MATHEMATICAL STUDIES OF PHOTOCHEMICAL AIR POLLUTION

Thesis by

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ABSTRACT

In Part I a new, comprehensive model for a chemically reacting plume, is presented, that accounts for the effects of incomplete turbulent macro- and micro- mixing on chemical reactions between plume and ambient constituents. This "Turbulent Reacting Plume Model" (TRPM) is modular in nature, allowing for the use of different levels of approximation of the phenomena involved. The core of the model consists of the evolution equations for reaction progress variables appropriate for evolving, spatially varying systems ("local phenomenal extent of reaction"). These equations estimate the interaction of mixing and chemical reaction and require input parameters characterizing internal plume behavior, such as relative dispersion and fine scale plume segregation. The model addresses deficiencies in previous reactive plume models. Calculations performed with the TRPM are compared with the experimental data of P.J.H. Builtjes (*) for the reaction between NO in a point source plume and ambient O_3, taking place in a wind tunnel simulating a neutral atmospheric boundary layer. The comparison shows the TRPM capable of quantitatively predicting the retardation imposed on the evolution of nonlinear plume chemistry by incomplete mixing. Part IA (Chapters 1 to 3) contains a detailed description of the TRPM structure and comparisons of calculations with measurements, as well as a literature survey of reactive plume models. Part IB (Chapters 4 to 7) contains studies on the turbulent dispersion and reaction phenomena and plume dynamics, thus exposing in detail the underlying concepts and methods relevant to turbulent reactive plume mod-

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* Builtjes, P.J.H. (1981) "Chemically Reacting Plume Experiments for the Wind Tunnel," Netherlands Organization for Applied Scientific Research, Division of Technology for Society, Ref. No. 81-013563, File No. 8710-20330.

eling. New formulations for describing in-plume phenomena, such as the "Localized Production of Fluctuations Model" for the calculation of the plume concentration variance are included here.

Part II (Chapter 8) presents a collection of distribution-based statistical methods that are appropriate for characterizing extreme events in air pollution studies. Applications to the evaluation of air quality standards, formulation of rollback calculations, and to the use of plume models are included here.

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PART IA

MATHEMATICAL MODELING OF TURBULENT REACTING PLUMES

General Theory,
Model Formulation and Evaluation

CHAPTER 1

PROBLEMS AND CONCEPTS OF REACTIVE PLUME MODELING

1.1 INTRODUCTION

All mathematical models of air quality offer an approximate description of actual meteorological–chemical systems that unavoidably relies on sets of simplifying assumptions. These assumptions are often based on specific information relevant to the phenomena to which they apply and thus their validity is supported by experience or theory (or both). However, in many cases simplifications are imposed on the mathematical formulation mainly by lack of adequate knowledge regarding the process considered. An example of the latter situation (often justified on an a priori requirement for simplicity) is the treatment of the effects of turbulent atmospheric mixing on the evolution of reactive systems by practically all large scale (urban or regional) models currently in routine use. The standard assumption involved in these models is that emissions are immediately mixed with the background air, in a perfectly uniform fashion, inside of some finite control volume (e.g. a computational cell of an Eulerian Grid model or an of "air parcel" following a Lagrangian trajectory). In this way the control volume is the analog of the ideal "stirred tank" of chemical reactor theory.

In fact pollutants emitted from strongly localized sources (industrial stacks) do not mix immediately with the background air at the molecular level but do so only after a certain time has elapsed and a corresponding distance from the source has been travelled. This fact results in the existence of both mean concentration gradients and incomplete fine scale mixing that may be controlling factors in the spatial and temporal evolution of multimolecular reactive systems. Thus, for example, the actual rate of a bimolecular reaction (with relatively fast intrinsic kinetics) between an emitted species and a constituent of the background air will depend on:

(a) The *mean values* of the concentration of both reactants which vary from point to point not only in the direction of the wind but also in every cross-section of the plume, especially in the vicinity of the source. (Here mean values will always refer to ensemble averages unless explicitly stated otherwise). This is a state of incomplete "macromixing" in the relevant fluid–mechanical terminology. For a reaction with nonlinear kinetics, rates and conversions evaluated with concentrations of the two species averaged over the plume cross-section (or over any finite volume) will differ from the actual average rates and conversions over the cross–section (or the finite volume).

(b) The *state of mixing at the molecular level* ("micromixing"). Even if the mean concentrations of the two species are steady and non-zero at a point, instantaneous fluctuations about these mean values, due to the fact that molecular diffusion has not yet mixed the reactants uniformly at the molecular level, will retard the reaction rate.(*)

The above facts are often ignored and in most existing reactive plume models (as well as in practically all large scale air pollution models, as it was mentioned earlier) it is typically assumed that plume constituents and background air are assumed uniformly mixed – i.e. there are flat concentration profiles and no concentration fluctuations – over some finite area or volume. This assumption is equivalent to

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(*) Reactions between species that coexist in the source emissions will also be influenced by concentration gradients and local fluctuations, although in that case delayed dilution of the reactive material with the background air will lead to higher actual rates than those predicted for a situation of complete mixing (as long as the reaction is of order higher than unity). Only monomolecular systems will be completely insensitive to these effects.

spatial averaging. Another type of averaging is implicitly introduced through the use of dispersion schemes that are relevant to *absolute* diffusion, and therefore to time–averaged concentration fields. However, when nonlinear reactions occur, temporal averages of reactant concentrations at a point do *not* give, when introduced into the dynamic equations that contain the nonlinearities, the corresponding averages of rates, conversions and product concentrations. This simple fact, which is often ignored in atmospheric modeling, dictates the use of statistics of instantaneous and not time-averaged realizations of the plume in the treatment of nonlinear reaction rates. Thus it is necessary to adopt transport closure schemes that account for the *non-local* character of turbulent dispersion and are able to discriminate between processes that affect the time averaged but not the instantaneous properties of the plume.

Various approaches, usually focusing on some particular aspect of the mixing–reaction problem, have appeared in the literature relevant to turbulent reactive plume (and in general turbulent reactive flow) modeling. However, these approaches have been either overly simplistic, thus corresponding to unrealistic descriptions of the processes involved, or, at the other extreme, overly complicated for routine use. In view of this situation the present work aims to develop a model that, while being fundamentally sound by accounting properly for the effects of macromixing, micromixing and implicit averaging on nonlinear plume chemistry, at the same time is computationally simple and easy to apply.(*)

The analysis that follows examines mainly the interaction of mixing and chemistry in the case of localized releases in ambient turbulence. Many of the concepts that are introduced and the equations that are formulated here are quite general,

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(*) In the general perspective of photochemical air pollution modeling, this work studies the importance of phenomena that are of "subgrid scale" from the viewpoint of urban scale airshed models, as well as the overall effect of atmospheric turbulence on chemical reactions (which, as will be shown, is especially important for localized sources) aiming to improve on the predictive methods that are currently applied. In particular, special attention will be given to a reactive system that is most sensitive to these phenomena because of its very fast reaction rate, while at the same time is among the most important that determine the evolution of complex photochemical air pollution processes, that is the ozone-nitrogen oxides photolytic cycle (see Section 1.3 and Chapter 3).

holding for arbitrary ambient flows and a wide range of source conditions. However, the applicability of the current operational version of the model (as summarized in Chapter 2) is necessarily limited to situations for which the flow dynamics are sufficiently simple so as to allow a reduction of the overall phenomenon to processes involving parameters that can be reliably estimated. More specifically, in the present work the focus is on a plume advected by a mean wind field that is either uniform over a significant period, or, in general, changes "smoothly enough" in space and time so that a mean plume centerline can be defined. Then atmospheric motions that do not contribute to the mean field (random fluctuations) are responsible for the spread of the instantaneous plume and for its meandering about the mean centerline (depending on the magnitude of the spatial scale of these motions relative to the local plune "diameter"). Bulk meandering motions are also assumed sufficiently "mild", following Gifford's (1959) classic "fluctuating plume model".

1.2 POINT SOURCES IN CONNECTION TO LARGE SCALE AIRSHED MODELING AND THE ATMOSPHERIC DIFFUSION EQUATION

The structure, capabilities and limitations of large (urban) scale models as well as various problems related to their formulation and application are discussed extensively elsewhere (see, e.g., Turner, 1979; Benarie, 1980; McRae et al, 1982) and, being beyond the scope of this work, will not concern us here except to identify briefly the points for which the present work attempts an improved treatment.

As it was stressed in the introduction of this chapter (Section 1.1), inherent in all urban and regional air quality models are procedures of temporal and spatial averaging of both the velocity and the concentration fields at scales that vary with the particular model formulation. Thus, *single-box* models assume that the total mass of pollutants emitted from both localized and distributed sources in the area covered by the box is immediately mixed uniformly into the atmospheric air mass of the box. *Lagrangian Trajectory* and *Eulerian Grid models* allow for more resolution of the atmospheric field under consideration; however again uniform mixing down to the molecular level is assumed to hold at all times inside the computational cells independently of the localized character of some sources.(*) Although the description can be improved in principle by reducing the size of cells near localized sources the assumption of immediate uniform mixing over a finite volume remains. The size of the cells employed in grid models depends not only on limitations set by the numerical procedure but also on the character of available inputs and the formulation of the basic model equations (Seinfeld, 1975).

(*) In some cases (see, e.g., McRae et al., 1982; Stewart and Liu, 1981) improvements have been introduced in the grid models by combining them with simple "plume calculations" that at least account for reduced mixing volume near the source. In these formulations the plume is assumed to expand gradually to the size of a computational cell. The qualitative principle of this coupling between airshed and plume models is shown schematically in Figure 1-1.

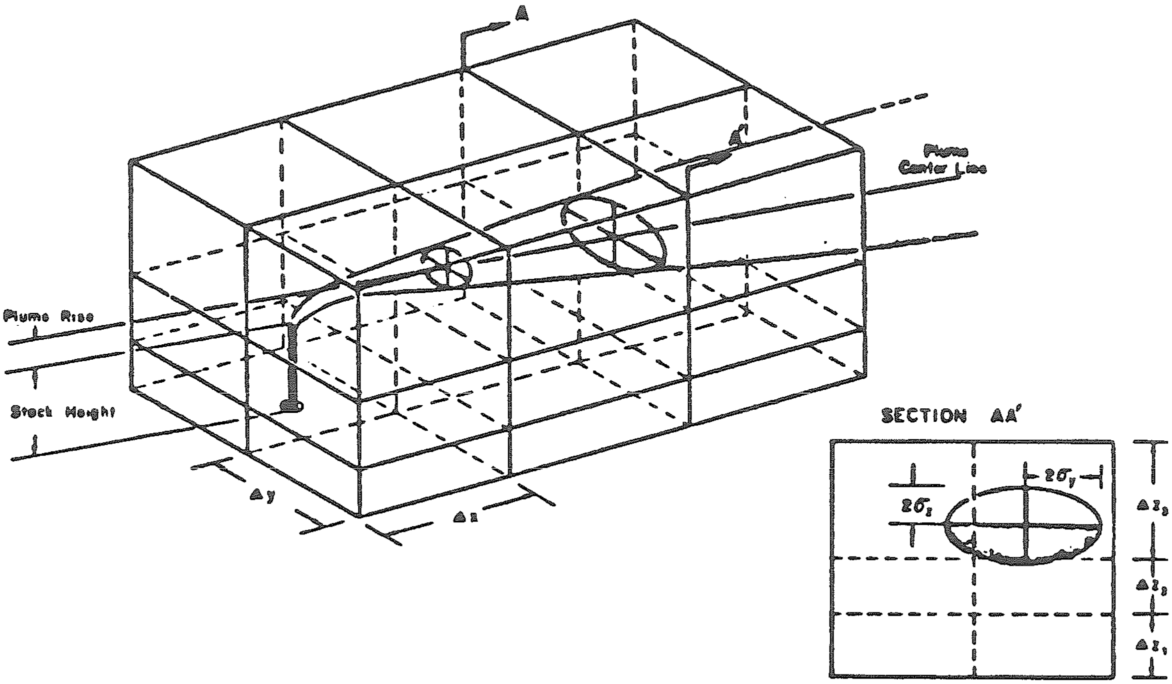

Figure 1-1

A Point-Source Plume Expanding in the Grid of an Airshed Model.

For example, models based on the atmospheric diffusion equation (ADE) introduce *implicitly* minimum resolution space-time scales, through the first order closure scheme (K-theory) for turbulent transport which formulates the ADE (see Figure 1-2 and Table 1-1) starting from an ensemble averaged form of the stochastic species transport equation (which is assumed to hold instantaneously and pointwise in the atmospheric continuum). Nevertheless, since higher order closure schemes are drastically constrained from routine applicability because of their high computational burden and limited range of verified parameters, the K-theories employed in the common ADE still offer the most practical description of atmospheric processes currently in use in urban scale airshed models. Conforming to the requirement for a "reasonable" computational effort the present work will also rely on special first order transport closure schemes that extend the validity of the ADE to localized emissions and fast nonlinear chemistry, subject of course to different restrictions in applicability.(*)

These closure schemes are based on the alternative view of local phenomena that is offered by the well known Gaussian plume formulas, commonly available for nonreacting species. These can be interpreted as solutions of ADE-type equations but with eddy diffusivities that depend on the distance from the point source (Csanady, 1973; Pasquill, 1974) and therefore do not represent properties of the turbulent flow field but of the particular plume (i.e. of the particular dispersion process).

The picture of the dispersion given by the Gaussian plume equation depends on the nature of the parameters that are used; it is usually a time averaged picture (the "plume envelope") corresponding to parameters that describe absolute diffusion. Nevertheless the Gaussian equations formally also apply to the *ensemble mean* of the instantaneous realizations of the plume with the direct introduction of parameters that describe the process of relative diffusion. This fact extends the applicability of

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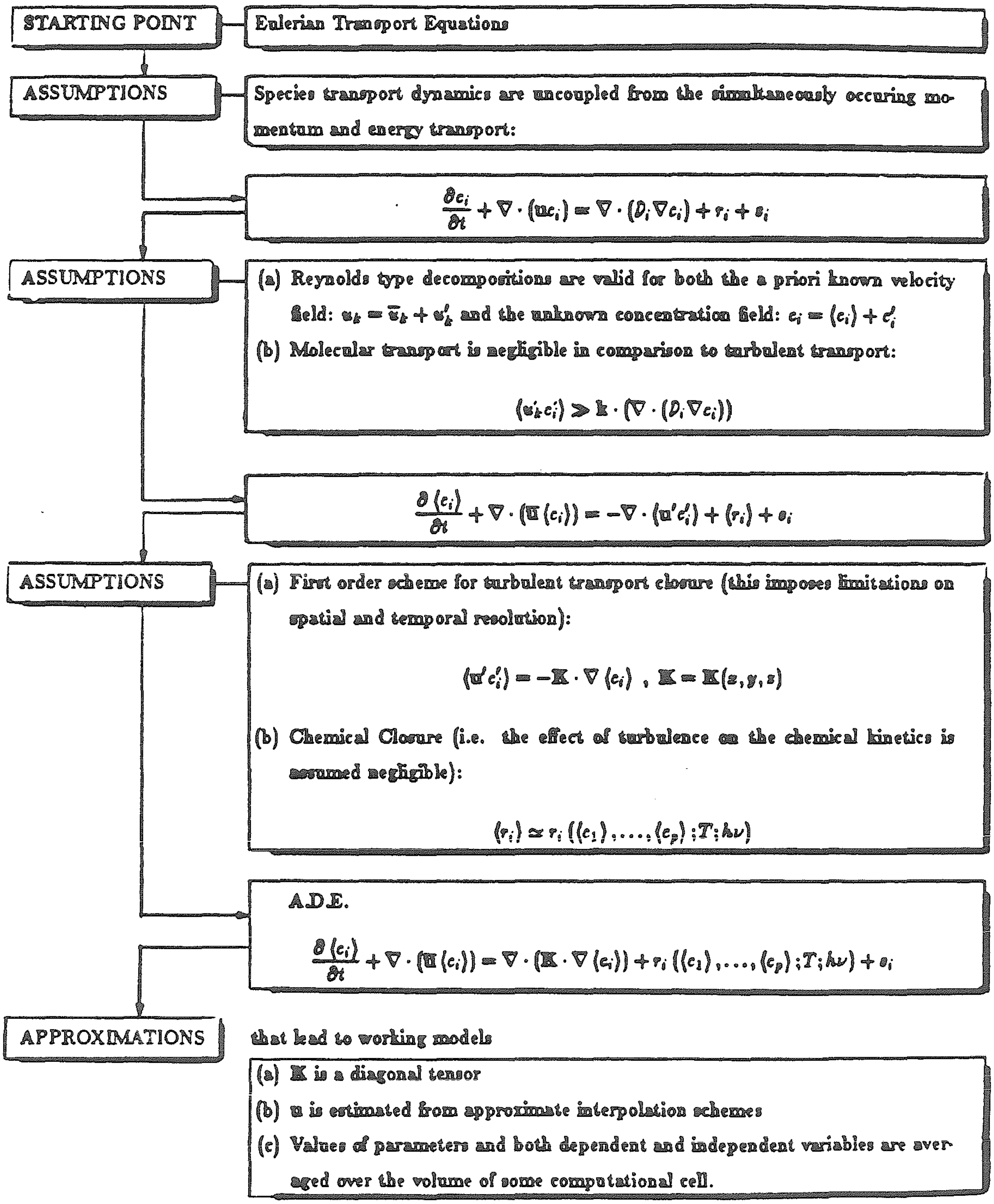
(*) The conditions for the validity of the common ADE are discussed extensively in other works (e.g. Lamb, 1973; Corrsin, 1974; Seinfeld, 1975, 1983; Goodin et al., 1976; McRae et al., 1982 etc.); a brief summary of its limitations – that can also be seen as "sources of error" in applications where these limitations are typically ignored – is presented in Table 1-1.



STARTING POINT — Eulerian Transport Equations

ASSUMPTIONS — Species transport dynamics are uncoupled from the simultaneously occuring momentum and energy transport:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (\mathbf{u} c_i) = \nabla \cdot (D_i \nabla c_i) + r_i + s_i$$

ASSUMPTIONS

(a) Reynolds type decompositions are valid for both the a priori known velocity field: $u_k = \bar{u}_k + u'_k$ and the unknown concentration field: $c_i = \langle c_i \rangle + c'_i$

(b) Molecular transport is negligible in comparison to turbulent transport:

$$\langle u'_k c'_i \rangle \gg \mathbf{k} \cdot (\nabla \cdot (D_i \nabla c_i))$$

$$\frac{\partial \langle c_i \rangle}{\partial t} + \nabla \cdot (\bar{\mathbf{u}} \langle c_i \rangle) = -\nabla \cdot \langle \mathbf{u}' c'_i \rangle + \langle r_i \rangle + s_i$$

ASSUMPTIONS

(a) First order scheme for turbulent transport closure (this imposes limitations on spatial and temporal resolution):

$$\langle \mathbf{u}' c'_i \rangle = -\mathbb{K} \cdot \nabla \langle c_i \rangle \ , \ \mathbb{K} = \mathbb{K}(x, y, z)$$

(b) Chemical Closure (i.e. the effect of turbulence on the chemical kinetics is assumed negligible):

$$\langle r_i \rangle \simeq r_i \left(\langle c_1 \rangle, \ldots, \langle c_p \rangle ; T ; h\nu \right)$$

A.D.E.

$$\frac{\partial \langle c_i \rangle}{\partial t} + \nabla \cdot (\bar{\mathbf{u}} \langle c_i \rangle) = \nabla \cdot (\mathbb{K} \cdot \nabla \langle c_i \rangle) + r_i \left(\langle c_1 \rangle, \ldots, \langle c_p \rangle ; T ; h\nu \right) + s_i$$

APPROXIMATIONS that lead to working models

(a) $\mathbb{K}$ is a diagonal tensor

(b) $\mathbf{u}$ is estimated from approximate interpolation schemes

(c) Values of parameters and both dependent and independent variables are averaged over the volume of some computational cell.

(See Seinfeld,1975; McRae et al.,1982 for notation and details)

Figure 1-2

Derivation of the Atmospheric Diffusion Equation

Table 1-1

Primary Sources of Error in the ADE and in Related Air Quality Models

	SOURCE OF ERROR	COMMENTS
A.	The true form of the turbulent fluxes is unknown; a first order scheme (K-theory) is introduced to describe them.	*Higher order closure schemes offer improved description over eddy diffusivities. However such closure methods lead to large computational requirements.*
B.	The closure approximation for turbulent transport limits the temporal and spatial resolution of the ADE. Inherent averaging leads to errors:	*Higher order closure schemes may allow formulation of equations with increased resolution capabilities. For point sources there is a simple first order closure alternative in the use of Gaussian plume models, corresponding to solutions of ADE-type equations, with eddy diffusivities that are functions of the travel time from the source. Proper selection of such diffusivities is needed for the description of instantaneous realisations of point source plumes.*
B.1.	in the case of strongly localised sources which cause steep gradients of the mean concentration fields	
B.2.	when combined with fast nonlinear chemical reaction rate terms.	
C.	Fine scale turbulent fluctuations of the concentration fields that induce higher order correlations in nonlinear chemical kinetic terms are neglected.	*Models of turbulent kinetic rates that account for the effects of fluctuations may be introduced when such effects are found to be important.*

the Gaussian plume concept (and of the related governing equations) to problems involving nonlinear phenomena. Meandering, which determines the random instantaneous position of the plume, will have to be considered a posteriori when temporal or spatial averages of dependent variables of the nonlinear phenomena are to be estimated from their (expected) instantaneous point values.

Conventional K theories (with eddy diffusivities independent of the travel time) describe only time averaged pictures of the dispersion phenomena and thus cannot discriminate the two different effects comprising dispersion for the separate treatment that is needed when nonlinear phenomena occur. A solution to the problem of describing the transport dynamics of an expected instantaneous realization of a reactive plume is to use generalized "eddy diffusivities" defined in terms of the relative dispersion parameters of a Gaussian plume. Thus the resulting "modified" ADE will describe a particular dispersion process determined by the initial and boundary conditions (or source terms) relevant to a specific localized source, and will not be a "concentration transport equation" in the traditional Eulerian sense. Essentially it will be an implicitly "non-local" equation, a fact that forbids superposition of forcing terms. The formal justification of this description (which is often a subject of discussion and – sometimes unsupported – criticism in the literature) and the underlying implications relevant to the nature of the processes involved are analyzed in more detail in Chapter 6.

Before closing this brief discussion we must stress the fact that the special problems associated with nonlinearities of plume phenomena are relevant only if the rates of time evolution of these phenomena are comparable to those of the processes of dispersion. This point is elaborated in the next section (and in more detail in Chapter 4) in connection with nonlinear rates of chemical reactions.

1.3 TURBULENT KINETICS AND THE ATMOSPHERIC DIFFUSION EQUATION

In typical application of the ADE in air quality models two critical assumptions are made with respect to chemical reaction terms. The first is an implicit one, regarding the approximation of ensemble means by spatial and temporal averages and is imposed by the nature of the common first order transport closure scheme, and can be circumvented by using the modified ADE, as discussed in the previous section. The second assumption is an explicit one, stating that (ensemble) mean reaction rates are functions of (ensemble) mean concentrations only and thus the latter replace directly instantaneous concentrations in the functional forms of the phenomenological kinetic laws:

$$\langle R\left(c_1, c_2, \ldots, c_n\right)\rangle = R\left(\langle c_1\rangle, \langle c_2\rangle, \ldots, \langle c_n\rangle\right)$$

Such an approach neglects altogether the effect of turbulence on nonlinear kinetic terms and the consequent need for chemical closure; it is actually the simplest and most drastic closure approximation. However the conditions for the validity of this approach are very restrictive (Lamb, 1973) requiring reaction time scales that are large compared to the time scales associated with the dispersion processes.

To provide perspective on this point, let us consider the problem of the release of species A in a turbulent background containing the species B. A and B react according to

$$A + B \rightleftharpoons P \qquad (1.3-1)$$

and the instantaneous–pointwiserate of (1.3-1) is expressed in terms of the instantaneous–pointwise concentrations as

$$R = k_f\, c_A c_B - k_b\, c_P \qquad (1.3-2)$$

Under conditions for which transport can be assumed practically decoupled from the simultaneous momentum and energy transfer that govern the velocity and temperature fields (Seinfeld, 1975 – Section 6.1), the instantaneous concentrations of A, B and P at any point will obey the species mass balance equations

$$\mathcal{L}^M c_S = r_S \tag{1.3 – 3}$$

(where S stands for A, B or P) with the appropriate boundary and initial conditions that also account for source terms. Here $\mathcal{L}^M$ represents the overall *Eulerian Mixing Operator* (a linear *stochastic* operator) which has the form (with the summation convention employed)

$$\mathcal{L}^M = \frac{\partial}{\partial t} + u_i \frac{\partial}{\partial x_i} - D_S \frac{\partial^2}{\partial x_i \partial x_i} \tag{1.3 – 4}$$

where u_i are the components of the random instantaneous velocity field and D_S is the molecular diffusivity of species S. r_S is the formation rate of species S. Obviously

$$r_A = r_B = -R, \quad r_P = R \tag{1.3 – 5}$$

Boundary and initial conditions are assumed deterministic in this formulation; thus all randomness is due to the turbulent velocity field.

In an Eulerian framework one starts typically by introducing Reynolds type decomposition of the random variables in mean and fluctuating components, that is $\mathbf{u} = \langle \mathbf{u} \rangle + \mathbf{u}'$, $c = \langle c \rangle + c'$ in the equations, where $\langle \cdot \rangle$ stands for ensemble averages. This leads to a moments closure problem, unavoidable in turbulence theory. (Eulerian formulations for evolution equations of the entire pdf have analogous closure problems). Nonlinear reaction rates produce *self-interaction* effects causing the appearance of new unknown correlations in the chemical part of (1.3-3) ("turbulent kinetic terms") in addition to the turbulent transfer correlations in the fluid-mechanical part. Thus

$$\left\langle \mathcal{L}^M c_A \right\rangle = -k_f \left(\langle c_A \rangle \langle c_B \rangle + \langle c_A' c_B' \rangle \right) + k_b \langle c_P \rangle \tag{1.3 – 6}$$

with

$$\left\langle \mathcal{L}^M c_A \right\rangle = \frac{\partial \langle c_A \rangle}{\partial t} + \langle u_i \rangle \frac{\partial \langle c_A \rangle}{\partial x_i} + \frac{\partial}{\partial x_i} \langle u_i' c_A' \rangle - D_A \frac{\partial^2 \langle c_A \rangle}{\partial x_i \partial x_i} \tag{1.3 – 7}$$

where incompressibility of the flow is assumed. Similar relations hold for the concentrations of B and P.

Now, unless

$$|\langle c_A \rangle \langle c_B \rangle| \gg |\langle c'_A c'_B \rangle|$$

is valid, calculations have to account for the effects of $\sigma_{AB} = \langle c'_A \, c'_B \rangle$ on the evolution of the system. An extensive literature has developed in relation to models that account for these effects either explicitly by deriving closure expressions for σ_{AB}, or, more commonly, by treating the phenomenon of incomplete mixing through various indirect approaches. Chapter 4 is devoted to the study of such modeling procedures, focusing on models appropriate to treat plume chemistry of either infinite or finite rate.

For the purpose of this introductory section it is sufficient to delineate the conditions under which $\langle c'_A \, c'_B \rangle$ is expected to be significant. If, for simplicity, it is assumed that $D_A = D_B$ and the linear reverse reaction is neglected one has the following equation for σ_{AB}:

$$\frac{\partial}{\partial t} \langle c'_A \, c'_B \rangle + \overbrace{\langle u_i \rangle \frac{\partial}{\partial x_1} \langle c'_A \, c'_B \rangle}^{(I)} =$$

$$= \overbrace{\langle u'_i c'_A \rangle \frac{\partial \langle c_a \rangle}{\partial x_i} + \langle u'_i c'_B \rangle \frac{\partial \langle c_B \rangle}{\partial x_i}}^{(II)} - \overbrace{\frac{\partial}{\partial x_i} \langle u'_i c'_A c'_B \rangle}^{(III)}$$

$$+ \overbrace{D \frac{\partial^2 \langle c'_A c'_B \rangle}{\partial x_i \partial x_i}}^{(IV)} - \overbrace{2D \left\langle \left(\frac{\partial c'_A}{\partial x_i} \right) \left(\frac{\partial c' B}{\partial x_i} \right) \right\rangle}^{(V)}$$

$$\overbrace{- k_f \left[\langle c'_A c'_B \rangle \left(\langle c_A \rangle + \langle c_B \rangle \right) + \left\langle c'_A {c'_B}^2 \right\rangle + \left\langle {c'_A}^2 c'_B \right\rangle + \left\langle {c'_B}^2 \right\rangle \langle c_A \rangle + \left\langle {c'_A}^2 \right\rangle \langle c_B \rangle \right]}^{(VI)}$$
$$(1.3-8)$$

As expected, new unknowns (third order correlations) appear in this equation as a consequence of the closure problem. However one can obtain a qualitative understanding of the processes that influence the evolution of σ_{AB} by examining the significance of the various terms in (1.3-8). These terms represent

(I) : convection of σ_{AB} by the mean velocity field.

(II) : generation of σ_{AB} by mean gradients in c_A and c_B.

(III) : transport of σ_{AB} by turbulent velocity fluctuations (that is turbulent diffusion of σ_{AB}).

(IV) : transport of σ_{AB} by molecular diffusion.

(V) : dissipation of σ_{AB} by molecular diffusion.

(VI) : production or decay of σ_{AB} due to chemical reaction.

In the absence of mean gradients the behavior of σ_{AB} is governed by the processes of fine scale mixing (term V) and chemical reaction (term VI); then the ratio of these terms can be used as an a priori measure of the intensity of interaction between mixing and reaction. We express the dissipation in terms of an an appropriate Corrsin length scale ℓ_d (Corrsin, 1952), which is a scale of magnitude intermediate to the micro- and macro- scales of the flow, analogous to the Taylor scale for velocity fluctuations, as

$$2D\left\langle\left(\frac{\partial c'_A}{\partial x_i}\right)\left(\frac{\partial c'_B}{\partial x_i}\right)\right\rangle \simeq \frac{mD\,\langle c'_A\,c'_B\rangle}{\ell_d^2}$$

where m is an integer commonly set equal to 2 (Donaldson and Hilst, 1972). In cases where the magnitudes of fluctuations can be assumed smaller than those of the mean values, term (VI) is approximated by $k_f\,\langle c'_A\,c'_B\rangle\,(\langle c_A\rangle + \langle c_B\rangle)$; then one can use

$$N_R = \mathrm{Da}_{\mathrm{II}} = \frac{k_f\,[\langle c_A\rangle + \langle c_B\rangle]\,\ell_d^2}{2D} \tag{1.3 – 9}$$

as a measure of chemistry—dispersion interaction. N_R is the ratio of characteristic time scales for mixing and reaction (a Damköhler dimensionless group); it allows the classification of 2nd order chemical reactions in *homogeneous* turbulent concentration fields (and with relatively low fluctuation levels) into slow, moderate and fast. When $N_R \gg 1$ ("instantaneous" or "very fast chemistry"), the characteristic time for chemical reaction is short compared to that for mixing, and the phenomenon is governed not by the kinetics but by the rate at which the reactants are brought together at the molecular level by dispersive processes. When $N_R \ll 1$ ("slow chemistry"), concentration fluctuations are dissipated before they can affect the kinetics; in this situation the mean reaction rate is satisfactorily predicted by $k_f \langle c_A \rangle \langle c_B \rangle$ (see also Lamb, 1973). In other words, if the dissipative scale of turbulence is small and the reaction rate is very slow, then molecular diffusion can be expected to keep A and B well mixed (at the molecular level) and the correlation term $\langle c'_A c'_B \rangle$ is negligible. For intermediate values of N_R a complex coupling between transport and chemistry requires elaborate schemes of modeling. (In the literature this regime is often referred to as "moderately fast" or "intermediate rate chemistry").

Representative values of N_R for some atmospheric reactions are given in Table 1-2. Typical values of $D = 0.17\text{cm}^2/\text{sec}$ and $\ell_d = 5$ and 20 cm were used in (1.3-9) for these estimates. One notices the wide range of N_R values relevant to atmospheric reactions as well as the sensitivity to the magnitude of the dissipation scale. It must be further stressed that in actual field situations, and in particular in plumes, even when segregation is small enough for (1.3-9) to provide a useful means for judging the coupling of transport and chemistry, ℓ_d as well as mean concentrations will vary significantly from point to point with subsequent large variations in the local value of N_R. Thus, the same reaction could be characterized as slow, moderate, or fast in different stages of plume evolution. Conditions such that *locally* $N_R = O(1)$ are possible for most of the reactions of Table 1-2; nevertheless it is obvious that certain reaction systems (such as the ozone – nitrogen oxides system) are most sensitive to fine scale concentration fluctuations.

Table 1-2

Typical Damköhler Numbers N_R for a Smog Chamber Experiment$^{(a)}$

REACTION	RATE CONSTANT	CONCENTRATION (ppm)		N_R $^{(b)}$	
A + B→	$(ppm^{-1}\ min^{-1})$	c_A	c_B	$l_d = 5cm$	$l_d = 20cm$
$NO + O_3 \rightarrow$	23.9	0.045	0.069	3.33	53.4
$NO_2 + O \rightarrow$	1.34×10^4	0.253	1.94×10^{-8}	4146	66474
$NO_2 + O_3 \rightarrow$	0.05	0.253	0.069	0.018	0.32
$NO + HO_2 \rightarrow$	1.20×10^4	0.045	1.56×10^{-6}	662	10588
$OLE + O_3 \rightarrow$	0.15	0.005	0.069	0.014	0.22
$O_3 + HO_2 \rightarrow$	1.5	0.069	1.56×10^{-6}	0.13	2.03

(a) Smog Chamber Experiment SUR-119J at 180 min (Pitts et al.,1976)

(b) Damköhler Number:

$$N_R = \frac{\text{Dispersion time scale}}{\text{Reaction time scale}} = \frac{k\,(c_A + c_B)\,\ell_d^2}{2\mathcal{D}}$$

$$(\mathcal{D} = 10.2\text{cm}^2\text{min}^{-1})$$

A final point that must be mentioned here is that in complex reaction networks (typical in photochemical air pollution) the importance of turbulent rates must be assessed in connection to "global" kinetic mechanisms involving the reacting species and not in connection to a single reaction step. Indeed, when a dispersion limited reaction is a member of a complex coupled system it may be so much faster than the other reactions that lowering its actual rate to the effective mixing rate will not change significantly the results of the overall kinetics.

1.4 REQUIREMENTS AND LIMITATIONS IN REACTIVE PLUME MODELING

As a conclusion of the discussion presented in the preceding sections it can be stated that the complexity of the various interacting phenomena taking place during the simultaneous mixing and reaction of point-source plumes in the atmosphere, and which must be taken into account in order that a model of the problem is realistic, will depend on:

(I) *The order of the chemical reactions under consideration.*

Monomolecular reactions (intrinsic linear kinetic rates) are insensitive to the state of mixing and are not affected by fine scale fluctuations. The existence of gradients of the mean concentration field in a plume cross-section results in locally varying rates and conversions but, since averaging procedures can be interchanged with other linear operators, the temporal and spatial averages of these quantities (rates, etc.) are the same independently of the way they were estimated. Of course prediction of local concentrations in the vicinity of the source requires a model other than the common ADE because of its inherent inability of the latter to handle highly localized sources.

Bimolecular (as well as higher order reactions) are affected by the state of mixing. Thus, if the reaction occurs faster than the plume mixes uniformly with the background air the actual rate will be controlled by dispersion effects. A priori averaging of the governing equations does not give the same average concentrations of products as a posteriori averaging of instantaneous pointwise concentrations of the same species. Hence instantaneous realizations of the plume must be considered in any computational scheme instead of time averaged plume envelopes.

(II) *The relative rates of reaction and dispersion processes.*

When the reaction is sufficiently slow the combined action of turbulent and molecular diffusion dissipates both mean concentration gradients and local fluctuations before appreciable conversion of reactants to products takes place. In such a case assumptions of well mixed cells are sufficient and the standard treatments of air pollution models are valid. When, however, the reaction rate is comparable or faster than that of the dispersion processes, a complex coupling of mixing and reaction phenomena occurs and schemes evaluating the results of this coupling must be introduced.

(III) *The initial state of the reactants.*

The interaction of mixing and chemistry is essentially different for the cases of initially premixed reactants (both constituents of the source effluent stream) and of initially non-premixed reactants (reaction between a constituent of the plume and the background air). Thus, for premixed reactants and reactions of order higher than one, turbulence creates positively correlated fluctuations and increases the overall rate as the reaction proceeds faster at the high concentration spots, whereas the action of molecular diffusion finally depresses the overall rate. For non-premixed reactants, and reactions of order higher than unity, turbulent fine scale fluctuations depress the reaction rate. Molecular diffusion is necessary to bring the reactants in contact and for fast reactions it may actually control the overall rate.

Thus when the (nonlinear) kinetic rate of a plume reaction is fast or comparable to that of the dispersion processes a reactive plume model must:

(i) be based on the instantaneous and not the time averaged realizations of the plume. These realizations must be modeled by uncoupling the effects of meandering (which does not interact with chemistry) from that of relative diffusion.

(ii) *not* ignore the existence of mean concentration gradients in any instantaneous plume cross-section (which are in fact much steeper than those present in the time averaged plume envelope).

(iii) estimate spatial and temporal averages of dependent variables in an a posteriori fashion from the instantaneous description of the reactive system (which means that after rates and conversions have been estimated for the instantaneous realization of the plume - which is in steady state - they must be "spread out" to the plume envelope volume in a proper probablistic manner).

(iv) include a scheme that estimates the effect of fine scale fluctuations on the chemical rate.

(v) include a scheme that estimates plume rise because of buoyancy and the distance from the source at which a final rise is obtained.

Further improvements on this formulation can be made by incorporating, if possible, schemes that evaluate buoyancy and wind shear effects on the dispersion of the plume, examining the effects of initial (thermal) source conditions on chemistry, etc.

The above requirements constitute a set of guidelines for the construction (and validation) of a Reactive Plume Model arising from the complexity of the physical phenomena and the need for their proper description.

A second set of requirements (or rather limitations) arises from the need that the model is sufficiently simple in order to be useful. Thus, a practically applicable Reactive Plume Model must:

(i) be simple and versatile,

(ii) require commonly available air quality, meteorological and source data as input parameters,

(iii) be compatible, if possible, with existing components of airshed models.

Therefore, a final working model, constructed on the lines specified by these two groups of requirements, must represent in some way a balance between

(A) *complexity that arises from an adequately realistic description of the physical processes, and*

(B) *simplicity and versatility, so that the model is useful for practical applications.*

Now, before proceeding to show how the scheme developed in the present work attempts to conform to these requirements – which is done in Chapters 2 and 3, with a detailed analysis regarding the modeling schemes and the parameters used following in Chapters 4 to 7– we present a brief summary of the current status of research in Reactive Plume Modeling.

1.5. REACTIVE PLUME MODELS : A LITERATURE SURVEY

Most atmospheric plume models in general fall in one of the following three major categories:

(i) Formulations dealing with the fluid-mechanical aspects of the problem in the near source region where the source buoyancy and "internal" plume turbulence are significant. These are the "plume rise models" resulting in a variety of schemes, from semi-empirical algebraic equations to complex numerical formulations (see Chapter 7).

(ii) Schemes, ranging from fitting of empirical data to large numerical experiments in either Eulerian or Lagrangian frameworks, that aim in the improvement of the parameterization of inert dispersion from point sources, for a variety of scales and averaging times (see Chapter 6), and,

(iii) Schemes that focus on the evolution of, most often linear – but sometimes complex, single phase or even multi-phase – reaction networks involving species emitted from point sources as well as constituents of the ambient atmosphere (Reactive Plume Models). The time scales relevant to this evolution correspond, almost exclusively, to the final or "atmospheric diffusion" phase of plume dispersion (i.e. typically beyond downwind distances of the order of magnitude of 100 stack diameters). Other physical removal processes (surface deposition, washout) may be included in these schemes.

At this point it must be mentioned that the resolution provided by some of the formulations commonly referred to as plume models is just that of urban (and even regional) models. Thus, certain of the currently available "plume" models, that consider complex nonlinear chemistry, are straightforward Lagrangian Trajectory models employing K-theory (despite the limitations discussed earlier) to describe turbulent transport inside the advected large Lagrangian volume; others employ Gaussian plume dispersion parameters but ignore the interaction of time averaging and nonlinearities. Appendix A1.2 contains a representative list of plume models, intended for

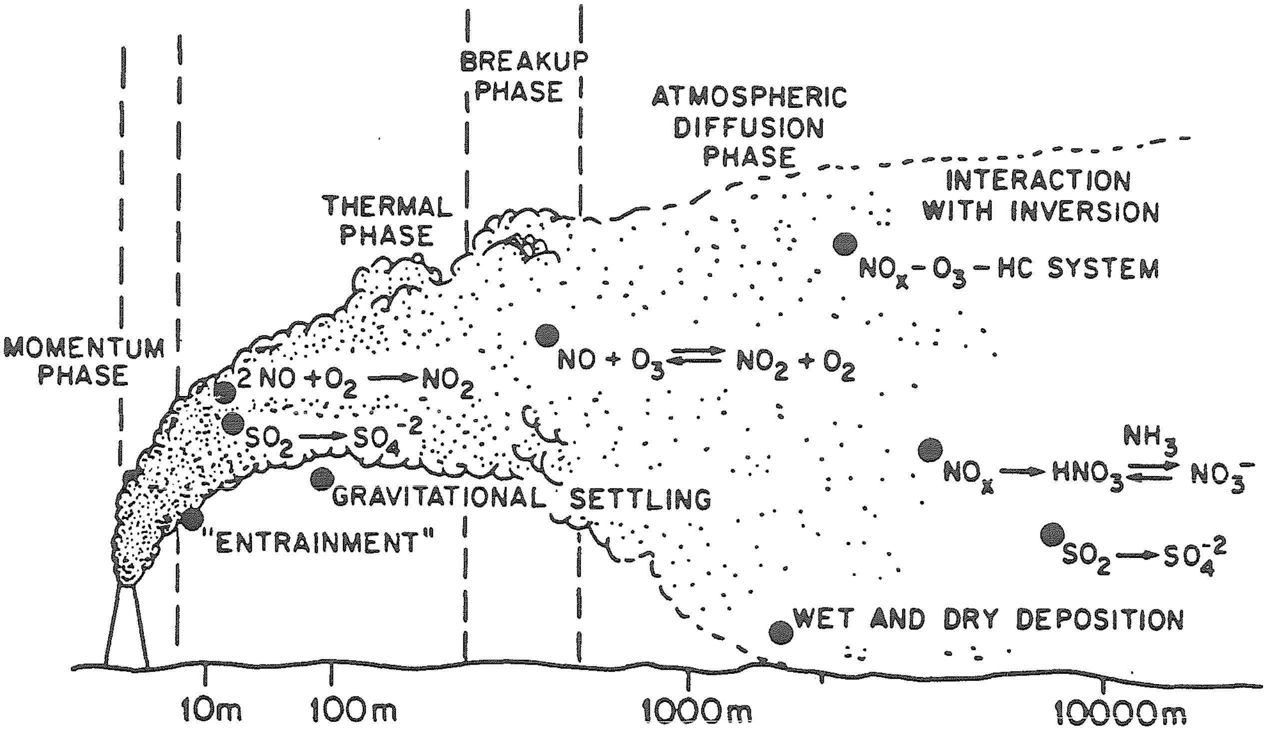


Figure 1-3

Schematic Representation of the Evolution

of the Various Typical "Phases" of Plume Physics and Chemistry

(and of the spatial scales associated with these phases).

routine use, that covers the typical range of available formulations; a brief description of each model is also presented there. More extended, comparative reviews of plume models and relevant references can be found in Liu et al. (1982) (see also Benarie, 1980).

Another point that cannot be overemphasized is the proper identification of the spatial/temporal range to which a particular model is relevant. To provide perspective on the importance of the different physical and chemical processes over various scales of the downwind distance from the source we give in Figure 1-3 a schematic representation of a "typical" plume evolving through successive "phases" where its initial momentum, its buoyancy, and, finally, the ambient turbulence, determine internal plume dynamics, rise, and expansion. (For further discussion of plume evolution and dominant processes in a given spatial range see Chapter 7 and Csanady, 1973).

Let us now focus attention on models that consider in-plume chemistry (in general more realistic than simple removal linearly related to the concentration level). Such models can be classified according to a variety of different criteria. A general review that examines different plume chemistry schemes and reactive plume models can be found in Burton et al. (1983); in the same volume (de Wispelaere, 1983) one can find summarized information on various aspects of particular in-plume processes. Typically, models incorporating large, complex, chemistry networks tend to simplify greatly the effects of the mixing processes. The most realistic and sophisticated representations of mixing are incorporated in formulations dealing with relatively limited reaction networks involving few reactions, most commonly with the NO–NO_2–O_3 photochemical system for which experience has shown the effects of mixing to be most important. Indeed, the fast reaction rates associated with this system and the fact that emissions from large industrial sources are in general rich in NO (and poor in hydrocarbons) make these reactions dominate plume chemistry in the earlier phases of dispersion where the volume of the plume gases is much smaller than that of typically sized cells of Eulerian grid (and most Lagrangian trajectory) models.

A review and classification of representative reactive plume models according to the way they treat mixing processes follows. (*) This classification is also summarized in Table 1-3 and, schematically, in Figure 1-4, where typical concentration patterns, as treated by the various models, are presented. (For some further discussion of the in-plume concentration patterns – resulting from the interaction of chemistry and mixing – see Chapter 3, and in particular Figure 3-2 and the comments relevant to it.)

Class I

> *Models that account only for reduced initial dispersion volume occupied by point source emissions (smaller than the resolution scale of the ADE or the computational grid of an urban scale model). Mixing is assumed uniform in this reduced volume (flat mean profiles - no fine scale fluctuations). Examples are: Liu et al. (1975), McRae et al. (1982), Forney and Giz (1981), Cocks and Fletcher (1979), Varey et al. (1978), Isaksen et al. (1978).*

Some of these models have been used in combination with urban scale airshed models, with the point source plume expanding gradually until it reaches the size of a computational cell. The expanding plume cross-section has been assumed either circular (Forney and Giz, 1981), rectangular (Liu et al., 1975) or elliptical (McRae et al., 1982). McRae et al. (1982) noted that the dispersion parameters determining the size of the elliptical cross-section must describe the instantaneous plume profile from relative dispersion and not the time averaged plume envelope. From the perspective of the present work it is very interesting to see how these simple models treat plume chemistry during the expansion of the plume; for this reason the formulation of McRae et al. (1982) is summarized in Appendix A1.1.

(*) This classification focuses on reactions with relatively fast nonlinear kinetics. As we have already noted slow reactions are adequately treated by conventional schemes that are currently in use (see McRae et al., 1982). Linear processes are naturally tractable (insensitive to the degree of micromixing) and analytical results are often available (e.g., Heines and Peters, 1973; Peterson and Seinfeld, 1977; Astarita et al., 1979; Alam and Seinfeld, 1981). However one should always keep in mind that the limitations on the validity of the ADE, regarding averaging and allowable temporal and spatial resolutions, are implicit in the results that are deduced from it, even when only linear processes are involved.

Table 1-3

Classification of Reactive Plume Models

DESCRIPTION OF MIXING	SELECTED REFERENCES
I. *Reduced initial dispersion volume (uniform mixing at any cross–section of this volume)*	Liu et al. (1975), Isaksen et al. (1978), Varey et al. (1978), Cocks and Fletcher (1979), Forney and Giz (1981), McRae et al. (1982)
II. *Divided perfectly mixed/unmixed dispersion volume*	Carmichael et al. (1981)
III. *Reduced Initial dispersion volume* and	
IIIA. *Sectionally homogeneous field at any cross section*	Lusis (1976), Melo et al. (1978), Stewart and Liu (1981), Hov et al. (1981), Seigneur et al. (1983)
IIIB. *Gaussian mean field at any cross section*	Peters and Richards (1977), White (1977), Hegg et al. (1977)
IV. *Turbulent fluctuations (no mean gradients)*	Donaldson and Hilst, (1972), Lamb (1976), Shu (1976), Shu et al. (1978), Bilger (1978), Kewley (1980)
V. *Mean field gradients and fine scale fluctuations*	Borghi (1974), Donaldson and Varma (1976), Kewley (1978)
VI. *Probability density evolution formulations*	Dopazo (1976), O'Brien et al. (1976), O'Brien (1980)

Class II

The partially perfectly mixed expanding volume: Carmichael and Peters (1981).

In the formulation of this model it is assumed that at every (circular) cross-section of the expanding plume only a fraction of the source effluent is perfectly mixed (flat profile—no fluctuations) with the environment. The rest remains pure source effluent forming a core surrounded by the perfectly mixed material. This core shrinks with distance from the source. The mixing process is viewed as a pseudo-kinetic step governed by empirical laws involving a mixing rate constant and the concentration of unmixed reactants. The advantage of such a model over those of Class I is only relative; completely empirical constants describing mixed and unmixed volume fractions must be introduced, and thus any improvement of predictions compared with those of the previous models is essentially a success in data fitting for the estimation of the constants.

Class III

Models that account for both reduced initial dispersion volume and inhomogeneous mean concentration fields (but consider no fine scale fluctuations) by:

Class IIIA:

assuming sectionally homogeneous fields or by

Class IIIB:

assuming Gaussian concentration fields inside the plume boundaries.

Thus, in models of Class IIIA the expanding plume volume is divided either in many expanding boxes of rectangular cross-section (Stewart and Liu, 1981; Seigneur et al., 1983; Hov et al., 1981), or in concentric elliptical rings (Lusis, 1976; Melo et al., 1978). In each of these sub-volumes the species are assumed perfectly mixed (flat profiles, no concentration fluctuations). The model of Stewart and Liu (1981) which is used in combination with an urban scale airshed model visualizes a cross-section of plume as an array of well mixed cells perpendicular to the plume centerline that expand in a prescribed fashion. The concentric elliptical rings model (Lusis, 1976; Melo et al., 1978) was developed for the $NO-NO_2-O_3$ system based on a similar model

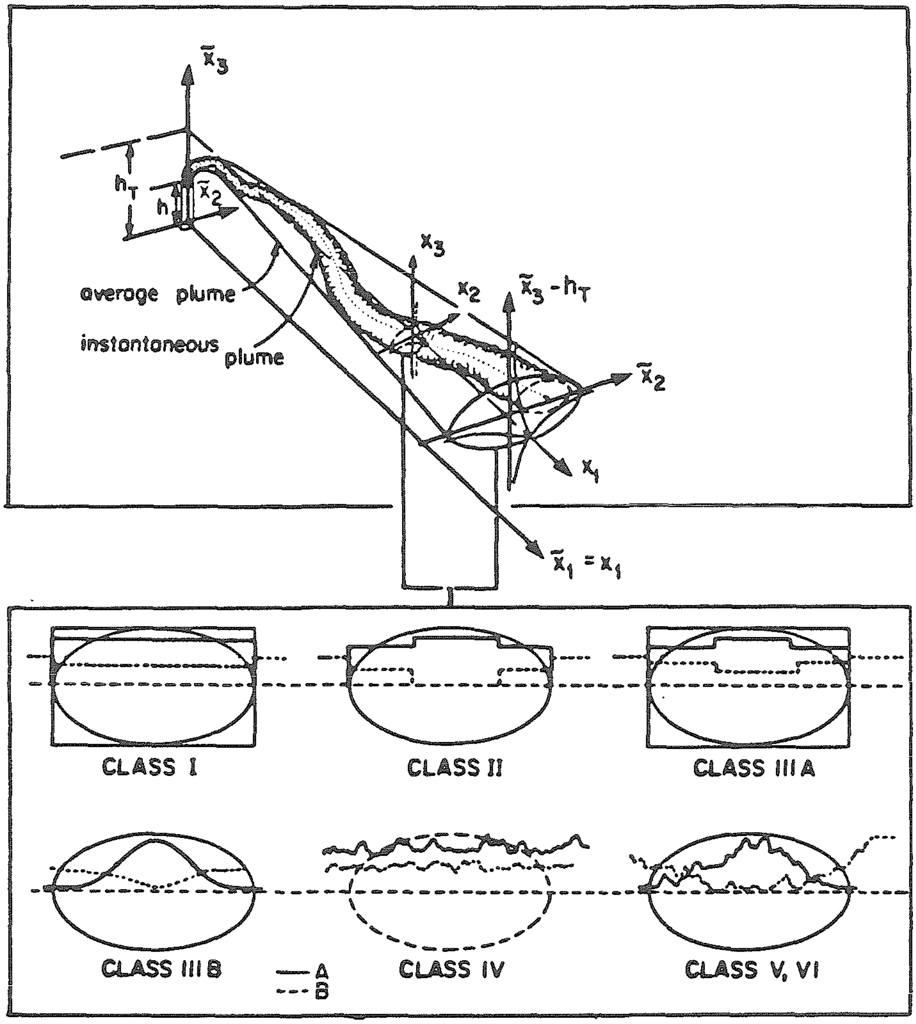


Figure 1-4
Schematic Representation
of the Basic Characteristics of Existing Reactive Plume Models
(according to the classification of Section 3)

The expanding plume is identified as a special control volume inside the atmospheric boundary layer (with the exception of the models of Class IV that consider uniform values of mean concentrations over the entire boundary layer), corresponding to either instantaneous plume realizations or (more often) to the time averaged envelope. (For models relevant to instantaneous realizations the mean concentrations must be ensemble averages and they can be in steady state only with respect to a frame of reference that follows the meandering centerline.) The cross-wind section of the plume is usually assumed to have elliptical shape (or rectangular in some of the models of Class I and IIIA); concentration profiles of the emitted and the ambient species (A and B respectively) that are typical in the various models are shown: Classes I to IIIB ignore the state of micromixing (local fluctuations) and assume profiles that are uniform (Class I), sectionally uniform (Class II, IIIA) or Gaussian (Class IIIB). Class IV takes into account fine scale fluctuations but ignores variations in the mean profiles. Finally Class V (and VI) consider the effects of both macromixing and micromixing.

by Freiberg (1976, 1978) who studied the oxidation of SO_2 in plumes. The model for the NO–NO_2–O_3 allows for turbulent exchange of material between adjacent rings. As far as the chemistry is concerned, it is assumed to be sufficiently slow so as not to be influenced by fine scale turbulent fluctuations.

Peters and Richards (1977) developed a model that belongs in Class IIIB. They assumed Gaussian profiles of concentration inside the plume and infinite rate chemistry and neglected completely concentration fluctuations. In order to obtain concentration profiles of the reactive species (reactants and products) they considered the transport of a conserved scalar (e.g., of a stoichiometric invariant of the reactive system). The transport equation of the conserved scalar is linear (no reaction term) and results in a Gaussian profile. Then the equilibrium relation (which is assumed to hold for mean concentration values since fluctuations are neglected) is used to obtain the reactive species concentrations. Although certain limitations of the atmospheric diffusion equation (see previous sections) were ignored, even so this model was a step beyond the perfectly mixed box models. White (1977) used the same principles to analyze the significance of experimental measurements.

Another model in Class III is that applied by Hegg et al. (1977), also in the analysis of experimental measurements. They assumed the reaction localized in the zone of highest concentration gradients and developed approximate schemes to obtain estimates of the time evolution of the reaction.

Class IV

Atmospheric fluctuations models (No consideration of mean concentration gradients): Donaldson and Hilst (1972), Bilger (1978), Kewley (1980), and Shu et al. (1978).

The studies of Donaldson and Hilst, Bilger, and Kewley refer to the effect of turbulent fluctuations on the nonlinear chemistry of a macroscopically mixed atmospheric volume where mean concentrations are uniform. Donaldson and Hilst (1972) were the first to show quantitatively the importance of fine scale fluctuations on nonlinear atmospheric chemistry. Bilger (1978) and Kewley (1980) used a version of the "probability density of conserved scalars approach" to study the nature of the NO–O_3–NO_2 photostationary state, providing insight on the actual behavior of the atmospheric reactive systems in a state of incomplete mixing. Lamb (1976), Shu (1976) and Shu et al. (1978) considered a source of NO in a background environment containing O_3, neglecting mean concentration gradients and averaging their governing equations over cross-sections of the control volume.

Class V

Models that account for both mean field gradients and fine fluctuations: Hilst et al. (1973), Borghi (1974), Donaldson and Varma (1976) and Kewley (1978)

The works of Borghi (1974) and Donaldson and Varma (1976) are representative of how models employed in combustion aerodynamics can be applied to atmospheric problems involving strongly localized sources. These models consider mean field gradients and treat the fluctuations terms by direct (higher order) closure schemes. Although these approaches are very informative, the models are complex, often involving higher order closure schemes, and formulated for specific conditions. Thus they cannot be considered as appropriate for routine use in atmospheric applications.

A simplified adaptation of the approaches used in combustion modeling to the atmospheric plume problem was presented by Kewley (1978) based mainly on the work of Bilger (1978). However the assumptions involved in certain steps of its formulation, although valid for the fluid mechanics of combustion devices, are definitely inappropriate for atmospheric conditions.(*)

Class VI

Probability density evolution formulations: O'Brien et al. (1976), Dopazo (1976), and O'Brien (1981).

This final class is included here for completeness; it consists of models that–at least in principle–attempt a complete characterization of the reacting system through estimation of the probability densities of the concentrations of all participating species. Evolution equations (based on methods from statistical mechanics) are constructed for the probability densities. However the works in this class are not yet in a form that would have practical use in atmospheric applications.

(*) The model of Kewley (1978) is a tractable formulation directly relating to atmospheric point source plumes (and in particular the ozone–nitrogen oxides system) that treats both mean concentration gradients and correlations of concentrations fluctuations. The method used to treat the fluctuations problem is a conserved scalar approach and is based on the assumption of infinite rate chemistry and pointwise equilibrium of the ozone–nitrogen oxides system wherever the reactants are mixed at the molecular level. There are however various weak points (besides this assumption of equilibrium) in the formulation of the model and the estimation of the parameters that are used. For example the common atmospheric diffusion equation is used as a starting point without consideration of time averaging effects and thus the transport closure approximation employed is not an appropriate one. Furthermore the variance of the concentration of an inert scalar, which accounts for local fluctuation effects by being used as a parameter in a clipped Gaussian probability distribution that is assumed to describe the conserved scalar field, is estimated on the basis of assumptions borrowed from the combustion literature that are not valid in atmospheric situations (see Chapter 5 for details). Of course even a better estimate of this variance would not help the situation that much, since, according to the preceding formulation of the model, the fluctuations would not be fluctuations about the correct quantity. Nevertheless, despite its points of invalidity this model is a rather simple approach that provides a qualitative understanding of certain of the phenomena that take place in a reactive plume.

1.6 CONCLUSIONS

The introductory analysis presented here showed that the evolution of systems of reactive pollutants in point source atmospheric plumes is determined in general by the combined action of both dispersive and reactive phenomena. These phenomena can lead to very complex physical situations as a consequence of the coupling of fast nonlinear kinetic rates with the turbulent nature of the flow field in which the reactions take place and the strongly localized character of the source.

All currently available theoretical studies of reactive plumes simplify – to different levels – the description of the complex system by introducing drastic assumptions, often wrong or misleading, about the importance and the nature of the coupling of the various interacting phenomena.

This first chapter considered both the nature of the reactive plume problem and the state of current research revealing the points that have not yet been treated properly; in the following we present the structure of a model that attempts to consider all the important aspects of the complex physical situation on the basis of explicitly stated assumptions.

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APPENDIX A1.1

Simple Models for Plume Mixing and Chemistry

The problem of release of species A in a background containing B (equations (1.3-1) to (1.3-5)) is often treated in atmospheric modeling practice by very simple methods. The most important example of this problem concerns the NO - NO_2 - O_3 system

$$NO_2 + h\nu \xrightarrow{k_1} NO + O$$

$$O + O_2 + M \xrightarrow{k_2} O_3 + M$$

$$O_3 + NO \xrightarrow{k_3} NO_2 + O_2$$

(see also Chapter 3) and most applications have focused on it.

Thus, one approach is to treat the reaction between NO and O_3, that produces NO_2, as a pseudo-linear step by assuming that the background O_3 concentration remains uniform and constant everywhere, which essentially means that dispersion processes are so much faster than chemical processes that are able to instantaneously "recover" all the ozone that is depleted by reaction inside the plume (see Builtjes, 1983). This method accounts for macromixing only through the non-uniform distribution (Gaussian) of NO_x and ignores completely any micromixing effects. Thus the NO_2 produced by the third of the above reactions at any point will be given by

$$c_{NO_2} = c_{NO_x}\left[1 - \exp\left(-k_3 c^b_{O_3}\right)\right]$$

In another approach, that (instead of assuming infinite rate of "recovery" of chemically depleted ozone) considers completely uniform mixing inside every cross-section of the plume and equilibrium of the NO - NO_2 - O_3 system, McRae et al. (1982) formulated nitrogen and excess oxygen balance as follows:

Nitrogen:

$$\begin{aligned} c_{NO_x}(t) &= c_{NO_2}(t) + c_{NO}(t) \\ &= D(t)c_{NO_x}(0) + [1 - D(t)]c^b_{NO_x} \qquad (A1.1-1) \end{aligned}$$

Excess Oxygen (ignoring $O(^3P)$):

$$\begin{aligned} c_{O_x}(t) &= c_{NO_2}(t) + c_{O_3}(t) \\ &= \mathrm{D}(t)[c_{NO_2}(0) + c_{O_3}(0) + [1 - \mathrm{D}(t)](c^b_{NO_2} + c^b_{O_3}) \end{aligned} \qquad (A1.1-2)$$

In those expressions $\mathrm{D}(t)$ refers to the plume dilution at time t, $c_{NO_x}(0)$ to the stack concentrations and the superscript "b" to the background values. The dilution is defined in terms of the change in the plume cross section area as a function of time. If the initial transverse area is A_0 and becomes $A(t)$ at some later time, t, then

$$\mathrm{D}(t) = \frac{A_0}{A(t)} \qquad (A1.1-3)$$

Thus there is a simple relation between the dilution and the growth of a cross-sectional segment of unit thickness:

$$\frac{1}{A(t)}\frac{dA(t)}{dt} = \frac{1}{\mathrm{D}(t)}\frac{d\mathrm{D}(t)}{dt} \qquad (A1.1-4)$$

In addition to the dilution $\mathrm{D}(t)$, the change in cross section area can be expressed in terms of the dispersion coefficients,σ_y and σ_z,

$$\frac{1}{A(t)}\frac{dA(t)}{dt} = \frac{1}{\sigma_y\sigma_z}\frac{d\sigma_y d\sigma_z}{dt} \qquad (A1.1-5)$$

If the ozone concentration in the source gases is negligible the excess oxygen balance can be written in the form

$$c_{O_3}(t) = c_A - c_{NO_2}(t) \qquad (A1.1-6)$$

where

$$c_A = \mathrm{D}(t)c_{NO_2}(0) + [1 - \mathrm{D}(t)](c^b_{NO_2} + c^b_{O_3}) \qquad (A1.1-7)$$

Then, writing the NO concentration as

$$c_{NO}(t) = c_B - c_{NO_2}(t) \qquad (A1.1-8)$$

where

$$c_B = \mathrm{D}(t)c_{NO_x}(0) + [1 - \mathrm{D}(t)]c^b_{NO_x} \qquad (A1.1-9)$$

one can utilize the equilibrium relation

$$c_{NO_2} = \frac{k_3}{k_1} c_{NO}\, c_{O_3} \qquad (A1.1-10)$$

to obtain a quadratic expression for c_{NO_2} the only physically realistic solution of which is

$$c_{NO_2}(t) = \frac{1}{2}\left\{\left(c_A + c_B + \frac{k_1}{k_3}\right) - \left[\left(c_A + c_b + \frac{k_1}{k_3}\right)^2 - 4c_A c_B\right]^{1/2}\right\} \qquad (A1.1-11)$$

The variables c_A, c_B can be calculated from measurements of c_{NO}/c_{NO_x} in the stack exhaust, the dilution, and the background concentration of NO, NO_2, and O_3.

Thus we see how the assumptions of uniform mixing (in a reduced and expanding volume) and infinitely fast reaction are combined to obtain a very simple result (but actually highly unrealistic) of conversion in the NO - NO_2 - O_3 system.

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for Appendix A1.1

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APPENDIX A1.2

Selected Plume Models

This Appendix contains a list of selected "Plume Models" (some of which take into account plume chemistry and other processes such as surface deposition, rain washout etc.) that are available in the public domain and have found wide application during the last decade. Most of them rely on the Gaussian plume concept; other formulations include applications of K-theory (either in a Lagrangian Trajectory or in an Eulerian Grid framework) or 2nd order closure methods. The majority of the models focuses on inert dispersion and linear removal mechanisms; among the models listed only IMPACT, PLMSTAR, RPM and TRACE take into account nonlinear chemistry. (However only RPM attempts to conform to the requirement of working with instantaneous plume statistics). Furthermore, only macromixing is included in these models; the interaction of turbulence and chemistry is ignored.

Some basic features of each model are listed as a brief description of its structure and capabilities; however it must be emphasized that some of these features may have been altered in more recent versions of the models. Thus this list is basically intended only to be indicative of the variety of approaches commonly employed in plume modeling. For further information, references and comparative discussion of plume models see Turner (1979), Benarie (1980), Liu et al. (1982), Burton et al. (1983) and Weber and Garrett (1984).

ADPIC

Lawrence Livermore Laboratory
University of California
Livermore, CA 94550

(R. Lange)

Comments: *ADPIC is a three-dimensional Lagrangian particle model (10^4 cells, 2×10^4 particles, 1 km/50m horizontal/vertical resolution); it calculates hourly averaged concentrations. The wind field is determined by the MATTHEW model (inverse-square-weighting for surface wind data; vertical extrapolation via mass conservation principle and a stability dependent power law; algorithm for minimization of divergence of wind field that takes into account the underlying terrain).*

- *Fluid particles released from a source follow a Lagrangian trajectory under the influence of the prevailing wind and a pseudovelocity representing turbulent diffusion. Each particle is tracked on an Eulerian grid, and the concentrations are computed by counting the total number of particles in a fluid cell. The horizontal dispersion coefficient is calculated using horizontal wind statistics; the vertical dispersion coefficient is assumed to obey a linear, height-dependent, relationship through the constant flux layer; both are functions of the distance from the source. Numerical solution is obtained by a modified particle in cell method.*
- *ADPIC considers chemically inert species but can be readily adapted to handle a linear chemical reaction; it treats surface deposition (flux proportional to product of surface concentration and deposition velocity) and washout and rainout (rate determined by product of concentration, rainfall rate, and a washout efficiency coefficient.)*

AQSTM

Illinois Environmental Protection Agency
Air Resources Analysis Section
2240 Churchill Road
Springfield, IL 62706

Comments: *AQSTM is a Gaussian model that estimates short term (1 to 24 hr avgs) inert species concentrations from multiple (up to 200) point sources. It takes into account plume rise (Briggs, post-1970 formulas) and inversion breakup, vertical wind variation (power law approximation), and provides an adjustment for non-flat terrain.*

- *The horizontal concentration profile is Gaussian; the vertical is initially Gaussian and finally uniformly mixed; power-law approximations to Pasquill-Gifford dispersion parameters (with sampling time correction) are used.*
- *The dispersing species are assumed completely inert (no chemical or physical removal processes).*

ARAP

Aeronautical Research Associates
of Princeton, Inc.
P.O. Box 2229
50 Washington Road
Princeton, NJ 08530
(W. S. Lewellen, C. duP. Donaldson)

Comments: *ARAP is a complex second-order-closure model that basically addresses the buoyant plume problem. It simulates evolution (in the near field) of plumes (either momentum or buoyancy dominated) into either a quiescent or windy atmosphere with stable, neutral and unstable stratification. ARAP is essentially a straightforward numerical scheme for plume rise (see Chapter 7).*

ATM

Oakridge National Laboratory
Oakridge, TN 37830
(W. M. Culkowski, M. R. Patterson)

Comments: *ATM is a discrete Gaussian model for point, line and area sources that estimates concentrations averaged over user-specified periods (larger than 1 hr). It is formulated for constant wind, flat terrain, and accepts user-specified plume rise.*

- *Horizontal concentration distribution is assumed uniform in each wind sector (22.5^0 sector averaging). Pasquill-Gifford-Turner and Hosker-Briggs-Smith dispersion coefficients (for distances up to 10 km and between 10 and 50 km respectively) are used for vertical dispersion.*
- *No chemical processes are considered. Dry deposition is treated through an effective source approach ("tilted plume approximation").*

ARGONNE

Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL 60439
(G. L. Mellor, T. Yamada)

Comments: *ARGONNE is a second-order-closure model intended to simulate the behavior of buoyant plumes from large cooling ponds, basically on a mesoscale range.*

BPM

Systems Applications, Inc.
101 Lucas Valley Road
San Rafael, CA 94903
(M. K. Liu, D. Durran, P. Mundkur M. A. Yocke, J. Ames)

Comments: *BPM is a two-dimensional model operating in two alternative modes (it either adopts an Eulerian approach with an Eulerian coordinate system spanning the downwind and vertical directions, or a trajectory approach with the cells spanning the crosswind and vertical direction). It employs K theory and calculates steady state concentrations (6×10^2 cells, 50m/30m horizontal/vertical resolution). BPM contains conservation equations for pollutant concentration and total mass as well as for momentum and energy; thus the wind fields are calculated internally.*

- *Horizontal and vertical eddy diffusivities are assumed equal; they are functions of the height (and boundary layer parameters) only.*
- *BPM considers inert species only (no removal mechanisms, either physical or chemical).*
- *Numerical solution is obtained through fractional steps with upstream-differencing scheme.*

CDM/CDMQC

U.S. Environmental Protection Agency
Office of Research and Development
Research Triangle Park, NC 27711
(A. D. Busse, J. R. Zimmerman)

Comments: *CDM is a kinematic model that estimates either short term (1 to 24 hr) or long term (1 mo to 1 yr) concentration averages from point and area sources. It accounts for plume rise from point sources (Briggs, pro 1970 formulas) and vertical wind variation (power law profile). It is formulated only for flat terrain.*

- *Concentration distribution is assumed uniform in each wind sector. Power law approximations for Pasquill-Gifford dispersion coefficients are used. Algorithms for estimating existence of stack downwash effects and vertical depth of the well mixed plume.*
- *The model can estimate constant exponential decay with user-assigned half life.*

CRSTER

U.S. Environmental Protection Agency
Office of Air Quality Planning
and Standards
Research Triangle Park, NC 27711
(J. H. Novak, D. B. Turner, J. R. Zimmerman)

Comments: *CRSTER is a Gaussian model; it estimates concentrations averaged over either short term (1 hr to 12 hr) periods or over a year. It estimates plume rise (Briggs, post 1970 formulas) and takes into account vertical wind variation (power law extrapolation). The terrain is assumed flat.*

- *Pasquill-Gifford-Turner dispersion coefficients are used to estimate horizontal and vertical dispersion. Vertical dispersion is constrained by ground surface and inversion base (multiple reflection); concentration is finally assumed uniform in the vertical.*
- *No removal mechanisms are considered.*

GEM

Science Applications, Inc.
875 Westlake Boulevard
Suite 212
Westlake Village, CA 91361
(A. Fabrick, R. Sklarew, J. Wilson)

Comments: *GEM is a kinematic model for hourly averaged concentrations from a single point source. Plume rise is estimated by Briggs (pro 1970 formulas), but the user must specify the appropriate formula. Wind speed may be provided by the numerical wind model WEST. Nonflat terrain can be considered.*

- *Concentration is assumed to be Gaussian in the near field (vertically uniform in the far field); the user specifies dispersion coefficients of his own choice or from a variety of model provided options.*
- *Only linear chemical processes can be taken into account.*

IMPACT

Science Applications, Inc.
875 Westlake Boulevard,
Suite 212
Westlake Village, CA 91361
(A. Fabrick, R. Sklarew, J. Taft,
J. Wilson)

Comments: *IMPACT is a (three-dimensional) Eulerian grid model (10^4 cells; 1 km/50 m horizontal/vertical resolution; hourly averaged concentrations) employing K theory. The wind field is obtained by a divergence minimization algorithm (that takes into account the underlying terrain).*

- *Vertical eddy diffusivities are calculated as functions of height and boundary layer parameters; horizontal eddy diffusivities are obtained from the vertical ones through multiplication by a stability-dependent coefficient.*
- *IMPACT uses a version of the Hecht-Seinfeld-Dodge mechanism for the chemical kinetics. Surface deposition is calculated by assuming the removal flux proportional to the product of surface concentration and a deposition velocity.*
- *Numerical solution is obtained through fractional steps (with second order flux correction) method.*

INTERA

Intera Environmental Consultants
2000 West Loop South, Suite 2200
Houston, TX 77027
(R. B. Lanz, K. H. Coats, C. Kloepfer)

Comments: *INTERA is a (three-dimensional) Eulerian grid model (10^4 cells; variable resolution, hourly-averaged concentrations) employing K theory. The wind field is obtained by a divergence minimization algorithm (flat terrain assumed).*

- *Horizontal diffusivities are assumed to be simple exponential function of height only (involving stability dependent exponents); vertical eddy diffusivities are then calculated through multiplication by a stability-dependent coefficient.*
- *Only a linear reaction and surface deposition can be treated by INTERA.*
- *Numerical solution is obtained through an upstream differencing scheme.*

ISC/ISCST

H. E. Cramer Company, Inc.
University of Utah Research Park
P. O. Box 8049
Salt Lake City, UT 84108
(J. F. Bowers, J. R. Bjorklund,
C. S. Cheney)

Comments: *ISC/ISCST is a kinematic model for point, line, area and volume sources; the averaging time is user-specified, up to 24 hours. The model estimates plume rise (Briggs, post 1970 formulas) and takes into account vertical variation in horizontal wind speed (power law extrapolation).*

- *Pasquill-Gifford-Turner dispersion coefficients are used for point sources without effects of building wakes; a modified set of coefficients is used for volume sources and point sources with effects of building wakes. (For $x < 100$ m no treatment is provided). Perfect reflection from inversion base and ground surface and finally uniform mixing in the vertical is assumed.*
- *Only linear processes can be treated.*

MESOGRID

Environmental Research and Technology, Inc.
696 Virginia Road
Concord, MA 01742
(C. S. Morris, C. W. Benkley, A. Bass)

Comments: *MESOGRID is a three-dimensional Eulerian grid model (2×10^3 cells; variable resolution; hourly or longer averaged concentrations) employing K theory. The wind field is assumed two-dimensional; observed winds are iteratively adjusted to remove the excessive divergence in the interpolated wind field. MESOGRID uses a special horizontal treatment that is more appropriate to mesoscale problems: vertical advection is assumed much smaller than vertical diffusion whereas horizontal advection is assumed to be much smaller than horizontal advection.*

- *MESOGRID does not use a horizontal eddy diffusivity; its vertical eddy diffusivity is calculated through an algorithm, similar to the ones employed in IMPACT, PDM and RADM, based on the similarity theory for the planetary boundary layer.*
- *MESOGRID was specifically designed to estimate atmospheric conversion of SO_2 to sulfate; surface deposition is also included.*
- *Numerical solution by the method of moments horizontally; forward-centered differencing vertically.*

MESOPUFF

Environmental Research and Technology, Inc.
696 Virginia Road
Concord, MA 01742
(C. W. Benkley, A. Bass)

Comments: *MESOPUFF is a regional scale kinematic model for point sources that provides concentrations averaged over a user-specified period (with minimum of 1 hour). It takes into account plume rise (Briggs, pro 1970 formulas) and fumigation. It uses gridded wind speed values input at each update interval; the whole puff is advected depending on winds at puff center. The terrain is assumed flat.*

- *PGT coefficients are used for vertical and horisontal dispersion for distances less than 100 km; for larger distances Heffter's dispersion coefficients are used. The user specifies condition of either multiple reflection or uniform mixing below the inversion base.*
- *The model treats linear decay of SO_2 to SO_4^{-2} and dry deposition of SO_2 and SO_4^{-2}.*

MPTER

U.S. Environmental Protection Agency
Meteorology and Assessment Division
Research Triangle Park, NC 27711
(T. E. Pierce, D. B. Turner)

Comments: *MPTER is a kinematic point source model providing averages over 1 to 24 hours. Plume rise is treated through Briggs formulas. An adjustment for non-flat terrain is provided.*

- *PGT horisontal and vertical coefficients are used; finally uniform mixing is assumed in the vertical.*
- *Constant exponential decay with user-assigned half-life.*

MSDM

Lawrence Livermore Laboratory
University of California
Livermore, CA 94550
(D. L. Ermak, R. A. Nyholm)

Comments: *MSDM is a kinematic model for point sources providing hourly, seasonal or annual concentration averages. Plume rise is treated by empirical formulas and vertical wind variation through a power law extrapolation.*

- *Coefficients based on the Pasquill-Gifford scheme are used. Horizontal dispersion is corrected for initial dilution effects. Initially multiple reflection and finally uniform mixing is assumed in the vertical. In the long term mode sector averaging is used.*
- *Linear chemistry (chains of up to three reactions) and dry deposition and gravitational settling (proportional to the ground level atmospheric concentration) are treated.*

MULTIMAX

Shell Development Company
Westhollow Research Center
P.O. Box 1380
Houston, TX 77001
(J. H. Moser –
modified by Koss and Condrey
at Tennessee Valley Authority)

Comments: *MULTIMAX is a kinematic model for point souces providing 1-, 3-, 24- hour and annual concentration averages. It uses Briggs formulas for plume rise and power-law extrapolation for the vertical variation in wind speed.*

- *Pasquill-Gifford-Turner horizontal and vertical coefficients are used with optional sampling time correction. Vertical dispersion is assumed constrained by ground surface and inversion base (multiple reflection).*
- *Only linear processes can be handled.*

PAL

U. S. Environmental Protection Agency
Meteorology and Assessment Division
Research Triangle Park, NC 27711
(W. B. Peterson)

Comments: *PAL is a kinematic model that calculates 1 to 24 hour-averages of concentrations from point, area and four types of horizontal line sources (straight and curved). Plume rise is taken (optionally) into account through Briggs (post 1970) formulas. A power law extrapolation is used for the vertical wind speed. The terrain is assumed flat.*

- *PGT dispersion coefficients are used; both horizontal and vertical coefficients are corrected for initial dilution effects. Multiple reflection and finally uniform mixing is assumed in the vertical.*
- *No removal processes are considered.*

PDM

Systems Applications, Inc.
101 Lucas Valley Road
San Rafael, CA 94903
(M. K. Liu, D. Durran, P. Mundkur,
M. A. Yocke, J. Ames)

Comments: *PDM is a hybrid three-dimensional, Eulerian, grid and trajectory puff model (a Gaussian puff module is incorporated in an Eulerian grid model to enhance the spatial resolution near strong point sources). It calculates hourly averaged concentrations* (10^4 *cells, 1 km/50 m horizontal/vertical resolution). The wind field is determined either (a) by interpolating observed surface winds–assumed constant with height–and then estimating vertical winds in terms of the horizontal divergence, or (b) by employing a wind model that is based on the mass-consistency principle.*

- *The horizontal eddy diffusivity is a user-specified constant. The vertical diffusivity is assumed a function of height (and boundary layer parameters) and is calculated through an algorithm that utilizes atmospheric similarity theory.*
- *PDM calculates atmospheric conversion of* SO_2 *to sulfate; surface deposition is also included.*
- *Numerical solution through a fractional steps (flux corrected) method.*

PLMSTAR

Environmental Research and Technology, Inc.
696 Virginia Road
Concord, MA 01742
(F.W. Lurmann et al.)

Comments: *PLMSTAR is a Lagrangian trajectory model estimating short term averages of concentration (variable horizontal and vertical resolution provided by a two-dimensional wall of cells advected by the mean wind). Wind field is determined by a divergence minimization algorithm; the validity of the trajectory approximation is also checked under the specific conditions relevant to the calculations.*

- *Vertical eddy diffusivities are functions of height and (stability dependent) boundary layer parameters; the horizontal diffusivities are then calculated by multiplying with a stability dependent coefficient. Alternatively, eddy diffusivities for dispersion from strong point sources are calculated in terms of (absolute) dispersion parameters that are functions of the travel time from the source.*
- *A reduced form of the ERT photochemical mechanism describes plume chemistry.*
- *Numerical solution is obtained by a scheme that discriminates between stiff and non-stiff ordinary differential equations.*

PTDIS

U. S. Environmental Protection Agency
Meteorology Assessment Division
Research Triangle Park, NC 27711
(D. B. Turner, A. D. Busse)

Comments: *PTDIS is a kinematic model for a single point source and 1 hr averaged concentration. Plume rise is either user specified or estimated by Briggs (post 1970) formulas. Wind speed is assumed constant with height and the terrain is assumed flat.*

- *PGT horizontal and vertical dispersion coefficients are used; multiple reflection is assumed in the vertical.*
- *No removal processes are considered.*

PTMAX

U. S. Environmental Protection Agency
Meteorology Assessment Division
Research Triangle Park, NC 27711
(D. B. Turner, A. D. Busse)

Comments: *PTMAX is a kinematic model for a single point source and 1 hr averaged concentration. Plume rise is either user specified or estimated by Briggs (post 1970) formulas. Wind speed is assumed constant with height and the terrain is assumed flat.*

- *PGT horizontal and vertical dispersion coefficients are used; vertical dispersion is constrained by ground reflection only.*
- *No removal processes are considered.*

PTMTP

U. S. Environmental Protection Agency
Meteorology Assessment Division
Research Triangle Park, NC 27711
(D. B. Turner, A. D. Busse)

Comments: *PTMTP is a kinematic model for multiple (up to 25) point source and 1 hr averaged concentration. Plume rise is either user specified or estimated by Briggs (post 1970) formulas. Wind speed is assumed constant with height and the terrain is assumed flat.*

- *PGT horizontal and vertical dispersion coefficients are used; multiple reflection is assumed in the vertical.*
- *No removal processes are considered.*

RADM

Dames and Moore
Advanced Technology Group
1100 Glendon Avenue, Suite 1000
Los Angeles, CA 90024
(A. K. Runchal, W. R. Goodin,
K. J. Richmond)

Comments: *RADM is a three-dimensional Lagrangian particle model* (2×10^4 *particles; hourly averaged concentrations; variable resolution) utilizing K theory. First the probability of finding a particle at a given location is calculated and then the concentration at a given location is determined from the distribution of particles in an Eulerian framework. The wind field is obtained by a divergence minimization algorithm (that takes into account the influences of both the underlying terrain and the vertical temperature gradient.)*

- *Vertical eddy diffusivities are a function of height and (stability dependent) boundary layer parameters; horizontal eddy diffusivities are assumed functions of stability dependent boundary layer parameters only. Calculations are based on a random walk approach.*
- *RADM estimates conversion of* SO_2 *to sulfate. Surface deposition is included.*

RAM

U. S. Environmental Protection Agency
Meteorology Assessment Division
Research Triangle Park, NC 27711
(D. B. Turner, J. H. Novak)

Comments: *RAM is a kinematic model for point and area sources. It calculates 1 to 24 hr averages. Plume rise is treated by Briggs (post 1970) formulas and wind speed variation in the vertical by power law extrapolation. The terrain is assumed flat.*

- *PGT horizontal and vertical coefficients are used for dispersion over rural areas; Briggs coefficients are used for urban areas. Multiple reflection is assumed in the vertical.*
- *Constant exponential decay with user assigned half-life.*

RPM

Systems Applications, Inc.
101 Lucas Valley Road
San Rafael, CA 94903
(M. K. Liu, D. A. Stewart,
T.W. Tesche)

Comments: *RPM is a two-dimensional trajectory puff model based on the Gaussian plume concept. A wall of rectangular vertical cells (perpendicular to the plume centerline) expands downwind, its total dimensions being four times the values of the relative dispersion parameters. Mass is reapportioned in the cells through an artificial diffusion mechanism.*

- *Horizontal and vertical dispersion parameters that determine the cell wall size are assumed to be functions of the dispersion time. The McElroy-Pooler parameterization scheme is adopted to estimate absolute dispersion. Then relative dispersion parameters are just assumed to be 1.5 times smaller than the corresponding absolute dispersion parameters (for all atmospheric stability classes). Artificial diffusion coefficients are used to account for mass transfer between cells. All cells are assumed uniformly mixed; thus the model provides only horizontal resolution.*
- *Modified formulations of the Carbon-Bond Mechanism are adopted in the various versions of the RPM family of models.*
- *Numerical solution is obtained by schemes appropriate for the solution of the stiff ordinary differential equations that describe* concentration evolution in each expanding cell.

SCIM

GEOMET, Inc.
15 Firstfield Road
Gaithersburg, MD 20760
(R. C. Koch)

Comments: *SCIM is a kinematic model for point and area sources. It calculates 1 hr to 1 yr averages. The model takes into account plume rise (Briggs, post 1970 formulas) and wind speed variation in the vertical (power-law extrapolation).*

- *PGT dispersion coefficients are used for rural areas; McElroy coefficients are used for urban areas. Perfect ground reflection and finally uniform mixing is assumed in the vertical.*
- *Constant exponential decay with user assigned half-time.*

STRAM

Battelle Pacific Northwest Laboratories
P.O. Box 99
Richland, WA 99352
(J. M. Hales, D. C. Powell, T. D. Fox)

Comments: *STRAM is a two-dimensional Lagrangian trajectory model (essentially a segmented Gaussian model, 5-20 cells; hourly or longer averaged concentrations, variable resolution). Each segment of the STRAM is mass-integrated in the crosswind and vertical direction. The rate of change of the integrated pollutant mass is controlled by the difference between the upstream inflow and downstream outflow area-integrated mass flux. A combination of (volume-integrated) chemical reaction, washout, and source and sink terms, is also included in the mass balance equations. The wind field is determined by direct interpolation (only horizontal wind speeds are required). STRAM is intended for long range transport problems (distances larger than 10 km from the source).*

- *Horizontal and vertical dispersion parameters are assumed to be functions of the downwind distance along the trajectory, described by simple exponential laws and stability dependent coefficients (the horizontal dispersion parameter exponent is taken equal to 0.9; the corresponding exponent for the vertical dispersion is assumed stability dependent).*
- *STRAM calculates atmospheric conversion of SO_2 to sulfate; surface deposition and washout-rainout are included.*
- *Numerical calculations employ Gauss-Laguerre quadrature; second-order Runge-Kutta integration.*

TCM

Texas Air Control Board
6330 Hwy 290 East
Austin, TX 78723
(R. A. Porter, J. H. Christiansen)

Comments: *TCM is a long term average (1 mo to 1 yr) model for point and area sources. Briggs plume rise equations under unstable or neutral conditions are used for all atmospheric conditions (only for the point sources). A power law is assumed for the vertical variation of the wind speed. The terrain is assumed flat.*

- *Uniform concentration distribution in the horizontal direction are assumed within each wind sector (22.5° sector averaging). Power-law approximation to Pasquill-Gifford curves are used for vertical dispersion; finally uniform mixing is assumed.*
- *Constant exponential decay with user assigned half-time.*

TEM

Texas Air Control Board
6330 Hwy 290 East
Austin, TX 78723
(R. A. Porter, J. H. Christiansen)

Comments: *TEM is a kinematic model providing short term (10-min, 30-min, 1-hr, 3-hr, 4-hr, 24-hr averages) concentration from multiple point (up to 300) and area (up to 200) sources. Briggs formulas are used to calculate plume rise and a power law extrapolation is used for wind variation in the vertical. The terrain is assumed flat.*

- *Power law approximations of Pasquill-Gifford coefficients are used; finally uniform mixing is assumed in the vertical.*
- *Constant exponential decay with user-assigned half-life.*

TRACE

AMI
Applied Modeling, Inc.
Los Angeles
(K.T. Tran)

Comments: *TRACE is a Lagrangian trajectory model providing short term averages of concentration (variable horizontal and vertical resolution of a two-dimensional wall of cells advected by the mean wind). Wind field is determined by a divergence minimization algorithm.*

- *Vertical eddy diffusivities are functions of height and (stability dependent) boundary layer parameters; the horizontal diffusivities are then calculated by multiplying with a stability dependent coefficient.*
- *The McRae-Seinfeld photochemical mechanism is employed for the description of the chemical kinetics.*
- *Numerical solution is obtained by a scheme that discriminates between stiff and non-stiff ordinary differential equations.*

VALLEY

U. S. Environmental Protection Agency
Office of Air Quality Planning
and Standards
Research Triangle Park, NC 27711

(E. W. Burt)

Comments: VALLEY is a kinematic model that calculates 24 hr, seasonal, and annual averages of concentrations from multiple (up to 50) point sources. It estimates plume rise (Briggs, post 1970) formulas and assumes constant wind speed with height. An adjustment for non-flat terrain is included.

- *Horizontally uniform concentration distribution is assumed in each wind sector (22.5° sector averaging). PGT coefficients (with near-ground source correction for urban areas) are used for the vertical dispersion. Multiple reflection and finally uniform mixing are assumed in the vertical.*
- *Constant exponential decay with user-assigned half-life.*

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for Appendix A1.2

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CHAPTER 2

THE TURBULENT REACTING PLUME MODEL (TRPM): STRUCTURE AND PARAMETERS

2.1 INTRODUCTION

In order to overcome deficiencies of currently available plume models, as they were described in Chapter 1, a new scheme, to be called the Turbulent Reacting Plume Model (TRPM), has been developed and is schematically presented in Figure 2-1 (page 67). The TRPM offers a comprehensive description of the evolution of atmospheric plumes, conforming to the requirement that models of nonlinear in-plume processes must:

(i) be based on ensembles of instantaneous and not time averaged realizations of the plume (avoid temporal averaging),

(ii) not ignore the existence of mean concentration gradients in the instantaneous plume cross sections (avoid spatial averaging), and

(iii) include a scheme that estimates the effects of fine scale fluctuations on the chemical rates.

In this treatment, and at the present level of development of the TRPM, the focus is on the quantitative analysis of the *interaction* of mixing and chemical processes. The approach followed discriminates between fluid-mechanical phenomena that interact with nonlinear chemistry (relative or two-particle dispersion due to small scale turbulence of the background air, possibly aided by the initial plume buoyancy and momentum) and phenomena that do not interact with chemistry (meandering, expected plume rise) and takes them into account separately.

The working model is a modular mathematical scheme that allows for alternative descriptions (at various levels of complexity) of the various processes involved in the reaction-dispersion phenomenon.

The core of the model is a "master module" that contains the differential evolution or algebraic local equations (depending on the assumptions appropriate for each specific system) for "progress variables" that describe the state of dispersion and reaction process. A new progress variable that utilizes spatially varying stoichiometry to reduce computational burden, and at the same time is a useful quantitative measure of the effect of mixing on reaction at each point, is introduced and used in this work; it is called the *"local phenomenal extent of reaction"* and the governing equations are formulated in terms of it. These equations represent the fundamental transport-reaction balances. They utilize

(a) a first order closure scheme for the turbulent dispersion (modified K theory: modified in the sense that the K's used are not properties of the flow field but, at any "receptor point," of the specific source-receptor pair, and the solution is relevant to expected instantaneous values and not temporally and spatially averaged quantities), and

(b) an indirect chemical closure scheme for the turbulent kinetic rates based on a "concentration field splitting" technique that accounts for the effect of fluctuations in the nonlinear terms. (For comparison calculations the model can ignore this effect and use conventional, non-turbulent kinetics.)

The calculations performed by the master module of the TRPM estimate expected pointwise concentrations of reactants and products inside the instantaneous plumes (relative to the center of mass of each cross-section). The required inputs for these calculations (to be called "inner level" parameters) are supplied by independent "peripheral modules" as follows:

(a) Dispersion coefficients that account for relative dispersion processes alone: A new iterative scheme that allows their estimation from observed atmospheric turbulence spectra has been formulated and is presented in Chapter 6. Alternatively available semi-empirical relations can also be used.

(b) The intensity of plume segregation (which measures completeness of fine scale mixing): This can be computed alternatively, from a first order closure numerical scheme for σ_c^2, or from the analytical expressions provided by the "Localized Production of Fluctuations Model" which has been developed for the needs of this work and is presented in Chapter 5.

Another peripheral module provides the information needed for the a posteriori calculation of averaged, or instantaneous, fixed point concentrations (needed to connect the plume model with more extended air quality models) by determining its mean path and local time-averaged size through "outer level" parameters. These define a translating coordinate system attached to the instantaneous plume centerline (i.e.,following its bulk bodily movements). Plume rise and meandering determine the position of this system. Meandering is modeled as a random (typically Gaussian) process through the fluid particle transition function of the turbulent field, and plume rise is simulated either by a comprehensive three-dimensional integral approximation scheme or, alternatively, by simple semi-empirical formulas.

The availability of alternative schemes for parameter estimation ensures flexibility of the overall formulation and allows control on the complexity of the working model and of the associated computational burden, in accordance with the quality of available inputs and the objective of the particular calculations. Application of the TRPM to the NO - NO_2 - NO_3 system of reactions, which is of particular importance in point-source atmospheric plumes, is presented in Chapter 3; comparison with available experimental data offers a satisfactory first evaluation of the model.

The following analysis focuses on the model problem described by equations (1.3-1) and (1.3-2) of Chapter 1, i.e. the second order reaction between the unpremixed species *A* (from the source) and *B* (from the background air). The objective is to transform the reaction–dispersion equation (1.3-6) in a solvable form via appropriate transport and chemical closure schemes, i.e. via a realistic parameterization of the turbulent fluctuation correlations appearing in equations (1.3-6) and (1.3-7).

2.2 BASIC ASSUMPTIONS AND APPROXIMATIONS

At the present stage of development of the TRPM it is assumed that the fine scale turbulence responsible for the phenomena of plume growth and entrainment is determined mainly by the fine scale dynamics of the ambient atmospheric flow field. Thus we neglect the effect that initial plume dynamics (buoyancy and momentum) may have on the evolution of the reactive system. The justification for this assumption is that in most practical cases the self-generated turbulence of the plume is a dominant factor in the mixing process only for travel times up to a few seconds for typical wind speeds (Csanady, 1973 - Section 6.12). Since the overall mixing of the plume with the background air will also be minimum during this stage of plume dispersion, it is therefore reasonable to conclude that no appreciable conversion of reactants to products has taken place in the initial phases that are dominated by the source dynamics. Naturally this assumption becomes more realistic in cases where initial buoyancy and momentum are actually small (as is the case in controlled wind tunnel experiments that can be utilized for initial model verification). If, however, the source effects are so intense that mixing at the initial phases of plume growth should be taken into account in a more precise way, then a first practical solution to this problem is to consider a virtual source at a sufficient distance upwind of the real source, such that background turbulence alone would have caused the same overall mixing at points downwind as self-generated turbulence acting for the actually traveled distances.

To meet the requirement that the governing equations must represent the *expected* instantaneous dynamics of the plume and not some time averaged envelope, we adopt a frame of reference with its origin always on the meandering centerline of the plume. A standard Galilean transformation is needed for the fixed frame equations to apply in the new coordinates. The mean concentration fields (*not* the corresponding stochastic fields) viewed from the moving frame are in a "true" steady state in the sense that they remain invariant with respect to infinitesimal time shifts. A time averaged field viewed from a fixed position would be in steady state only for averaging times long enough to incorporate and "smooth out" meandering effects of various scales. Thus the steady state of the plume envelope as viewed from a ground observer is a different concept from the steady state that is considered here and that actually refers to isolated relative diffusion.

For a continuous steady release one has $\partial \langle \cdot \rangle / \partial t = 0$ in the meandering coordinates. For notational convenience it is subsequently assumed that all dependent and independent variables are defined in the moving frame. In this way random bodily movements of the plume are "extracted" from the mean mixing operator $\langle \mathcal{L}^M \rangle$, (modeled through a Lagrangian scheme) which still describes advection and relative turbulent as well as molecular diffusion phenomena. The assumption that this operator remains of the same form in the fixed and the randomly meandering frames is discussed in detail in Chapter 6 (by considering essentially the operator's Green's function), and is justified for the idealized case of point source and homogeneous-stationary turbulence; for more realistic (and therefore complicated) situations one expects this assumption to be valid for relatively *mild meandering.*

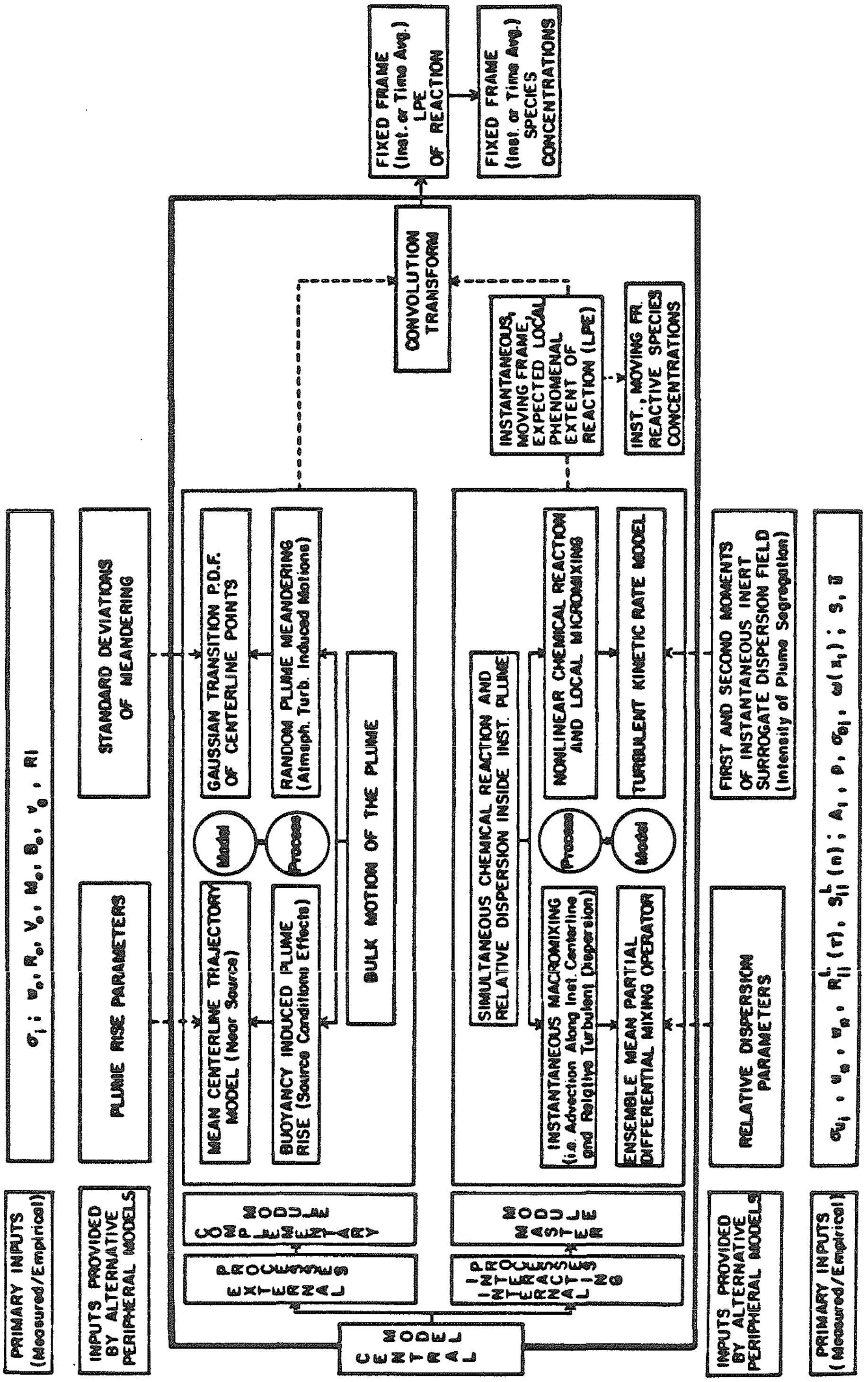

Figure 2-1

Structure of the Turbulent Reacting Plume Model (TRPM)

2.3 MODELING THE GOVERNING EQUATIONS: THE MIXING TERM

$\langle \mathcal{L}^M \rangle$ must be modeled in such a way that after the introduction of the closure approximation it still describes mean instantaneous realizations of the plume. Exclusively "fluid particle dispersion" will be associated with $\langle \mathcal{L}^M \rangle$ on the assumption that molecular diffusion is negligible in comparison to turbulent transport. Special attention must be given to this step. Molecular diffusion is by no means a "negligible" or unimportant phenomenon in the structure of the overall process. On the contrary, it may control the overall rates of chemical conversions. However, its major effect consists of *homogenizing* the mixture of plume gases and background air at local scales and not in transporting material macroscopically. Thus molecular diffusion affects the steady state distribution of fluctuations rather than of mean concentrations, which are determined by turbulent diffusion. In this sense we "neglect" the molecular diffusion term in the l.h.s. of equation (1.3-6); actually the effects of molecular diffusion will be *incorporated implicitly* in the r.h.s. of this equation, in a phenomenal kinetic rate that accounts for the effects of fine scale fluctuations.

The theoretical basis for the development of closure schemes that take into account the scale–dependent properties of the mixing process, and therefore reflect the *nonlocal* character of turbulent dispersion, is reviewed in the monograph of Leslie (1973 – Chapters 8 and 12) and in Monin and Yaglom (1975 – Section 24); more recent developments are discussed in Jiang (1985). These schemes lead to the development of integrodifferential equations for $\langle c \rangle$ (more exactly for the transition probability density of fluid particles) that involve the mixed space–time correlations of either Eulerian or Lagrangian velocity fields. However, the current formulation of the TRPM adopts the simplest version of this approach by utilizing a dispersion equation with "apparent" eddy diffusivities that depend on the travel time (see Csanady, 1973 – Section 3.8; Berlyand, 1975 – Section 2.6). A formal construction of this model is possible, e.g. starting from Roberts' (1961) equation (equation 24.8 of Monin and Yaglom, 1975), and reducing it to a partial differential equation by assuming

(i) velocity fields that are delta correlated in space (see also Runca et al., 1983), and

(ii) that the fluid particles' positions constitute first order Markovian processes.

A more detailed discussion of the assumptions and problems associated with the apparent eddy diffusivities concept is presented in Chapter 6.

Introducing the eddy diffusivities in terms of the instantaneous plume description, i.e. as

$$K_i(t) = \frac{1}{2}\frac{{\sigma_{R_i}}^2}{dt} \qquad (2.3-1)$$

where σ_{R_i} is the dispersion parameter for relative diffusion, the ensemble mean form of the mixing operator will be

$$\left\langle \mathcal{L}^M(\cdot) \right\rangle \simeq \mathcal{L}^M_K \langle\cdot\rangle = \frac{\partial\langle\cdot\rangle}{\partial t} + \langle u_i\rangle \frac{\partial\langle\cdot\rangle}{\partial x_i} - K_i \frac{\partial^2\langle\cdot\rangle}{\partial x_i \partial x_i} \qquad (2.3-2)$$

A further *optional* assumption in the TRPM is that of negligible turbulent diffusion in comparison to advection in the direction of mean wind speed (the commom "slender plume approximation"). This assumption of no back-mixing implies that plume species will interact chemically only with the background air and not with plume material of different "age" (which is at a different stage of dilution and chemical conversion). Since recirculation eddies inside the plume will necessarily mix "fresh" effluent with "older" material, the validity of this approximation will depend on the magnitude of the mean wind speed and the atmospheric stability conditions.

Thus, for example, for steady and relatively strong mean wind speed $\overline{u}_1$ in the x_1-direction, the mean mixing operator will be approximated by

$$\mathcal{L}^M_K \langle\cdot\rangle = \overline{u}_1 \frac{\partial\langle\cdot\rangle}{\partial x_1} - K_2(x_1)\frac{\partial^2\langle\cdot\rangle}{\partial x_2^2} - K_3(x_1)\frac{\partial^2\langle\cdot\rangle}{\partial x_3^2} \qquad (2.3-3)$$

2.4 MODELING THE GOVERNING EQUATIONS: THE REACTION TERM

(a) The Chemical Closure Problem

Modeling the r.h.s. of equation (1.3-6), i.e. introducing a closure scheme for the second order turbulent kinetics, has been the explicit or implicit objective of an extensive amount of research in several fields of science and engineering; the relatively few and recent applications in the field of air pollution modeling were mentioned in the review of Chapter 1.

At this point one must realize that a knowledge of the fundamental concepts underlying the various approaches that have been proposed to provide closure to turbulent kinetics equations (and of the relative merits and limitations of these approaches) is a prerequisite in selecting the most appropriate method for a given application; for this reason a review and classification of existing modeling methods, with the focus on their potential applicability to the atmospheric plume problem, is presented in Chapter 4.

To summarize some basic ideas of Chapter 4, approaches that deal explicitly with global Eulerian statistical transport-reaction equations of the form of (1.3 - 3) and (1.3 - 6) can be classified as "direct", when correlations (or joint pdf's) of reacting species concentrations such as c_A, c_B are modeled directly through algebraic or differential equations, and as "indirect" or "mixing-reaction-decoupling" approaches, in which the quality of mixing (at both macroscopic and microscopic scales) is studied separately, in terms of some auxiliary variables, commonly called "conserved scalars", that are not affected by the chemical reaction, and is subsequently related to the observed phenomenal chemical rate.

The indirect closure method is presently at a better state of development and in general leads to more tractable schemes than direct methods; it was actually originated as early as 1928 (Burke and Schumann, 1928) and has often been reintroduced since then (Hawthorne et al., 1949; Toor, 1962). In the case of infinitely fast ("instantaneous") reactions, closure is needed only for correlations or pdf's of the conserved scalars (e.g. Kewley's (1978) model). When the chemical rate is finite, parameterization of expressions involving both conserved scalars and reaction sensitive variables is also necessary. Such an approach was adopted by Shu (1976), Lamb (1976), and Lamb and Shu (1978); however, their analysis was restricted to macroscopically cross- sectionally uniform concentration fields and thus limited the applicability of their model to one-dimensional problems (i.e. considering variations of mean concentrations only in one, spatial or temporal, dimension).

A general formulation of the method, in a way that holds for pointwise defined instantaneous consentrations in arbitrary, non-uniform, fields is briefly presented next; some further discussion can be found in Chapter 4 and in Appendix A4.1.

(b) The "Concentration Field Splitting" Method

Let $c_A^I(\mathbf{x},t)$, $c_B^I(\mathbf{x},t)$ be the hypothetical concentrations of A and B that would exist at the space-time point $(\mathbf{x},t)$ if they did not react with each other but, still, were transported in the field by exactly the same molecular and convective mechanisms. We can define these new variables as concentrations of fictitious *inert surrogates* A^I, B^I, of A and B. c_A, c_B as well as c_A^I, c_B^I at any $(\mathbf{x},t)$ are random variables. The approach proposed in this work accounts for the possible states of mixing of the two species by viewing each of the above concentration fields not only as random functions of $(\mathbf{x},t)$ but also as *functionals* of the entire ensembles of realizations of the inert surrogate of their "mixing partners" at $(\mathbf{x},t)$. Indeed, the possible micromixing states of, say, A or A^I at any point depend on the probabilistic characteristics of the conentration of B^I at this point. Thus $c_A(\mathbf{x},t)$ and $c_A^I(\mathbf{x},t)$ are functionals of the ensemble of all possible values of $c_B^I(\mathbf{x},t)$. This dependence is expressed formally through the following integral representation of each random realization of, say, $c_A(\mathbf{x},t)$:

$$c_A\left(\mathbf{x},t;[c_B^I(\mathbf{x},t)=\gamma_B^I]\right)=\int c_A\left(\mathbf{x},t;[c_B^I]\right)\,\delta\left(\gamma_B^I-c_B^I(\mathbf{x},t)\right)\,dc_B^I \qquad (2.4-1)$$

Then, defining

$$a = c_A\left(\mathbf{x}, t; [c_B^I = 0]\right), \quad \alpha = c_A\left(\mathbf{x}, t; [c_B^I = \gamma_B^I \neq 0]\right) \qquad (2.4-1a)$$

and similarly a^I and α^I for c_A^I, b and β for c_B, and b^I and β^I for c_B^I, one has

$$\begin{aligned} c_A(\mathbf{x},t) &= a(\mathbf{x},t) + \alpha(\mathbf{x},t) \\ c_A^I(\mathbf{x},t) &= a^I(\mathbf{x},t) + \alpha^I(\mathbf{x},t) \\ c_B(\mathbf{x},t) &= b(\mathbf{x},t) + \beta(\mathbf{x},t) \\ c_B^I(\mathbf{x},t) &= b^I(\mathbf{x},t) + \beta^I(\mathbf{x},t) \end{aligned}$$

The advantage of this representation ("concentration field splitting") lies in the fact that the evolution of a, α etc., and of their statistical moments and correlations, is more easily predictable than of the reactant concentrations themselves.

One can use (2.4-1) and the ensemble averaged form of (1.3-3) to deduce relations between correlations of c_A, c_B and a, α, b, β, a^I, α^I, b^I and β^I (see Chapter 4). Thus, when the forward reaction in (1.3-1) dominates the backward (a situation which is expected to be valid in the near field of plume dispersion), and therefore $\left\langle c_A^I(\mathbf{x},t)\right\rangle \geq \langle c_A(\mathbf{x},t)\rangle$, $\left\langle c_B^I(\mathbf{x},t)\right\rangle \geq \langle c_B(\mathbf{x},t)\rangle$, it can be shown that

$$\langle c_A c_B\rangle = \langle \alpha\beta\rangle, \quad \left\langle c_A^I c_B^I\right\rangle = \left\langle \alpha^I \beta^I\right\rangle \qquad (2.4-2)$$

and

$$\langle a(\mathbf{x},t)\rangle = \left\langle a^I(\mathbf{x},t)\right\rangle, \quad \langle b(\mathbf{x},t)\rangle = \left\langle b^I(\mathbf{x},t)\right\rangle \qquad (2.4-3)$$

In this case, with the introduction of the *mixing functions*

$$M_{c_1 c_2} = \frac{\langle c_1 c_2\rangle}{\langle c_1\rangle \langle c_2\rangle}, \quad M_{c_1 c_2}^I = \frac{\left\langle c_1^I c_2^I\right\rangle}{\left\langle c_1^I\right\rangle \left\langle c_2^I\right\rangle} \qquad (2.4-4)$$

one can obtain the expression:

$$\langle c_A c_B\rangle = \frac{\varphi}{\mu_A \mu_B} M_{AB}^I \left[\langle c_A\rangle - (1-\mu_A)\left\langle c_A^I\right\rangle\right] \left[\langle c_B\rangle - (1-\mu_B)\left\langle c_A^I\right\rangle\right] \qquad (2.4-5)$$

where φ is the *reaction parameter* and μ_A, μ_B are the *mixing parameters* defined by

$$\varphi = \frac{M_{\alpha\beta}}{M^I_{\alpha\beta}} \tag{2.4 – 6}$$

and

$$\mu_A = \frac{\langle \alpha^I \rangle}{\langle c^I_A \rangle}, \quad \mu_B = \frac{\langle \beta^I \rangle}{\langle c^I_B \rangle} \tag{2.4 – 7}$$

In the special case of macroscopically uniformly mixed fields μ_A and μ_B represent the fractions of the total quantities of the fictitious inert surrogates of A and B that coexist in completely micromixed volumes.

Equation (2.4-5) is an exact relation. It expresses the unknown correlation in terms of mean values of the unknowns and in terms of parameters all of which except one, namely φ, depend only on inert scalar mixing. The problem of course has been transformed into the problem of estimation of these parameters.

A substantial simplification of (2.4-5) can be obtained in the case where $\langle c_B(\mathbf{x}, 0) \rangle$ is nonzero for all $\mathbf{x}$. This of course means that $\langle c^I_B(\mathbf{x}, t) \rangle$ is also nonzero for all $\mathbf{x}$ and t and therefore $\langle a^I(\mathbf{x}, t) \rangle \equiv 0$, $\langle \alpha^I(\mathbf{x}, t) \rangle \equiv \langle c^I_A(\mathbf{x}, t) \rangle$, which give $\mu_A = 1$ for all $(\mathbf{x}, t)$ (notice, however, that $\mu_B \neq 1$ in general). This result can be utilized for a typical atmospheric plume where the emissions of A (e.g. NO) have near source concentrations that are orders of magnitude higher than those of B (e.g. O_3). The fact $\langle c_A \rangle \gg \langle c_B \rangle$ near source implies that it will make no observable difference to the conversions of A if it were assumed that B is perfectly mixed with the emissions at the source, at a concentration equal to that of the ambient (in agreement with the idealization of the point source). Indeed, in such a case it does not make an appreciable difference to the overall evolution of reaction and the observed conversions of A if A and B are initially premixed or unpremixed. This further means that fine scale segregation of A and B inside the plume is induced mainly by the chemical reaction. This simplifies the analysis considerably, especially if it is assumed that the reaction is not infinitely fast and a local steady state with microscopic coexistence of

A and B prevails. It is then possible using intuitive arguments to suggest that

$$\mu_B \simeq \frac{1}{M^I_{AA}}, \text{ and } M^I_{AB} \simeq 1$$

are acceptable *closure assumptions*. It can further be shown, by examining the significance of the participating correlations under the aforementioned conditions, that φ should be of order one. This is corroborated by the analysis of Shu (1976),Lamb and Shu (1978), and Shu et al. (1978) for monodimensional systems.

Hence, to recapitulate, in the case of a point release of A into an initially uniform field of B, and under the assumption that the concentrations of A, at least near the plume axis, are much greater than the background concentration of B, we can approximate the term $\langle c_A c_B \rangle = \langle c_A \rangle \langle c_B \rangle + \langle c'_A c'_B \rangle$ by

$$\langle c_A c_B \rangle \simeq M^I_{AA} \langle c_A \rangle \langle c_B \rangle + \left(1 - M^I_{AA}\right) \langle c^I_B \rangle \langle c_A \rangle \qquad (2.4-8)$$

where M^I_{AA} is a function characteristic of the state of *inert* species mixing in the plume.

Alternatively,if we consider the fluctuations $c^{I\,\prime}_A$ about $\langle c^I_A \rangle$, M^I_{AA} can be written as $M^I_{AA} = 1 + I^I_A$ where

$$I^I_A = \frac{\left(\sigma^I_A\right)^2}{\left\langle c^I_A \right\rangle^2} \text{ where } \left(\sigma^I_A\right)^2 = \left\langle (c^I_A)'^2 \right\rangle \qquad (2.4-9)$$

is the relative intensity of concentration fluctuations of an inert emitted species in a plume, or *"intensity of stream segregation"* (see Chapter 4 for a more detailed discussion).

Introducing I^I_A we can write (2.4-8) as

$$\langle c_A \, c_B \rangle \simeq \langle c_A \rangle \langle c_B \rangle + I^I_A \langle c_A \rangle \left(\langle c^I_B \rangle - \langle c_B \rangle\right) \qquad (2.4-10)$$

which of course is equivalent to

$$\langle c'_A \, c'_B \rangle \simeq I^I_A(\langle c^I_B \rangle - \langle c_B \rangle)$$

The overall mean rate of reaction (1.3-1) at a point will therefore be

$$\langle R\rangle \simeq \tilde{R} = k_f \langle c_A\rangle \langle c_B\rangle - k_f I_A^I \langle c_A\rangle \left(\langle c_B^I\rangle - \langle c_B\rangle\right) - k_b \langle c_P\rangle \qquad (2.4-11)$$

Hence, all the effects of turbulence (or incomplete mixing) on the chemical kinetics have been incorporated in the second term of (2.4-11) which involves

(i) the mean concentrations of the reactive species $\langle c_A\rangle$, $\langle c_B\rangle$ which are the actual unknown variables we want to estimate,

(ii) the mean concentrations of inert surrogate species $\langle c_A^I\rangle$, $\langle c_B^I\rangle$, and

(iii) the variance of fluctuations of an inert emitted species.

The form of the second term of (2.4-11) suggests that it can be interpreted as representing a *fictitious reverse reaction* that retards the overall kinetic scheme in comparison to perfectly mixed conditions. The kinetic constant $k_f I_A^I$ of this "reaction" will depend on position in the plume because I_A^I shows a strong dependence on axial and radial position. The "reactants" participating in this fictitious step are A and the portion of B at any point that has already undergone chemical reaction (and therefore it is not actually available at that point). Thus the term $\langle c_B^I\rangle - \langle c_B\rangle$ can be viewed as representing "occupied" or "de-activated" B molecules that participate in a backward reaction with A, with a kinetic constant that is determined by the intensity of turbulent fluctuations. The behavior of this term is determined by the relative magnitude of I_A^I, $\langle c_A\rangle$ and $\left(\langle c_B^I\rangle - \langle c_B\rangle\right)$.

Thus, the initial problem of solving the system of equations of type (1.3-6) with $\mathcal{L}^M$ given by (1.3-7) has been reduced to solving

$$\mathcal{L}_K^M c_{A,B,P} = \tilde{r}_{A,B,C} \ \text{ with } \tilde{r}_A = \tilde{r}_B = -\tilde{r}_P = -\tilde{R} \qquad (2.4-12)$$

where $\tilde{R}$ is given by (2.4-11) and $\mathcal{L}_K^M$ is given by (2.3-2).

2.5 THE WORKING COMPUTATIONAL SCHEME

2.5.1 Reduction of the Number of Equations: The Local Phenomenal Extent of Reaction

When the number of independent reactions is smaller than the number of reacting species, stoichiometric relations can be combined with the concept of inert surrogate concentrations to reduce the number of partial differential equations needed to describe the evolution of multimolecular systems in turbulent, incompletely mixed, fields.

The conventional *extent* or *degree of advancement* of reaction is a useful tool in utilizing stoichiometric relations to simplify the kinetic description of chemical systems that evolve either in space or in time. For such systems the number of governing equations for the evolution of concentration fields can always be reduced to the number of independent reactions between the species. Then, at steady state, simple algebraic expressions relate the concentrations of all species to the extents of independent reactions. (Such a formulation is obviously useful when the number of reacting species is larger than the number of independent reactions). When however chemical reaction and macroscopic, as well as microscopic, dispersion effects are coupled and evolve *simultaneously in space and time*, the conventional formulations are no longer useful. For this reason we introduce here the concept of a local phenomenal extent for a spatially distributed reaction, which incorporates both stoichiometry and diffusion effects to simplify the description of a simultaneously reacting and diffusing mixture of species. Suppose the p species $A_1, A_2, \dots, A_p$ participate in the reaction

$$0 = \sum_{i=1}^{p} \nu_i A_i$$

where $i = 1, 2, ..., p$ and ν_i is the stoichiometric coefficient of species A_i, that takes place in an arbitrary flow field. In general the reactants will not be uniformly mixed at a microscopic or perhaps and at a macroscopic level. Therefore the concentration c_i of species A_i will be in general a function of position and time, $c_i = c_i(\mathbf{x}, t) = c_i(x_1, x_2, x_3, t)$. Furthermore, when the reaction occurs in a turbulent flow field the concentrations of species A_i, $i = 1, 2, ..., p$ will also constitute stochastic fields. Thus in general we can write $c_i(\mathbf{x}, t) = \langle c_i(\mathbf{x}, t) \rangle + c_i'(\mathbf{x}, t)$. Introducing the concept of an *inert surrogate* A_i^I for each of the species A_i, that is of a fictitious inert species emitted from the same sources and having the same dispersion properties as A_i, we can define the hypothetical instantaneous and mean inert surrogate concentration fields $c_i^I(\mathbf{x}, t)$ and $\langle c_i^I(\mathbf{x}, t) \rangle$. Then a phenomenonal extent of reaction, which will be a stochastic function of position in the reaction field, can be defined by the relation

$$\xi(\mathbf{x}, t) = \frac{c_i(\mathbf{x}, t) - c_i^I(\mathbf{x}, t)}{\nu_i} \qquad (2.5-1)$$

Notice that for species participating in a "forward" reaction ("reactants") the stoichiometric coefficient ν_i will be by definition negative while for species participating in a "backward" reaction ("products") ν_i will be positive.

The "physical" meaning of ξ can be interpreted as the extent or degree of advancement that would characterize a reaction at a point $\mathbf{x}$ and time t if this reaction would take place in a hypothetical perfectly mixed volume in which the initial uniform concentrations of reactants would correspond to the concentrations that diffusion processes acting *alone* would have created at $(\mathbf{x}, t)$. Hence ξ does not correspond directly to any actual state of conversion of reactive species, nor can it characterize by itself the state of evolution of a chemical process. It is rather an artifact depending on the whole structure of the system (dispersion phenomena, distribution of sources, etc.) and can simplify significantly — as we will show in the following — the complexity of its description when there are more reacting species than independent reactions.

Once the dynamic equations for the evolution of $\langle \xi(\mathbf{x}, t) \rangle$ as well as of the inert surrogate mean concentration fields $\langle c_i^I(\mathbf{x}, t) \rangle$ have been formulated and solved, then the mean concentration of any reacting species is calculated directly by

$$\langle c_i(\mathbf{x}, t) \rangle = \langle c_i^I(\mathbf{x}, t) \rangle + \nu_i \langle \xi(\mathbf{x}, t) \rangle \qquad (2.5-2)$$

Thus, for the reaction $A + B \rightleftharpoons P$ we will have at any point $\mathbf{x}$ $\langle c_A \rangle = \langle c_A^I \rangle - \langle \xi \rangle$, $\langle c_B \rangle = \langle c_B^I \rangle - \langle \xi \rangle$, and $\langle c_P \rangle = \langle c_P^I \rangle + \langle \xi \rangle$. Thus, instead of solving the system of equations (2.4-12) we need only solve one dynamic equation for $\langle \xi \rangle$:

$$\mathcal{L}_K^M \langle \xi \rangle = \tilde{R} \tag{2.5 – 3}$$

with $\mathcal{L}_K^M$ given by (2.3-3).

The approximate reaction rate given by equation (2.4-11) can be written as a quadratic expression in $\langle \xi \rangle$, the coefficients being functions of properties of the inert surrogate fields:

$$\tilde{R} = \tilde{R}_1(\mathbf{x}, t) \langle \xi \rangle^2 + \tilde{R}_2(\mathbf{x}, t) \langle \xi \rangle + \tilde{R}_3(\mathbf{x}, t) \tag{2.5 – 4}$$

where

$$\begin{aligned} \tilde{R}_1 &= k_f (1 + I_A^I) \\ \tilde{R}_2 &= k_f \langle c_A^I \rangle (1 + I_A^I) + k_f \langle c_B^I \rangle + k_b \\ \tilde{R}_3 &= k_f \langle c_A^I \rangle \langle c_B^I \rangle - k_b \langle c_P^I \rangle \end{aligned} \tag{2.5 – 4a}$$

In situations relevant to atmospheric plumes, inert concentration fields can often be assumed to be described adequately by appropriate Gaussian formulas; in this case it is obvious that the computational burden involved in the solution of (2.4-12) is reduced significantly. Further, in cases of infinite rate chemistry, where pointwise equilibrium is assumed for the instantaneous concentrations and the mean rate is equal to zero, $\langle R \rangle = 0$ then only estimates for the inert surrogate concentration fields and the variance of inert species fluctuations are needed for the direct algebraic calculation of the reactive species concentration fields.

2.5.2 Estimation of Fixed Frame Concentrations

The mean location of the plume and the statistical properties of its meandering motion can be used to estimate reactive concentrations at any fixed point once the corresponding concentrations in the translating frame are calculated by the master module.

The problem is as follows: We seek the expected instantaneous concentration, $\langle \tilde{c} \rangle$ at the point $(\tilde{x}_1, \tilde{x}_2, \tilde{x}_3)$ of a fixed reference frame and let (x_1, b_2, b_3) be the fixed frame random coordinates (at time t) of the center of mass of a vertical plume cross-section passing through $x_1 \equiv \tilde{x}_1$. The instantaneous random concentration $\tilde{c}$ at $(x_1, \tilde{x}_2, \tilde{x}_3)$ is of course exactly the concentration c of the moving frame measured at $(x_1, \tilde{x}_2 - b_2, \tilde{x}_3 - b_3)$: $\tilde{c}(x_1, \tilde{x}_2, \tilde{x}_3) \equiv c(x_1, \tilde{x}_2 - b_2, \tilde{x}_3 - b_3)$, and hence $\langle \tilde{c}(x_1, \tilde{x}_2, \tilde{x}_3) \rangle \equiv \langle c(x_1, \tilde{x}_2 - b_2, \tilde{x}_3 - b_3) \rangle$. Now if $P_k(x_1; b_2, b_3)\, db_2\, db_3$ represents the probability that the center of mass of the vertical plume cross-section at x_1 is in the area element (b_2, b_3) to $(b_2 + db_2, b_3 + db_3)$, then

$$\langle \tilde{c}(x_1, \tilde{x}_2, \tilde{x}_3) \rangle = \int_{b_2} \int_{b_3} \langle c(x_1, \tilde{x}_2 - b_2, \tilde{x}_3 - b_3) \rangle \, P_k(x_1; b_2, b_3)\, db_2\, db_3 \qquad (2.5-5)$$

The probability density function $P_k(x_1; b_2, b_3)$ can be expressed in terms of the transition probability density for fluid particles in a turbulent field which is a quantity extensively studied in analyses of turbulent flows (Monin and Yaglom 1971, 1975; Hinze 1975; Seinfeld 1975). Typically $P_k(x_1; b_2, b_3)$ is assumed Gaussian,

$$P_k(x_1; b_2, b_3) = \frac{1}{2\pi \sigma_{M_2} \sigma_{M_3}} \exp\left(-\frac{b_2^2}{2\sigma_{M_2}^2} \right) \exp\left(-\frac{b_3^2}{2\sigma_{M_3}^2} \right) \qquad (2.5-6)$$

where the σ_M's are the standard deviations of meandering at x_1. Then, relation (2.5-5) estimates $\langle \tilde{c} \rangle$ in a fixed frame through a convolution transform of the moving frame concentration $\langle c \rangle$, the transform having a Gaussian kernel (a Weierstrass transform – see Zemanian, 1968).

2.5.3 Summary of the Computational Scheme

To summarize the overall TRP Model, its equations, as applied to the problem A(plume species) $+B$(in ambient)$\rightleftharpoons P$, are given in Table 2-1 together with the parameters involved.

Numerical implementation of the scheme of Table 2-1 involves the following three-step sequence:

STEP 1: *Preprocessor settings - Peripheral Models Activation*

This initial step consists of selecting the appropriate method ("peripheral model") for calculating the inner level parameters to be utilized by the mixing-reaction equations (i.e. the relative dispersion parameters, the inert surrogate means and the plume intensity of stream segregation). The available options in the current version of the TRPM are discussed in Section 2.6.

STEP 2: *Master Module Calculations*

This step consists of the calculation of spatial reaction evolution in a meandering/rising frame of reference. In the model problem (three species - one independent reaction) the master module consists of the evolution equation for $\langle \xi \rangle$, a set of algebraic equations relating reactive species concentrations to $\langle \xi \rangle$, plus the calculations for the inert mixing problem, i.e. for the mean and the variance of the inert surrogate of the plume species.

The evolution of $\langle \xi \rangle$ is described by a reaction-diffusion equation, the chemical kinetics term being a second degree polynomial in ξ (equations (2.5-3), (2.5-4)). The coefficients of this polynomial are functions of position inside the plume and involve the aforementioned properties of the inert surrogate; these are calculated either from analytical expressions, when the inert dispersion problem allows for such solutions (e.g. Gaussian type formulas for the mean and the Localized Production of Fluctuations formulas) or from numerical solution of linear transport equations with apparent eddy diffusivities given by (2.3-1). An Alternating Direction Implicit finite difference scheme, that is appropriate for handling the nonlinearity of (2.5-3), is adopted for the grid solution of the equations for $\langle \xi \rangle$, $\langle c_A^I \rangle$ and $\left(\sigma_A^I\right)^2$ (see Appendix

Table 2-1

The TRPM Applied to the Model Problem $A + B \rightleftharpoons P$

(Intrinsic Chemical Reaction Rate $R = k_f c_A c_B - k_b c_P$)

A. GOVERNING EQUATIONS FOR TURBULENT MIXING AND REACTION: MASTER MODULE

(i) *Dynamic Evolution Equations (for steady release of A in ambient B)*

(ia) *Auxilliary Calculations*

$$\mathcal{L}_K^M \left\langle c_A^I \right\rangle = 0\ ;\ \left\langle c_A^I \right\rangle = S\delta(\mathbf{x}) \text{ at } \mathbf{x} = 0,\ \left\langle c_A^I \right\rangle \to 0 \text{ at } x_2 \to \pm\infty,\ x_3 \to \infty,\ \frac{\partial \left\langle c_A^I \right\rangle}{\partial x_3} = 0 \text{ at } x_3 = -h_T$$

$$\left\langle c_B^I \right\rangle = \langle c_B \rangle^0\ ,\ \left\langle c_P^I \right\rangle = \langle c_P \rangle^0$$

$$\mathcal{L}_K^M \left(\sigma_A^I\right)^2 = 2K_i \left(\frac{\partial \left\langle c_A^I \right\rangle}{\partial x_i} \right)^2 - \frac{\left(\sigma_A^I\right)^2}{kt};\ \left(\sigma_A^I\right)^2 = 0 \text{ at } \mathbf{x} = 0,\ \left(\sigma_A^I\right)^2 \to 0 \text{ at } x_2 \to \pm\infty,\ x_3 \to \infty,\ \left(\sigma_A^I\right)^2 = 0 \text{ at } x_3 = -h$$

(ib) *Local Phenomenal Extent of Reaction Calculations*

$$\mathcal{L}_K^M \langle \xi \rangle = R_1(\mathbf{x}) \langle \xi \rangle^2 + R_2(\mathbf{x}) \langle \xi \rangle + R_3(\mathbf{x})\ ;\ \langle \xi \rangle = 0 \text{ at } \mathbf{x} = 0,\ \langle \xi \rangle \to 0 \text{ at } x_2 \to \pm\infty,\ x_3 \to \infty,\ \frac{\partial \langle \xi \rangle}{\partial x_3} = 0 \text{ at } x_3 = -h_T$$

where

$$\mathcal{L}_K^M \langle \cdot \rangle = -\bar{u}_1 \frac{\partial \langle \cdot \rangle}{\partial x_1} + K_{R_2} \frac{\partial^2 \langle \cdot \rangle}{\partial x_2^2} + K_{R_3} \frac{\partial^2 \langle \cdot \rangle}{\partial x_3^2},\quad K_{R_i} = \frac{\bar{u}_1}{2} \frac{d\sigma_{R_i}^2}{dx_1}$$

and

$$\tilde{R}_1(\mathbf{x}) = k_f (1 + I_A^I);\quad \tilde{R}_2(\mathbf{x}) = k_f \left[\left\langle c_A^I \right\rangle (1 + I_A^I) + \left\langle c_B^I \right\rangle \right] + k_b;\quad \tilde{R}_3(\mathbf{x}) = k_f \left\langle c_A^I \right\rangle \left\langle c_B^I \right\rangle - k_b \left\langle c_P^I \right\rangle$$

$$I_A^I = \frac{\left(\sigma_A^I\right)^2}{\left\langle c_A^I \right\rangle^2} \text{ with } \left(\sigma_A^I\right)^2 = \left\langle \left(c_A^I\right)'^2 \right\rangle$$

(ii) *Local Stoichiometry at* $\mathbf{x}$

$$\langle c_A \rangle = \left\langle c_A^I \right\rangle - \langle \xi \rangle\ ,\ \langle c_B \rangle = \left\langle c_B^I \right\rangle - \langle \xi \rangle\ ,\ \langle c_P \rangle = \left\langle c_P^I \right\rangle + \langle \xi \rangle$$

B. ESTIMATION OF FIXED FRAME CONCENTRATIONS: COMPLEMENTARY MODULE

(i) *Plume Rise Effects*

Plume Rise Model gives $\langle b_3 \rangle = \langle b_3(x_1) \rangle$

(*Alternatives:* (i) Brigg's formulas, (ii) Schatzmann's integral scheme)

(ii) *Meandering Effects*

$$\langle \bar{c}(x_1, \bar{x}_2, \bar{x}_3) \rangle = \int_{b_2} \int_{b_3} \langle c(x_1, \bar{x}_2 - b_2, \bar{x}_3 - b_3) \rangle\, P_k(x_1; b_2, b_3)\, db_2\, db_3$$

$$P_k(x_1; b_2, b_3) = \frac{1}{2\pi \sigma_{M_2} \sigma_{M_3}} \exp\left(-\frac{b_2^2}{2\sigma_{M_2}^2} \right) \exp\left(-\frac{b_3^2}{2\sigma_{M_3}^2} \right)$$

Notation: A in-plume species; B ambient species; $\left\langle c_i^I \right\rangle$ mean inert surrogate concentration; $\langle c_i \rangle^0$ mean ambient concentration; c_i' instantaneous fluctuation about the mean value; k_f and k_b forward and backward reaction rate constants; ξ local phenomenal extent of reaction; $\left(\sigma_A^I\right)^2$ and I_A^I variance and intensity of segregation for the inert surrogate of A. $\bar{x}_i$ fixed frame coordinates; x_i meandering frame coordinates; b_i coordinates of instantaneous centerline; σ_i, σ_{R_i} and σ_{M_i}: absolute dispersion, relative dispersion and meandering parameters; $\bar{u}_1$ mean wind field along the plume centerline; P_k Gaussian fluid particle position pdf; h_T effective source height.

A3.1). In the case analytical expressions are used for $\langle c_A^I \rangle$ and $\left(\sigma_A^I\right)^2$, one can avoid the grid solution and obtain an estimate of $\langle \xi \rangle$ at any arbitrary point of the field by direct transformation of (2.5-3) into integral form and application of an iterative method (see Chapter 3, Section 3.3.3).

STEP 3: *Post-Processing Calculations*

In this final step, expected (or time averaged) reactive species concentrations at points fixed relative to the ground are estimated. More specifically, this step consists of:

3A. Selecting the outer level parameters, i.e.,

(i) specifying the plume rise model to be used for determining the mean plume path, and

(ii) estimating the meandering parameters.

(The available options are discussed in the next section).

3B. Calculating fixed frame concentrations via the convolution relation (2.5-5).

Further calculations such as estimation of spatial (e.g., crosswind plane) average concentrations can also be readily performed simultaneously with Step 3.

2.6 DETERMINATION OF PARAMETERS IN THE REACTIVE PLUME MODEL

In this section we summarize basic information regarding the parameters that are needed in the TRPM for quick reference and in order to provide an overview of the entire computational procedure (and the possible alternative choices in this procedure) that must be followed for an application of the model. A more detailed exposition can be found in Chapters 5, 6 and 7.

2.6.1 Inner Level Parameters

(a) Relative Dispersion Parameters

(See also Chapter 6)

Methods providing estimates of relative or two-particle dispersion parameters can be classified as:

(i) Similarity theory combined with empirical information from field and laboratory measurements of puffs or instantaneous plume realizations (Plate, 1982; Hanna et al., 1982; Hanna, 1984).

(ii) Analytical and numerical Lagrangian studies of fluid particle motion based on Langevin equations (Gifford, 1982; Durbin, 1980; Sawford, 1982; Lee and Stone, 1983ab).

(iii) Fluid particle transition probability density methods (Leslie, 1973-Sections 8.6 and 12.2; Lundgren, 1981; Jiang, 1985).

(iv) Spectral methods - An analysis of the motion of fluid particle pairs shows that the relative dispersion parameters cannot be expressed directly in terms of velocity spectra because the correlation of relative fluid particle velocities is not stationary (*). Indirect techniques, based on appropriate filtering of spectral functions were originated by Smith and Hay (1961). More recent attempts to obtain information on

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(*) The two-particle dispersion counterpart of Taylor's formula will involve weighted integrals of the temporal correlation of the relative two-particle acceleration (Lin and Reid, 1963).

relative dispersion and meandering through a direct single-step filtering of measured one-dimensional Eulerian velocity spectra have produced contradictory results (Sheih, 1980; Rowe, 1981; Mikkelsen and Troen, 1981).

We will adopt the following two options for relative dispersion parameters:

(1) Use of simple similarity or empirical relations (Csanady, 1973; Hanna, 1984) in power law form.

(2) Use of an iterative filtering algorithm to deduce information from observed velocity spectra. This algorithm is briefly described in the next paragraph; for further discussion see Chapter 6.

Atmospheric field measurements during the last two decades have resulted in reliable universal forms of Eulerian velocity spectra (see, e.g., Caughey, 1982; Panofsky and Dutton, 1984-pp174-228). Given the Eulerian velocity spectral density in the i-th direction $S^E_{ii}(n)$ (normalized), and the corresponding velocity variance $\left[u'^2_i\right]_{\infty,0}$ where the subscripts ∞, 0 denote sampling of instantaneous values over an infinite sampling time, and utilizing the Hay-Pasquill (1959) hypothesis for the relation among Eulerian and Lagrangian quantities, one obtains the following relation for the absolute dispersion parameters,

$$\sigma_i^2 = \left[u'^2_i\right]_{\infty,0} t^2 \int_0^\infty S^E_{ii}(n) \frac{\sin^2 \pi n(t/\beta)}{\left(\pi n\,(t/\beta)\right)^2} dn \qquad (2.6-1)$$

where $\beta = a\overline{u}_1 \left[u'^2_i\right]^{-1/2}_{\infty,0}$, with $a \simeq 0.4$ to 0.6. Then, using a low frequency filter we obtain a first estimate of the relative dispersion parameter through

$$\sigma_{R_i}^2 = \left[u'^2_i\right]_{\infty,0} t^2 \int_0^\infty S^E_{ii}(n) \frac{\sin^2 \pi n(t/\beta)}{\left(\pi n\,(t/\beta)\right)^2} \left[1 - \frac{\sin^2 \pi n\tau}{(\pi n\tau)^2}\right] dn \qquad (2.6-2)$$

where the averaging time τ is taken equal to

$$\tau = \frac{2\sqrt{2}\sigma_i}{\overline{u}_1} \qquad (2.6-3)$$

Then we refine the estimate of σ_{R_i} by replacing σ_i in the expression for τ with the estimate of σ_{R_i} This procedure is repeated until convergence is achieved.

The spectral functions of Kaimal (1973) and Hojstrup (1982) for stable and neutral-unstable conditions, respectively, can be adopted for use with this approach.

(b) Inert Surrogate Means and the Intensity of Segregation

(See also Chapter 5)

The chemical closure scheme for point source plume-unpremixed reactants involves mean concentrations of inert surrogates and the fine scale intensity of stream segregation for the instantaneous plume. In the present work the latter quantity was defined as the ratio of the variance to the square of the mean concentration of an inert surrogate of the emitted reactant, at every point inside the instantaneous plume boundaries. Thus estimates for the first two moments of the instantaneous concentration field are needed.

Calculation of mean concentrations is, of course, a widely studied problem in atmospheric diffusion theory. At the present level of development of the TRPM the two alternatives of using Gaussian type analytical expressions or solving $\mathcal{L}_K^M \left\langle c_A^I \right\rangle = 0$ numerically are available.

The variance $\left(\sigma_A^I\right)^2$ of c_A^I is also calculated either

(i) from the analytical expressions provided by the Localized Production of Fluctuations Model (which is presented in detail in Chapter 5), when a Gaussian formula offers an adequate description of the mean instantaneous field, or

(ii) from numerical solution of the $\left(\sigma_A^I\right)^2$-transport equation:

$$\mathcal{L}_K^M \left(\sigma_A^I\right)^2 = 2K_i \left(\frac{\partial \left\langle c_A^I \right\rangle}{\partial x_i} \right)^2 - \frac{\left(\sigma_A^I\right)^2}{kt} \qquad (2.6-4)$$

(summation convention implied), with k a constant in the range 1/3 to 3/2, sbject to boundary conditions requiring that $\left(\sigma_A^I\right)^2$ vanishes at the ground surface.

Other alternative schemes either resulting from simplifications of (2.6-4) (e.g. Csanady, 1973), or, empirically, from measurements (e.g. Wilson et al, 1982ab), that may be appropriate for use with the TRPM under special conditions, are also discussed in Chapter 5 and its appendices.

2.6.2 Outer Level Parameters

(a) Mean Plume Path (Plume Rise)

(See also Chapter 7)

Determining the path and expansion of an actual plume in the near-source region requires analyzing the problem of the merging of two turbulent flows, i.e., of the emissions flow, possibly associated with significant momentum and buoyancy fluxes, and of the ambient, density stratified turbulent atmospheric flow, up to that point in time where the properties of the ambient completely dominate the system (Briggs, 1975, 1984; List, 1982; Gebhard et al., 1984).

For use with the TRPM two alternatives are provided:

(1) Use of Briggs' (1975) formulas that are the most widely accepted in applications (Hanna et al., 1982). These formulas result from a combination of field observations, dimensional analysis, and simple entrainment hypotheses.

(2) Use of a two- or three-dimensional version of Schatzmann's (1978, 1979) integral model that is formulated for arbitrary temperature and density differences inside the plume and for arbitrary stratification (Appendix A7.2).

(b) Meandering Parameters

(See also Chapter 6)

Meandering parameters σ_{M_i} are determined through

$$\sigma_{M_i}^2 = \sigma_i^2 - \sigma_{R_i}^2$$

Other processes that may contribute to the total variance, such as shear and buoyancy are assumed negligible here; in a more detailed calculation, one can use estimates of the contribution to the variance of these processes as reported, e.g., in Csanady (1973)and Pasquill (1974, 1975). The σ_{R_i}'s are calculated as described in Subsection 2.6.1; a variety of possible alternatives is available in the literature for the σ_i's (see, e.g., Hanna et al., 1982; Seinfeld, 1983, for recent reviews). The "best" estimate for use must be chosen on the basis of the information that is relevant to the particular application. If velocity spectra are available, then the spectral forms of Taylor's formula (equation (2.6-1)) offer a procedure that relies on theory and utilizes a rich source of information on atmospheric turbulence, i.e., its spectral density.

2.7 CONCLUSIONS

A modular scheme for describing reaction evolution in plumes has been developed, focusing on the construction of a method that accounts for the effects of mixing on bimolecular reactions between constituents of the plume and the background air.

A major advantage of the present approach is that all fine scale mixing effects are incorporated in the chemical kinetic terms and that the transport part of the governing equations has to account only for macromixing. Consequently, even if the bimolecular reaction under consideration is coupled with a network of other physical or chemical processes involving the participating species, only terms corresponding to the above reaction will have to be modified via the adopted chemical closure scheme. Another important point is that, because of the "decoupling of mixing and reaction" character of the closure scheme, even if more than one independent bimolecular reactions between unpremixed reactants occurs in the system, the parameters of the chemical closure, involving inert surrogate properties, will have to be estimated only once. Further, the equations governing these parameters are not coupled with the equations for the reaction progress variables. In conclusion, the TRPM provides a flexible scheme appropriate for assessing the effects of incomplete mixing on nonlinear atmospheric reactions. The "core" of the model, contained in the master module, is relatively simple - considering the variety of phenomena it addresses. Indeed, the chemical closure approximation does not require further evolution equations for high order concentration correlations; instead, it requires parameters that can all, optionally, be expressed by closed analytical formulas and provides a direct substitute of the correlation of fluctuation in the mean kinetic term. Further, the concept of the local phenomenal extent of reaction improves the computational efficiency of the model, also providing a means for describing the local level of the interaction between dispersive and reactive phenomena.

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CHAPTER 3

THE TURBULENT REACTING PLUME MODEL (TRPM): APPLICATION TO THE NO - NO_2 - O_3 SYSTEM

3.1 INTRODUCTION

In this chapter we present a first evaluation of the Turbulent Reacting Plume Model (TRPM) that was described in Chapter 2. The reaction considered is that between NO, emitted from a point source, and ambient O_3. This particular system of reactants was chosen because (see also Chapter 1):

(i) it is typically the most important system in the near field dispersion phase of plumes from large combustion sources (McRae et al., 1982; Burton et al., 1983),

(ii) its kinetics are characterized by time scales that are of comparable magnitude to those of the atmospheric mixing processes and, consequently, its evolution is determined by a strong and complex coupling of reaction and dispersion phenomena, and

(iii) there are available detailed data bases that show explicitly the effects of the aforementioned coupling as well as the inability of simple formulations to describe it.

A set of laboratory data is chosen to compare with TRPM predictions for the effects of incomplete macro- and micro- mixing on nonlinear chemistry. The controlled conditions to which these data are relevant, and the relatively ample amount of information regarding the characteristics of the flow and the dispersion process, allow for quantitative conclusions and avoid the uncertainties associated with complex field flows and, necessarily, incomplete or limited measurements. The simple geometrical characteristics of the experimental flow under study, combined with the modular formulation of the TRPM, lead to the construction of a rather simple computational scheme that provides a direct testing of the "master module" of the TRPM.

3.2 ATMOSPHERIC MIXING AND THE O_3 - NO - NO_2 SYSTEM

The three principal reaction steps involved in the O_3–NO–NO_2 photolytic cycle are (*)

$$NO_2 + h\nu \xrightarrow{k_1} NO + O$$

$$O + O_2 + M \xrightarrow{k_2} O_3 + M$$

$$O_3 + NO \xrightarrow{k_3} NO_2 + O_2$$

The value of k_1 depends on light intensity and it varies between 0 and 0.6 min^{-1} for typical sunlight intensities. The values of k_2 and k_3 are obtained from the following relations (Hampson and Garvin, 1978) at 1 atm pressure with T in degrees K:

$$k_2 = \frac{0.246}{T^2}\exp\left(\frac{510}{T}\right) \ \text{ppm}^{-2}\,\text{min}^{-1}$$
$$k_3 = \frac{9.2 \times 10^5}{T}\exp\left(\frac{-1450}{T}\right) \ \text{ppm}^{-1}\,\text{min}^{-1}$$

Under most commonly encountered conditions the above reactions proceed at a rate nearly two orders of magnitude faster than any of the other steps in photochemical smog formation that involve ozone (Stedman and Jackson, 1975). Since the combustion products from large point sources are rich in nitrogen oxides and typically have low concentrations of reactive hydrocarbons (McRae et al., 1982), the near source plume chemistry is dominated by the above O_3–NO_x cycle. Thus there arises the need for estimating the fraction of nitric oxide (NO) that is converted to nitrogen dioxide (NO_2) during the initial phase of plume dispersion, before the plume has

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(*) An additional source of nitrogen dioxide in plumes is the thermal oxidation of nitric oxide by oxygen. This process is only significant for very high nitric oxide concentrations and is usually omitted in photochemical rection mechanisms or just used to correct the source concentration ratio of nitrogen oxides; an exposition of the latter approach, based on McRae et al., (1982), is given in Appendix A3.2.

grown to the size of a typical computational cell of an airshed model. After that point a complete reaction mechanism considering hydrocarbon and radical interactions will have to be employed.

The main oxidizing reaction $O_3+NO \rightarrow NO_2+O_2$ for typical atmospheric concentrations would have a half life of approximately 30 seconds for well mixed volumes. Under such conditions many investigators have made the assumption that the ozone production and decay rates are in equilibrium and derived the photostationary state approximation, PSSA, (Leighton, 1961)

$$k_3\, c_{NO} c_{O_3} = k_1\, c_{NO_2} \qquad (3.2-1)$$

This relation will hold locally for systems that are mixed at the molecular level (e.g., smog chambers). One however will not be able to substitute in this equation temporally or spatially averaged concentrations $\bar{c}_{NO}$, $\bar{c}_{NO_2}$, $\bar{c}_{O_3}$ obtained from real atmospheric situations where the mixing of pollutants with air is not complete (Seinfeld, 1977; Bilger, 1978). This fact (which is also true for ensemble means of concentrations) is due to the macroscopic and microscopic inhomogeneities of real concentration fields. Thus, ensemble averaging of (3.2-1), where k_1, k_3 are assumed non-random, (*) does not lead to a relation of the form $k_3 \langle c_{NO} \rangle \langle c_{O_3} \rangle = k_1 \langle c_{NO_2} \rangle$ but to

$$k_3 \langle c_{NO} \rangle \langle c_{O_3} \rangle + k_3 \langle c'_{NO} c'_{O_3} \rangle = k_1 \langle c_{NO_2} \rangle \qquad (3.2-2)$$

The parameters usually employed to depict the invalidity of relation (3.2-1) for averaged concentrations are the so-called photostationary state parameter (PSSP) λ, defined in terms of averaged concentrations (see e.g., Bilger, 1978):

$$\lambda = \frac{k_3}{k_1} \frac{\langle c_{O_3} \rangle \langle c_{NO} \rangle}{\langle c_{NO_2} \rangle} \qquad (3.2-3)$$

(*) Actually random fluctuations in light intensity and, to a lesser degree, in temperature cause inevitable variations of the rate constants. One can incorporate this variation in the kinetic equations by decomposing the rate coefficients into mean and fluctuating components: (see, e.g. Kewley, 1978, and Appendix A3.3

and the photostationary state number (see e.g., Stedman and Jackson, 1975) which is simply the inverse of λ. From (3.2-2) one obtains

$$\lambda = \frac{1 - k_3}{k_1} \frac{\langle c'_{O_3} c'_{NO} \rangle}{\langle c_{NO_2} \rangle} \tag{3.2 – 4}$$

Deviations of λ from unity (which is the value it would assume if defined in terms of instantaneous random concentrations) depend on the sign and magnitude of the correlation $\langle c'_{O_3} c'_{NO} \rangle$. For the initial stages of plume dispersion (in general for the admixing of fresh emissions) we expect the correlation to be negative and hence λ to be greater than unity. For smoggy air mixing with clean air one can expect a positive correlation and therefore λ less than unity. (If one also considers fluctuations in light intensity–which affect k_1–one would expect a negative correlation of these fluctuations with c_{NO_2} and therefore a reducing effect on the value of λ.)

Measurements in polluted atmospheres have produced values of λ ranging from 0.3 to 7.5. Eschenroeder and Martinez (1972), from measurements in Los Angeles, report values of λ less than unity (down to 0.3) at low ambient ozone concentrations. These values increase drastically with increased mean ozone concentrations (e.g., they report values of λ greater than 7 for ozone concentrations in the range of 24 pphm). Stedman and Jackson (1975) report on values of $1/\lambda$ from measurements of ambient air quality in Detroit. Using 400 data sets they found that $1/\lambda$ was equal to 1.01 with a standard deviation of 0.2 and a standard error of the mean equal to 0.01. Other experimental results obtained during the Sydney Oxidant Study (Kewley and Post, 1978) also show variations of λ both above and below unity. Theoretical analyses of the problem in terms of simple descriptions of the state of incomplete mixing in the atmosphere have been presented by Calvert (1976), Seinfeld (1977), Bilger (1978), Kewley (1978, 1980), Kewley and Bilger (1979); formulations relevant to these analyses are also incorporated in some of the existing reactive plume models.

During the night reaction $NO_2 \rightarrow NO + O$ does not take place and the evolution of the system is determined by reaction $O_3 + NO \rightarrow NO_2 + O_2$. No photostationary state approximation can be invoked in this case but of course the conversion of NO to NO_2 is still retarded by the mixing processes. With respect to modeling, the absence of a "reference" equilibrium state, that provides a first approximation to the solution of the problem, in general makes the case of the irreversible system described by $O_3 + NO \rightarrow NO_2 + O_2$ more difficult to handle (unless an "infinitely fast rate" assumption is invoked).

Various sets of field data relevant to nitrogen oxides-ozone chemistry in point source plumes are available (see, e.g., Burton et al., 1983, for a list and discussion of various field studies), the most widely referenced probably being those of Davis et al. (1974) and Hegg et al. (1977). However, incomplete information regarding the complex flow field and various aspects of the dispersion process, variations in temperature and light intensity, the possibility of changing source conditions, and the presence of hydrocarbons in the atmosphere, prohibit the quantitative association of observed effects with the fundamental underlying processes. Consequently, comparison of field data with theoretical calculations is presently meaningful only in a qualitative manner; proper initial testing and validation of a reacting plume model requires comparison with well controlled laboratory data where the uncertainty of "side effects" is kept to a minimum.

Laboratory studies of the reaction between nonpremixed O_3 and NO have been conducted by Shea (1977) for a turbulent O_3 jet in a NO environment, by Builtjes (1981, 1983) for a nonbuoyant NO plume in an O_3 environment, in a wind tunnel simulating a neutral atmospheric boundary layer, and by Komori and Ueda (1984) for a NO jet into a nonturbulent coflowing stream containing O_3 and for a NO plume into a grid-generated turbulent stream.

The set of data most appropriate for testing the capability of the TRPM to calculate the effect of mixing on plume chemistry, under conditions relevant to atmospheric flows, seems to be provided by the experiments of Builtjes and is briefly discussed in the next section, in relevance to the needs of the present work.

3.3 THE EXPERIMENTAL DATA BASIS AND THE TRPM EQUATIONS

3.3.1 The Nature of the Experimental Data

The experimental data basis provided by the work of Builtjes (1981, 1983) consists of averages over sets (to be seen as statistical samples from the perspective of this work) of short term point measurements of NO, NO_x and O_3 concentrations, for an elevated, non-buoyant, "point" source plume in a wind tunnel. The wind tunnel (with a test section 10 m long and a cross-section of 2.65×1.2 m^2) simulated a neutral atmospheric boundary layer above grassland at a scale 1:500. The respective ratio of time scales of processes in the wind tunnel and in the atmosphere was estimated to be approximately 1:35. Details of the atmospheric boundary layer simulation can be found in Builtjes and Vermeulen (1980). The details of the reacting plume experiments are given in Builtjes (1981) and are further discussed in Builtjes (1983); the essential parameters of these experiments are given here in Table 3-1.

The source NO_x was entirely in the form of NO, a constant mean background conentration of O_3 was maintained, and the experiments were performed "in the dark"; no measurable quantities of hydrocarbons were present in the wind tunnel. Thus reaction $O_3+NO \rightarrow NO_2+O_2$ was governing the system as the sole producer of NO_2. Transverse (horizontal) concentration profiles of NO, NO_x and O_3 were measured at the height of the source at various distances downwind. At each point of these transverse profiles, and for each experiment, the statistical sample of mesurements contains ten 30-second averaged O_3 values together (a) with five 1-minute averaged NO_x values, and, (b) with five 1-minute averaged NO values, as well as five 30-second averaged O_3 values without the NO plume present. These data were averaged, leading to one O_3, NO_x, NO and NO_2 = NO_x-NO concentration value at that point. The reproducibility of the measurements was approximately 15 % for O_3, 25 % for

Table 3-1

Parameters for the Wind Tunnel Experiment

(Builtjes, 1981, 1983)

NO Source Data

S (pure NO) $= 0.0110\ \mathrm{m^3\,s^{-1}}$

$\bar{c}_{NO}$ at $x = 0$ $= 3900$ ppm

source height $h = 0.14$ m

source exit velocity $u_e = 0.4\ \mathrm{m\,s^{-1}}$

source diameter $= 0.003$ m

Ambient Data

ambient ozone concentration $\bar{c}^{env}_{O_3} = 0.350$ ppm

integral length scale (at $z = h$) $= 0.3$ m

average turbulence intensity (at $z = h$) $= 0.1$

mean wind velocity (at $z = h$) $= 0.4\ \mathrm{m\,s^{-1}}$

boundary layer thickness $= 0.8$ m

(Typical Temperature Range: 16 °C–20 °C)

NO_x and 30 % for NO, with a subsequent very large scatter in the estimated NO_2 values. (The reproducibility was in general better along and close to the centerline). These facts suggest that the O_3 sample averages should be better approximations of theoretical ensemble means of instantaneous values than the corresponding averages of NO and NO_x. Subsequent comparisons with TRPM calculations will therefore focus mainly on O_3 values.

In addition to the measurements of concentrations and ambient flow properties the experimental data base contains some direct information regarding the dispersion process. This information will be used as "validated input" in the calculations, reducing the uncertainty associated with dispersion related parameters and allowing to focus on the testing of the master module of the TRPM.

3.3.2 Parameters for the TRPM Calculations

(a) Dispersion Parameters and Mean Surrogate Concentrations

The wind-tunnel plume showed only insignificant meandering. Thus in the following the plume envelope is assumed practically indistinguishable from the *expected* boundaries of the instantaneous plume. The dispersion parameter in the y (transverse horizontal) direction for the inert plume was estimated from measurements (of SF_6, of NO in an O_3-free environment and of total NO_x in an environment containing O_3) as $\sigma_y = 0.072x^{0.907}$ where x is the downwind distance from the source (x and σ_y in meters). Data related to the distribution of concentrations in the vertical (z) direction are not available; in the absence of other relevant information it was assumed that $\sigma_z = 1/2\sigma_y$, which is a classic choice in the case of neutral boundary layers (Csanady, 1973 - Section 3.12). The values of concentrations along the centerline (for all the aforementioned releases) exhibit good agreement with Gaussian plume calculations for these values of the dispersion parameters σ_y and σ_z. Figure 3-1 contains the centerline calculations together with the measured values of total NO_x in the reactive plume experiments.

Direct comparison of predictions with observed transverse profiles is difficult because of the inherent randomness of the concentration data. Figure 3-2a shows crosswind values of total NO_x (non-dimensionalized with the associated theoretical centerline concentration), measured horizontally at source height at various distances downwind, in comparison with the corresponding Gaussian estimates, versus the dimensionless distance y/σ_y from the centerline. Each depicted experimental value in this figure is the average of five short term measurements at a point, as mentioned earlier; different values at approximately the same y/σ_y correspond to measurements at different downwind positions. (It is obvious from the existing scatter in the data that averages over five values are very poor approximations to ensemble means.) When however one averages the different data corresponding to the same y/σ_y, thus improving the approximation of the relevant ensemble mean value, one discovers a satisfactory agreement between measurements and calculations, as shown in Figure 3-2b. (Actually averages were taken over data in the intervals 0 to $0.2y/\sigma_y$, $0.2y/\sigma_y$ to $0.4y/\sigma_y$, etc., since the dimensionless positions of the measurements at different downwind distances were not usually identical). It can therefore be claimed that the Gaussian plume equation

$$\langle c_{NO_x} \rangle = \frac{S}{2\pi\sigma_y\sigma_z\overline{u}} \exp\left(-\frac{y^2}{2\sigma_y^2}\right) \left\{ \exp\left[-\frac{(z-h)^2}{2\sigma_z^2}\right] + \exp\left[-\frac{(z+h)^2}{2\sigma_z^2}\right] \right\} \tag{3.3 – 1}$$

with the source located at $(x,y,z) = (0,0,h)$, is a valid model for the expected concentrations of the inert surrogate of NO (which in the present case is identical to total NO_x).

(b) The Intensity of Segregation

The second auxilliary calculation, besides that of the mean $\langle c_{NO_x} \rangle$, required by the master module of the TRPM, is that of the variance σ_c^2 of instantaneous total NO_x concentrations. (The intensity of stream segregation, involving these two quantities, participates in the turbulent kinetics expression of the TRPM). Since a

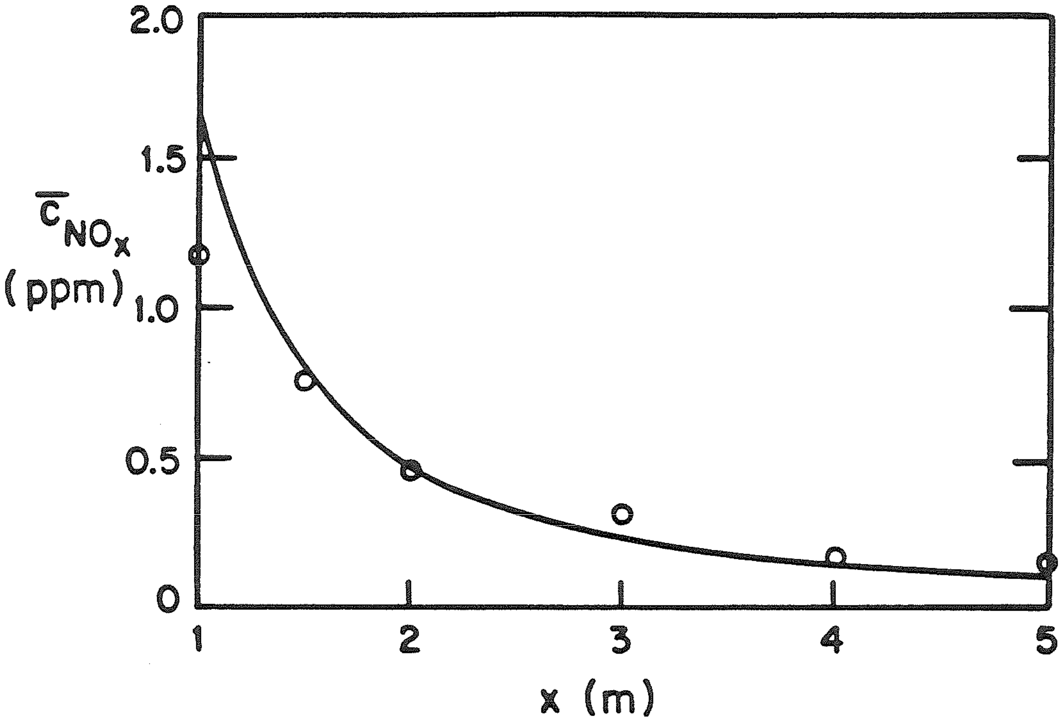

Figure 3-1

Total NO_x Concentrations along the Plume Centerline:
Data of Builtjes (1981) and Gaussian Plume Calculations.

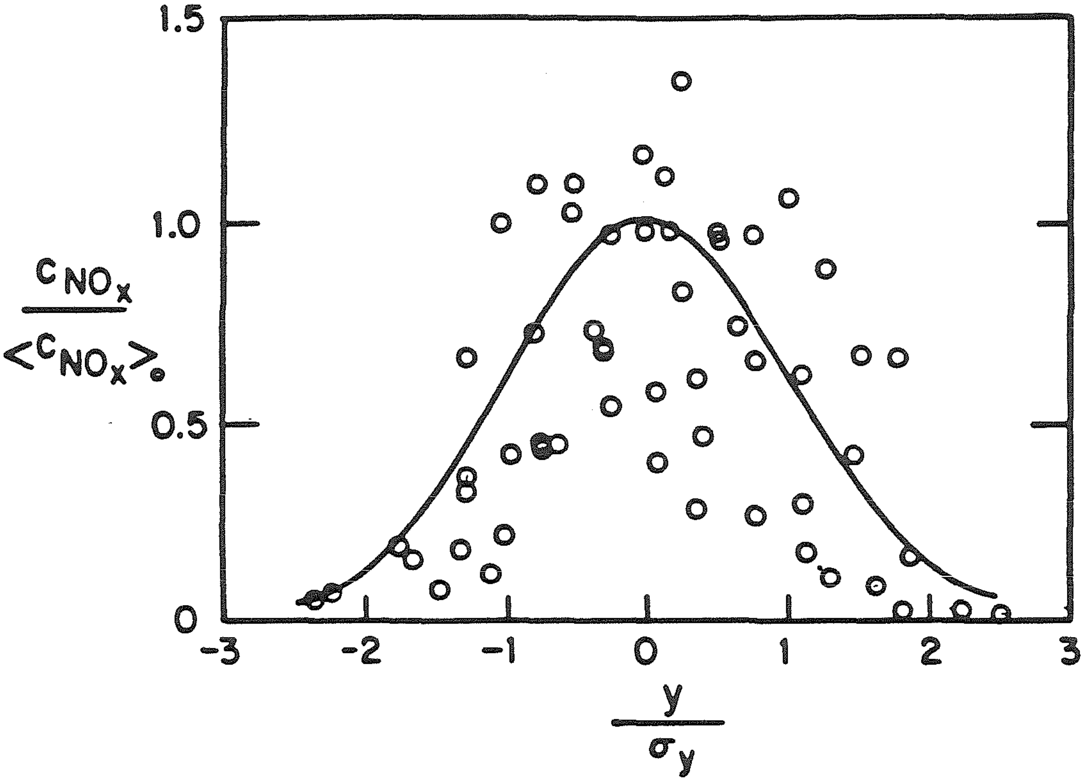

Figure 3-2a

Total NO_x Concentrations

Horizontally at Source Height and at Various Downwind Distances (1 to 5 m):

Data of Builtjes (1981) and Gaussian Plume Calculations

(both normalized with respect to the theoretical centerline value)

vs the Dimensionless Crosswind Distance y/σ_y from the Plume Centerline.

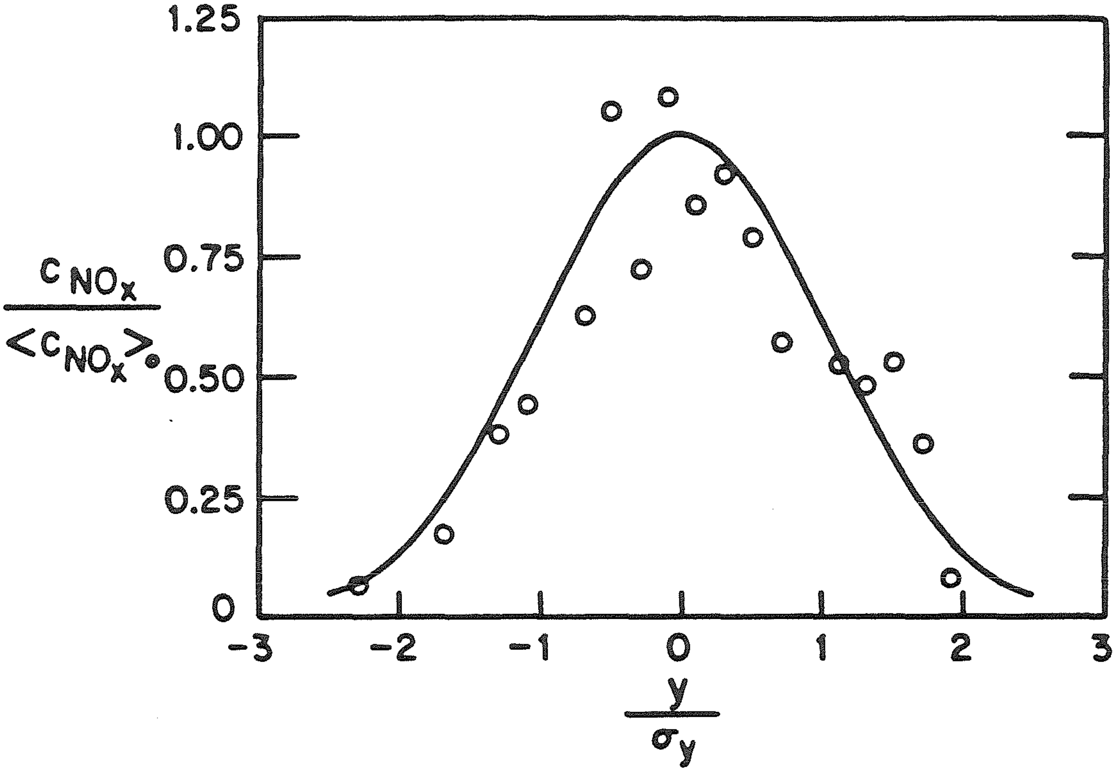

Figure 3-2b

Total NO_x Concentrations as in Figure 3-2a,

with the Experimental Values Replaced by the Averages of Measurements

(corresponding approximately to the same y/σ_y)

(See text for details)

Gaussian formula is assumed to provide an adequate description of the mean of the "instantaneous" NO$_x$ field in the present case, we adopt the Localized Production of Fluctuations Model for σ_c^2 (Chapter 5):

$$\sigma_c^2(x,y,z) = \left(\frac{S}{2\pi\overline{u}}\right)^2 \frac{p\,\omega^{A_1-1}}{\sigma_y(\varsigma)\,\sigma_z(\varsigma)\,\sigma_y(x-\varsigma)\,\sigma_z(x-\varsigma)} \exp\left(-\frac{y^2}{2\sigma_y^2(x-\varsigma)}\right) \times$$
$$\times \exp\left(-\frac{ab}{2\sigma_y(x-\varsigma)\,\sigma_z(x-\varsigma)}\right)\left[\exp\left(-\frac{(z-h)^2}{2\sigma_z^2(x-\varsigma)}\right) I_0\left(\frac{\sqrt{a^2(z-h)^2+b^2y^2}}{\sigma_y(x-\varsigma)\,\sigma_z(x-\varsigma)}\right)\right.$$
$$\left. -\alpha \exp\left(-\frac{(z+h)^2}{2\sigma_z^2(x-\varsigma)}\right) I_0\left(\frac{\sqrt{a^2(z+h)^2+b^2y^2}}{\sigma_y(x-\varsigma)\,\sigma_z(x-\varsigma)}\right)\right] \qquad (3.3-2)$$

where I_0 is the modified Bessel function of order zero, ω is the dimensionless localization parameter (between 0 and 1), $\varsigma = \omega x$, p is the exponent in the power law for σ_y, σ_z (i.e. $p = 0.907$ here), $a = 3/4\sqrt{\pi}\sigma_y(\varsigma)$, $b = 3/4\sqrt{\pi}\sigma_z(\varsigma)$, and A_1 is a constant factor (between 1.5 and 3.0) relating the fluctuations dissipation time scale to the dispersion time. The parameter α equals unity for a "perfectly absorbing boundary", i.e. for $\sigma_c^2 = 0$ at the ground surface, and would be zero in the absence of ground effects.

Measurements in the reacting plume experiments show that the centerline intensity of segregation $I_s^c = I_s(x,0,0)$, where $I_s = \sigma_c^2/\langle c_{NO_x}\rangle$, remains approximately constant after the first 1.5 meters of dispersion ($\sqrt{I_s^c} = 0.5 \pm 0.15$); this is the only direct information concerning σ_c^2 and I_s in the available data. The approximately constant value of the segregation suggests that, in the downwind range of available measurements, the floor of the wind tunnel does not affect the variance significantly, at least close to source height, and allows the estimation of a constant value of ω (in terms of p and A_1). A value of $A_1 = 3p$ is assumed for the calculations according to the analysis for constant I_s^c and self-similarity of variance profiles (Chapter 5), and this choice determines directly the value of ω. However, as will be discussed in the next section, extensive calculations for varying values of the parameters show the overall effect of the exact choice (within their acceptable range) of A_1 (as well as of α) on the final results of the TRPM to be only minor, at least under the conditions of the present study. The same was found to be true for the I_s^c varying within its limits of uncertainty.

Another problem related to modeling σ_c^2 is the description of its evolution towards the profile given by (3.3-2) (which for constant ω and $\alpha \simeq 0$ reduces to a self similar form). This is a major problem in the fluid mechanical analysis of plume segregation and no general answer is known. However, the assumptions leading to the construction of the TRPM in its current form are associated with an artificial description of the evolution of segregation to which we will conform here. Indeed, in the formulation of the TRPM it is assumed that initially O_3 has a uniform concentration everywhere, i.e. it exists even in the source gases at its background concentration. This approximation is justified by the very large difference between the source concentration of NO and the background concentration of O_3 (3900 ppm versus 0.35 ppm in the present case). Obviously, the overall conversion of NO downwind will only be negligibly affected by the fictitious amount of O_3 that was assumed present in the emissions, and which will be practically consumed during a very short time interval after emission. Thus, in our approach the segregation is seen as induced by the chemistry very close to the source. So, as a first approximation, we assume that

$$\frac{\sigma_c}{\langle c_{NO_x} \rangle} = I_s^{1/2} \sim \frac{\langle c_{NO_2} \rangle}{\langle c_{NO_x} \rangle}$$

and for constant background ozone concentration $\langle c_{O_3} \rangle^{\mathrm{env}}$

$$\frac{\sigma_c}{\langle c_{NO_x} \rangle} \sim 1 - \exp\left(-k_3 \langle c_{O_3} \rangle^{\mathrm{env}} t\right)$$

which presents $\sqrt{I_s}$ as evolving towards its final value with a characteristic e-folding time determined by chemistry. (One must notice here that this chemical time scale $k_3 \langle c_{O_3} \rangle^{\mathrm{env}}$ equals 2.5 times the Lagrangian integral time scale estimated for the wind tunnel experiments, an indication of the fact that chemical and macromixing processes proceed at rates of comparable magnitude). It should be kept in mind that the preceding approach is introduced for consistency with the complete set of approximations involved in the TRPM and it is *not* aimed at explaining the details of the actual processes of mixing of point source plumes; it is a useful scheme for the specific purposes of the present reacting plume simulation and under the aforementioned restriction of very large concentration differences. From a practical viewpoint, calculations show that only the assumption of a characteristic time scale $k_3 \langle c_{O_3} \rangle^{\mathrm{env}}$ for the attainment of the values given by (3.3-2) plays a significant role in the overall TRPM results. Indeed, the difference obtained from assuming $\sqrt{I_s^c}$ increasing according to the above "1-exp" law and from assuming e.g. $\sqrt{I_s^c} \sim t$ or $\sqrt{I_s^c} \sim \sqrt{t}$ was negligible for practical purposes.

At this point it is useful to discuss some aspects of the process of plume mixing and clarify the relevance of certain assumptions involved in our approach. Actual sources deviate from the idealization of the "point" concept in the initial phases of dispersion, even in the highly simplified case when emissions do not differ in momentum or buoyancy from the ambient turbulent flow, because the finite dimensions of the source obviously dictate a separate initial flow that merges gradually with the ambient. During this process of flow merging the background ozone must diffuse through the plume boundaries and mix down to the molecular level with the NO rich regions in order that chemical reactions occur. As turbulent dispersion processes mix the plume with the background air a "macromixed zone" in which both NO and O_3 are present – in the sense that their mean concentration values are nonzero – is created near the plume boundaries. O_3 is diffusing from the plume edges inwards but is largely consumed by NO before the centerline is reached and NO_2 peaks will be formed in the macromixed zone, which at any given plume cross-section will have the form of a ring whose outer circle defines the reacting plume boundaries (Hegg et al., 1977). The width of this ring increases downwind until it covers the entire cross-section of the plume and the NO_2 peaks eventually disappear (see Figure 3 - 3).

In Builtjes' experiments such NO_2 peaks were observed very close to the source (although the scatter of the data does not allow quantitative estimates of the magni-

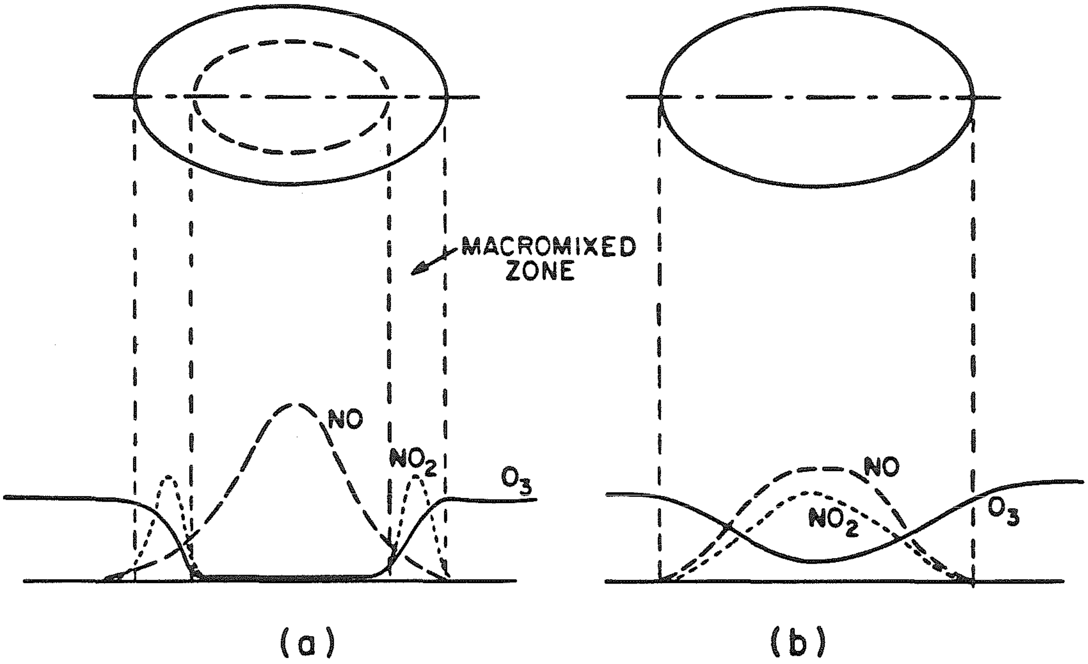

Figure 3-3

Evolution of Macromixing in a NO Plume:

Mean Profiles of NO, NO_2 and O_3

at Two Downwind Distances.

tude and position of these peaks); nevertheless this ring-type structure dissapears in the first 2 meters of the plume dispersion. Builtjes (1983) notes that for practical applications it is not necessary to use a model that is capable of calculating the observed NO_2 peaks, although it should be able to estimate the retardation in the reaction rate caused by incomplete macromixing and micromixing in the atmospheric dispersion phase of plume evolution. This suggestion was adopted in the present version of the TRPM and source size effects are neglected, based on the fact that the details of the initial merging process will have negligible effects on the overall conversion of NO to NO_2 that is observed further downwind.

3.3.3 The TRPM Equations

The equation governing the NO–NO_2–O_3 system under the assumptions stated, and for the specific conditions relevant to the data base described, assumes the form

$$\overline{u}\frac{\partial\langle\xi\rangle}{\partial x} - K_y(x)\frac{\partial^2\langle\xi\rangle}{\partial y^2} - K_z(x)\frac{\partial^2\langle\xi\rangle}{\partial z^2} =$$

$$= \tilde{R}_1(x,y,z)\langle\xi\rangle^2 + \tilde{R}_2(x,y,z)\,\langle\xi\rangle + \tilde{R}_3(x,y,z) \qquad (3.3-3)$$

(or, in compact form, $\mathcal{L}_K^M = \tilde{R}$) where

$$K_i(x) = \frac{\overline{u}}{2}\frac{d\sigma_i^2}{dx} \qquad (3.3-4)$$

and

$$\begin{aligned} \tilde{R}_1 &= k_3(1+I_s) \\ \tilde{R}_2 &= k_3\,\langle c_{NO_x}\rangle\,(1+I_s) + k_3\langle c_{O_3}\rangle^{\mathrm{env}} \\ \tilde{R}_3 &= k_3\,\langle c_{NO_x}\rangle\,\langle c_{O_3}\rangle^{\mathrm{env}} \end{aligned} \qquad (3.3-5)$$

with $\langle c_{NO_x}\rangle$ and σ_c^2 given by (3.3-1) and (3.3-2) respectively.

Here $\langle\xi\rangle$ is the *local phenomenal extent* of reaction $NO + O_3 \rightarrow NO_2 + O_2$ (Chapter 2), and for the specific experimental system under consideration

$$\langle c_{NO_2}\rangle = \langle\xi\rangle\,,\ \langle c_{NO}\rangle = \langle c_{NO_x}\rangle - \langle\xi\rangle\,,\ \langle c_{O_3}\rangle = \langle c_{O_3}\rangle^{\mathrm{env}} - \langle\xi\rangle \qquad (3.3-6)$$

The boundary conditions associated with (3.3-3) are

$$\langle \xi \rangle = 0 \text{ at } (x, y, z) = (0, y, z) \tag{3.3-7}$$

$$\langle \xi \rangle \to 0 \text{ at } y \to \pm\infty, z \to \infty, \quad \frac{\partial \langle \xi \rangle}{\partial z} = 0 \text{ at } z = 0 \tag{3.3-8}$$

Numerical solutions of (3.3-3) were obtained through

(i) an Alternating Direction Implicit (ADI) finite difference scheme, and,

(ii) through iterative solution of the associated integral equation.

The ADI method is especially suitable for the problem described by (3.3-3) since the nonlinearity appears only in the kinetic term. This term is calculated directly in each step using the value of $\langle \xi \rangle$ estimated in the immediately preceding iteration, performed in the alternative direction. The simple geometry of the simulated experimental system and the homogeneous boundary conditions also allow a reduction of the computational burden because of the existing symmetry with respect to the $(x, 0, z)$ plane. Thus, calculations for each x-step only have to be performed in, say, the positive $(y, 0, z)$ half-plane under the restriction $\partial \langle \xi \rangle / \partial y = 0$ at $y = 0$. (The basic finite-difference equations for the present calculations are summarized in Appendix A3.1).

The alternative choice of a feasible iterative point solution is allowed by the fact that, in the case under consideration, analytical expressions are available for all the parameters involved in (3.3-3), and the analytical form $G^M(x, y, z|x', y', z')$ of the Green's function of the partial differential operator/boundary conditions of (3.3-3) is known:

$$G^M(x, y, z|x', y', z') = \frac{1}{2\pi\sigma_y(x - x')\sigma_z(x - x')\overline{u}} \exp\left[-\frac{(y - y')^2}{2\sigma_y^2(x - x')} - \frac{(z - z')^2}{2\sigma_z^2(x - x')}\right] \tag{3.3-9}$$

Using as an initial first approximation for $\langle \xi \rangle$ the value corresponding to the pseudo-linear version of the problem, i.e. the solution obtained under the assumption that the mean ozone concentration remains everywhere constant at its background value,

$$\langle \xi \rangle^{(0)}(x, y, z) = \langle c_{NO_x} \rangle \left[1 - \exp\left(-k_3 \langle c_{O_3} \rangle^{\text{env}}\right)\right] \tag{3.3-10}$$

one obtains a first approximation for $\tilde{R}$:

$$\tilde{R}^{(0)}\left(\langle\xi\rangle;x,y,z\right)=\tilde{R}\left(\langle\xi\rangle^{(0)};x,y,z\right)$$

The next approximation for $\langle\xi\rangle$ is obtained through

$$\langle\xi\rangle^{(1)}(x,y,z)=\int_0^x\left[\int_{-\infty}^{\infty}\int_0^{\infty}G^M(x,y,z|x',y',z')\,\tilde{R}\left(\langle\xi\rangle^{(0)};x',y',z'\right)\,dz'dy'\right]dx' \tag{3.3 – 11}$$

and so on, until convergence to a steady value of $\langle\xi\rangle$ is obtained.

3.4 RESULTS AND DISCUSSION

In this section we present results of the numerical calculations compared with the experimental data of Builtjes (1981). The most important comparisons are presented in Figures 3-4 and 3-5 that refer to calculations and measurements along the centerline of the plume. Both calculations and data are presented in dimensionless form, as ratios of concentrations, and therefore give directly the dependence of conversions on downwind distance or travel time. The farthest downstream available measurements in the wind tunnel were taken at 5 m, which at a wind speed of 0.4 m/s corresponds to a travel time of 12.5 s. The respective quantities for a field situation would be approximately a 2.5 km downwind distance (or 7.5 min of travel time) with an average wind speed of 5.7 m/s.

Figure 3-4 contains the measured values of the ratio of NO to total NO_x as well as three calculated curves:

(a) *turbulent kinetics calculations,* of $\langle c_{NO} \rangle \, / \, \langle c_{NO_x} \rangle$ i.e. results from the TRPM considering the effects of both macromixing and micromixing, with parameters estimated as described in the previous section,

(b) *conventional kinetics calculations,* i.e. results from the common reaction–diffusion equation (to which the TRPM reduces for $I_s = 0$), that incorporate solely the effects of macromixing, and,

(c) *modified Gaussian plume calculations,* i.e. results from the pseudo-linear reaction assumption (equation (3.3-10)) which views plume macromixing in a very simplistic manner, that is with ozone profiles unaffected by the plume, and, of course, ignores micromixing effects. The same dispersion parameters were used in all the three different models. The 50% conversion time predicted by the TRPM is 9.0 s (of the order of 5.3 min for the comparable field situation), in very good agreement with the wind tunnel measurements. The respective calculations from the conventional reaction–diffusion equation gave a 50% conversion time equal to 6.5 s (3.8 min in the field stuation), i.e. about 28% shorter than the observed time, and the modified Gaussian plume model predicted 4.75 s (2.8 min in the field), that is almost 47% less than the observed value.

Figure 3-5 shows the measurements of the ratio of O_3 concentration (under reactive conditions) to the corresponding background value along the centerline, again compared with calculations that assume turbulent and conventional kinetics. (The relevant assumption of the modified Gaussian plume model is that $\langle c_{O_3} \rangle = \langle c_{O_3} \rangle^{\mathrm{env}}$ and the ratio shown in Figure 3-5 is always unity). The narrow peak of the calculated results at the origin arises from the assumption $\langle c_{O_3} \rangle = \langle c_{O_3} \rangle^{\mathrm{env}}$ for all (y, z) at $x = 0$ that was discussed in the previous section; the fast descent of the calculated ratio to a near zero value serves as an a posteriori justification of this approximation.

Comparisons of the transverse profile measurements and calculations are presented in Figures 3-6a to 3-6e for downwind distances 1, 2, 3, 4 and 5 m. The O_3 data were selected as being the more reproducible and less scattered. Again dimensionless ratios of concentrations are given, for easier comparison with other situations, plotted against the dimensionless distance y/σ_y from the plume centerline. The corresponding numerical solutions of the reaction-diffusion equation with conventional kinetics are also given in these figures. Although the scatter of the transverse data is significant, Figures 3-6a to 3-6e corroborate the basic conclusion arising from the comparison presented in Figures 3-4 and 3-5, i.e. that the TRPM indeed can provide a quantitative estimate of the effects of both macro- and micro- mixing on the evolution of plume reactions.

The primary parameters implicit in the calculations presented in the above figures were either

(a) measured, or estimated so as to fit dispersion measurements (σ_y, σ_z or the exponent p),

(b) the "most typical" among possible alternatives, corresponding to first-choice conventions of the peripheral models employed (i.e. $A_1 = 3p$), or

(c) the average values of randomly fluctuating quantities that were measured in the

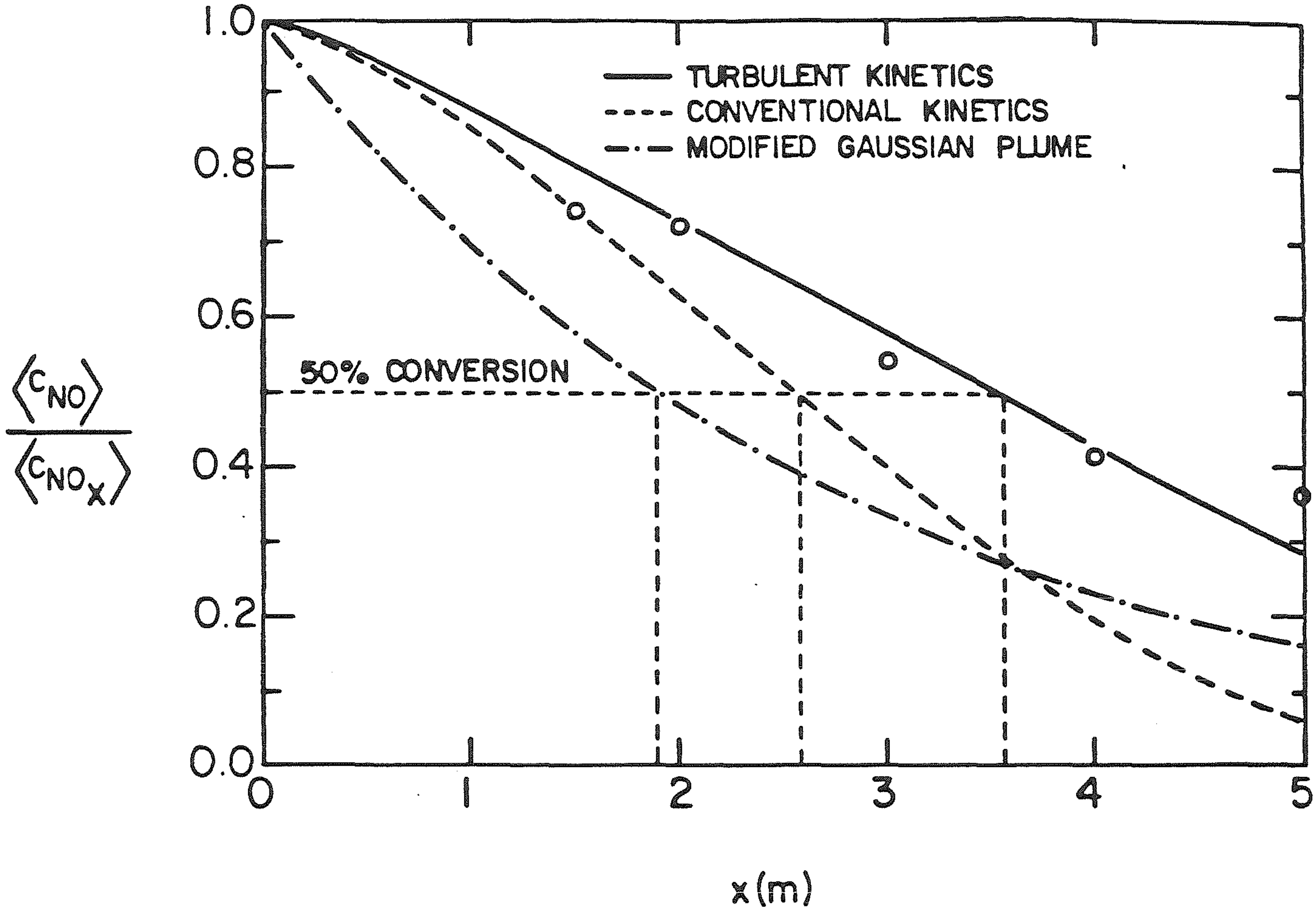

Figure 3-4

Ratio of NO to Total NO_x Concentration along the Plume Centerline:
Data of Builtjes (1981) and Calculations
(i) for Turbulent Kinetics (the complete TRPM equations),
(ii) for Conventional Kinetics (ignoring the effects of micromixing), and
(iii) from a Modified Gaussian Plume Model.

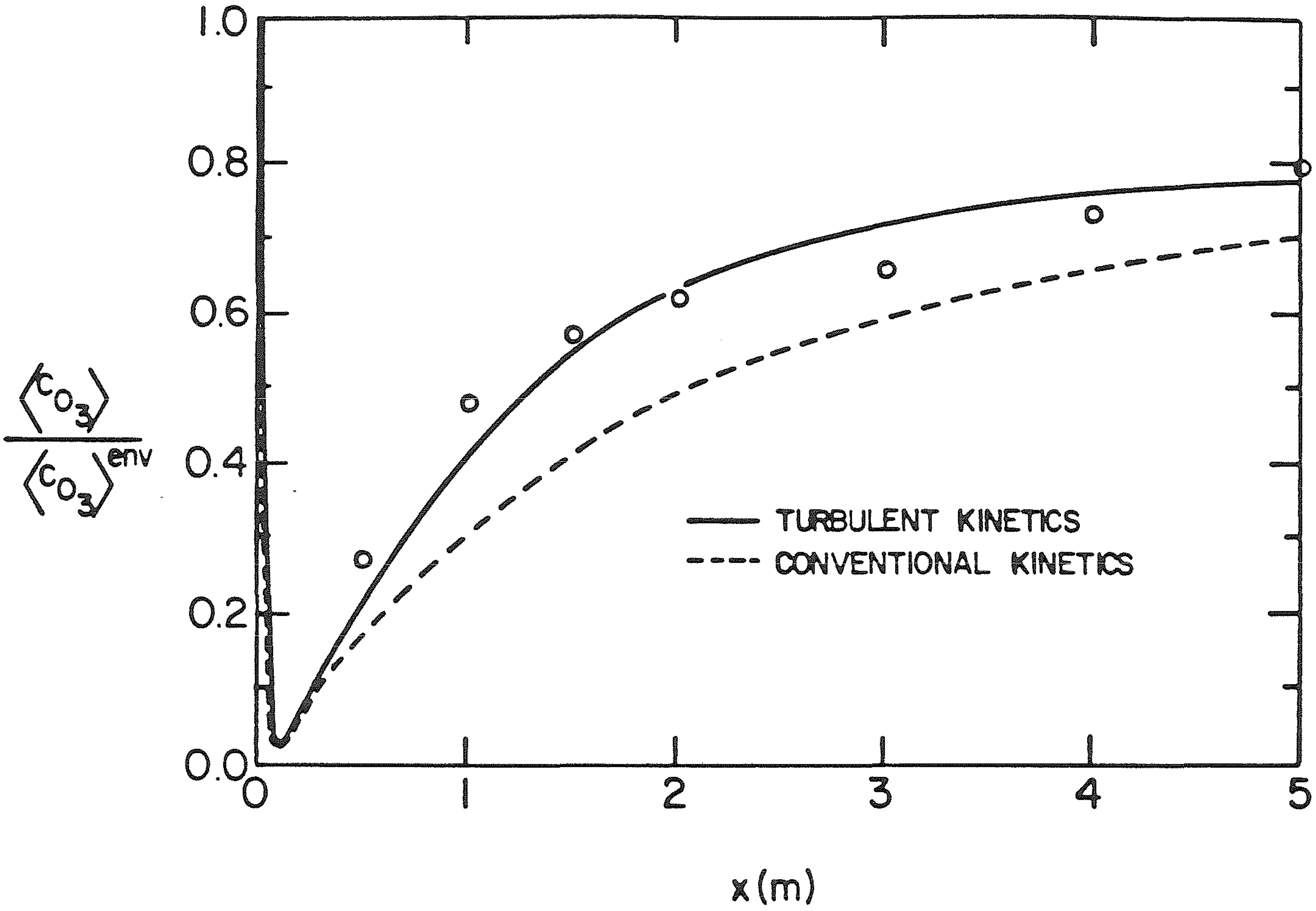

Figure 3-5

Ratio of O_3 Concentration (under reactive conditions)
to the Corresponding Background Value ($\langle c_{O_3} \rangle^{env}$) along the Plume Centerline:
Data of Builtjes (1981) and Calculations
(i) for Turbulent Kinetics (the complete TRPM equations), and
(ii) for Conventional Kinetics (ignoring the effects of micromixing).

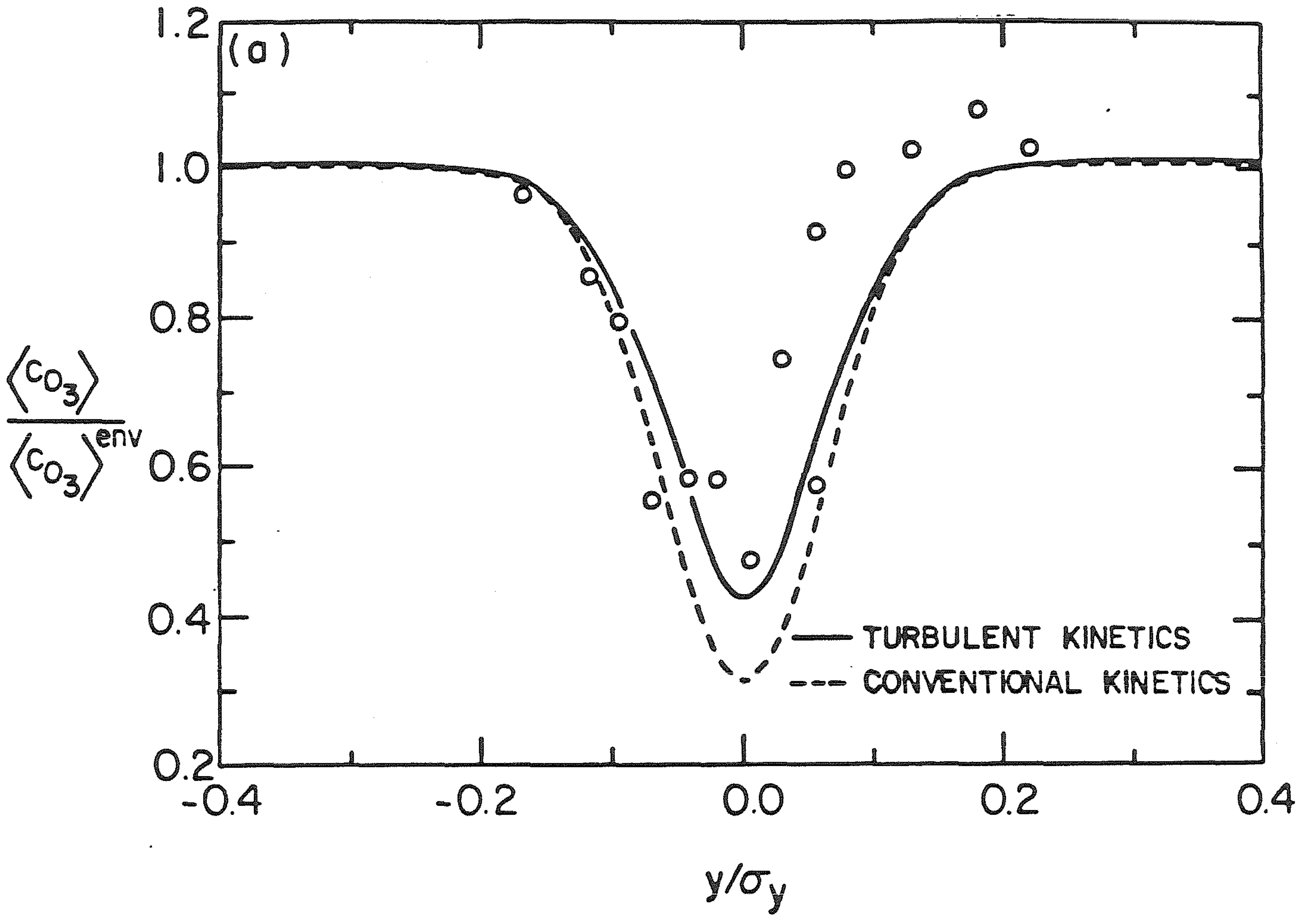

Figure 3-6a

Ratio of O_3 Concentration (under reactive conditions)
to the Corresponding Background Value ($\langle c_{O_3}\rangle^{env}$)
Horizontally at Source Height at $x = 1$ m Downwind:
Data of Builtjes (1981) and Calculations
(i) for Turbulent Kinetics (the complete TRPM equations), and
(ii) for Conventional Kinetics (ignoring the effects of micromixing)
vs the Dimensionless Distance y/σ_y from the Centerline.

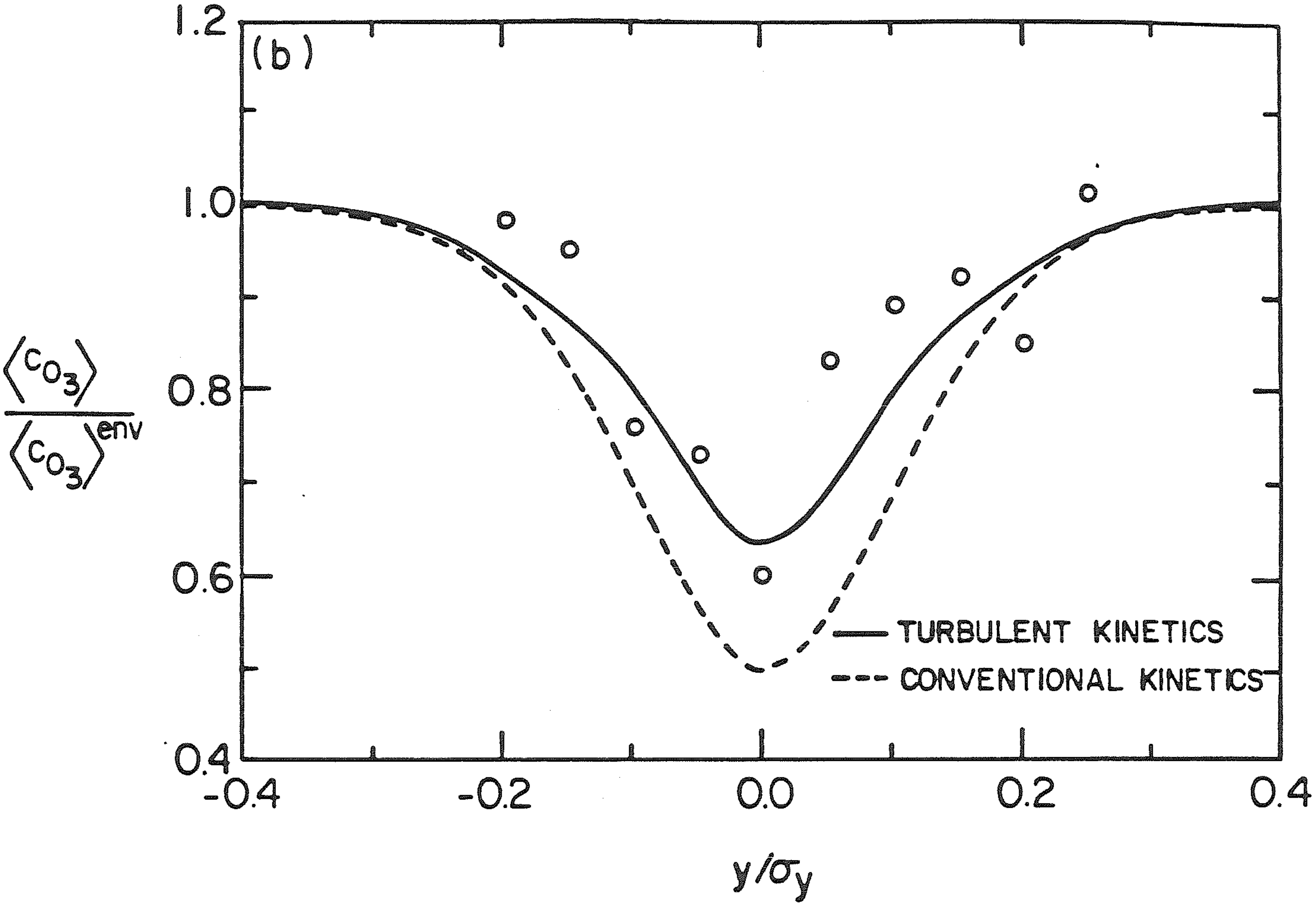

Figure 3-6b

As in Figure 3-6a, at $x = 2$ m

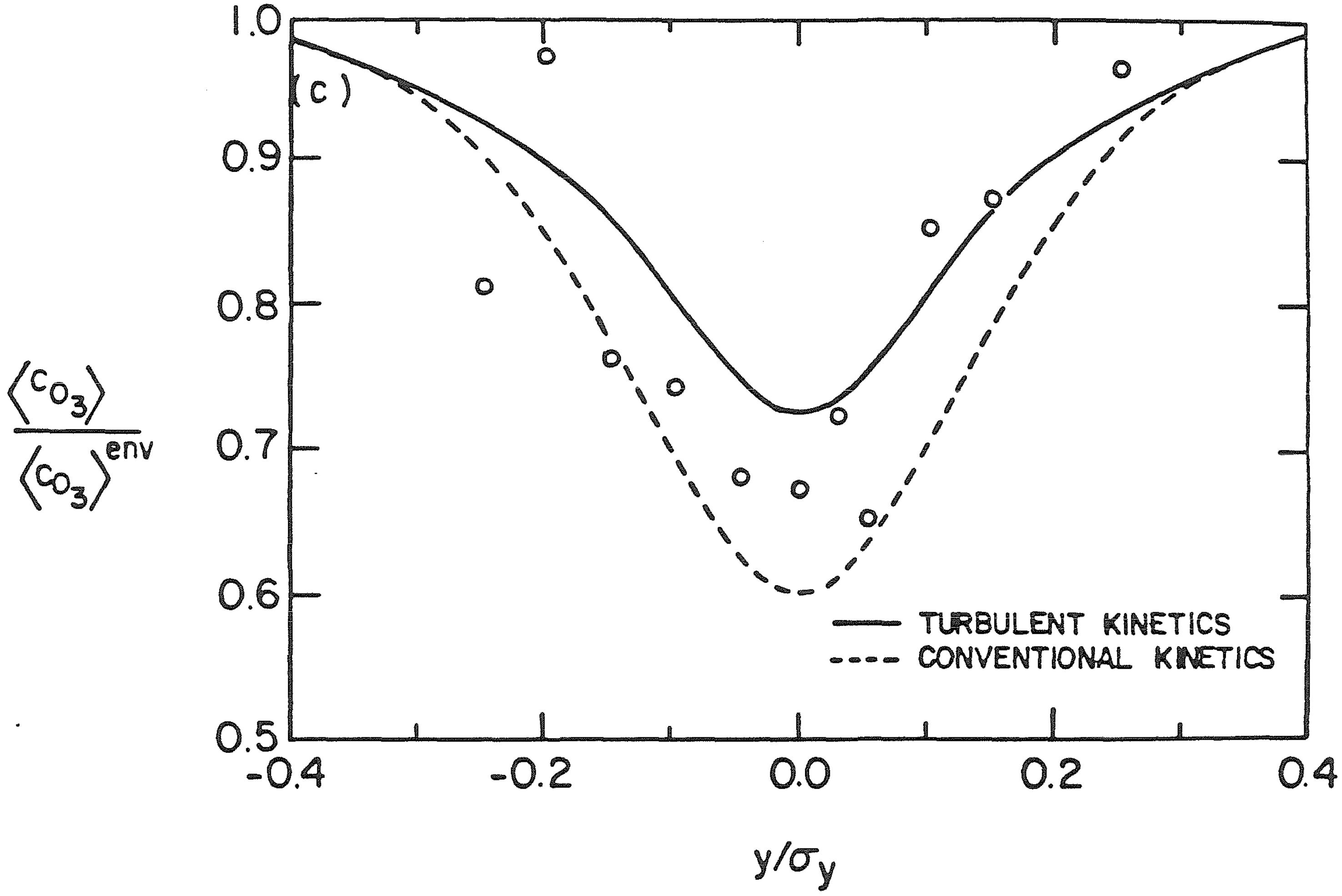

Figure 3-6c

As in Figure 3-6a, at $x = 3$ m

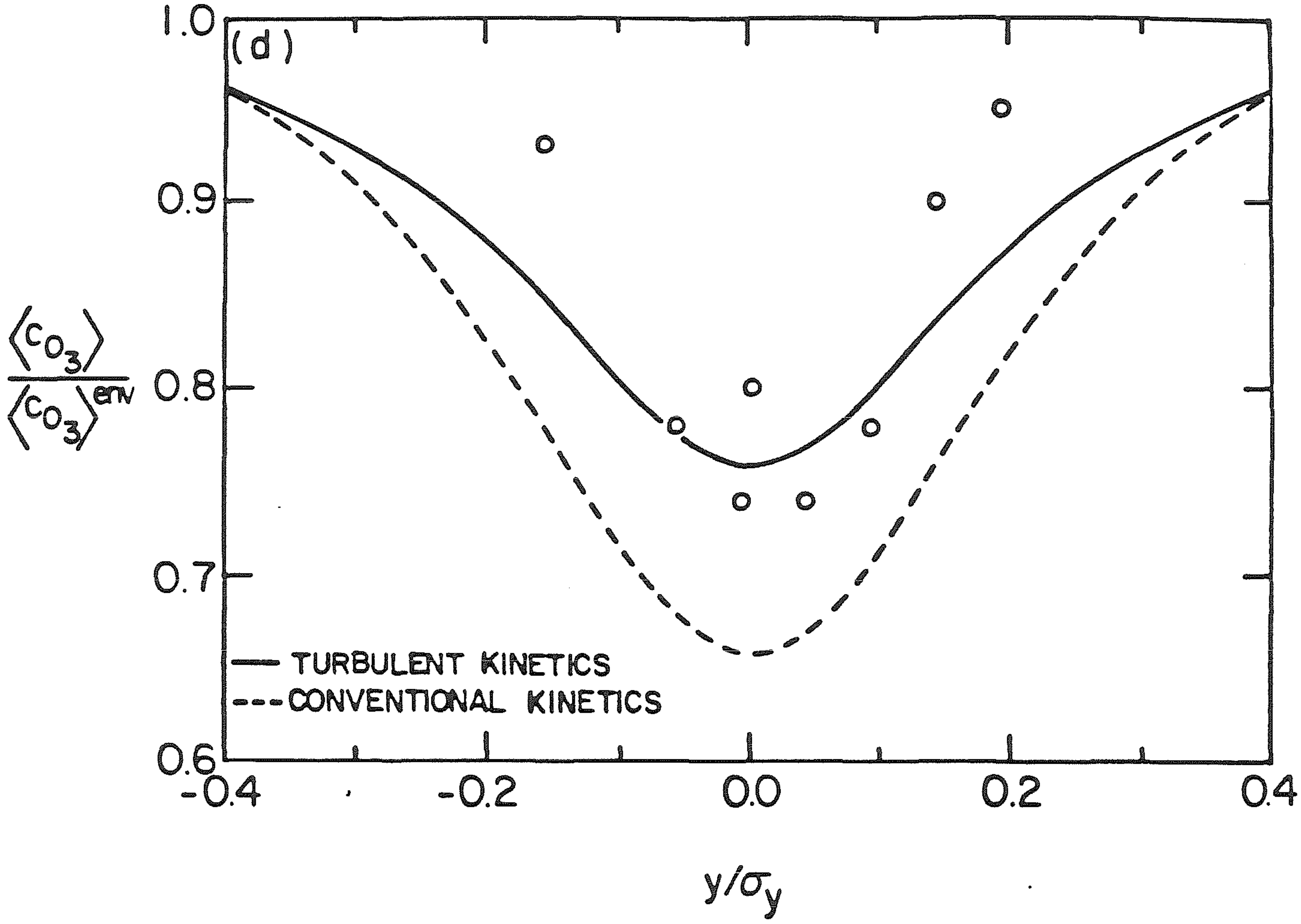

Figure 3-6d

As in Figure 3-6a, at $x = 4$ m

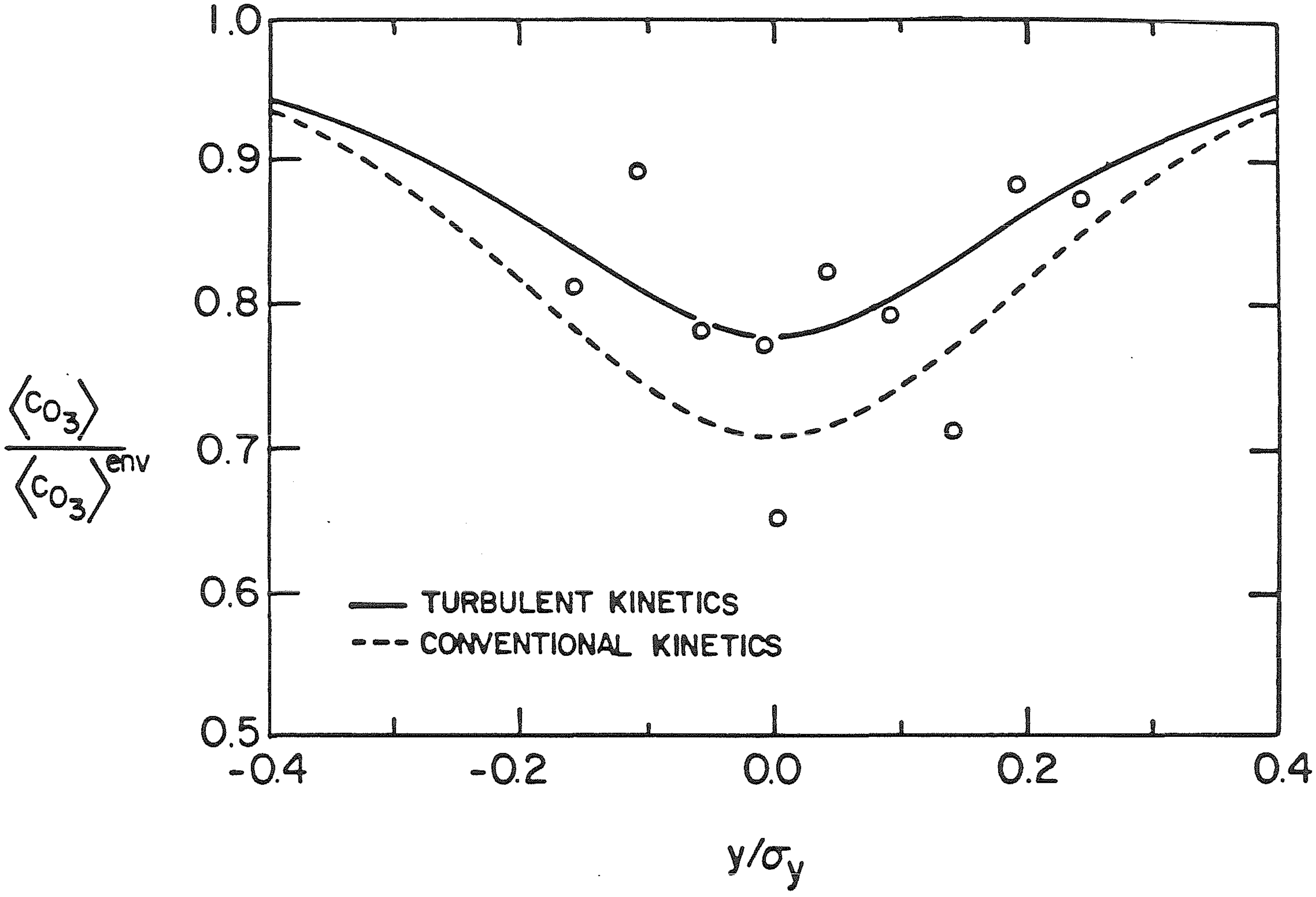

Figure 3-6e

As in Figure 3-6a, at $x = 5$ m

wind tunnel (e.g. the average temperature in the wind tunnel was used to calculate the rate coefficient k_3 and the average value of centerline intensity of segregation I_s^c was used to fix parameters in the segregation profiles).

Extensive sets of calculations were performed for varying values of the primary parameters, especially for those in categories (b) and (c) above, in order to assess the sensitivity of the TRPM to their values. The results of these calculations show that the TRPM is quite robust with respect to the parameters involved and allows for a reasonable amount of uncertainty in their estimation; they futher show that the present agreement between measurements and theoretical predictions does not arise from any type of "fine tuning" of parameters. As an example, the effect of $\sqrt{I_s^c}$ variation between its extreme observed values in the steady state range (approximately 0.35 to 0.65), is shown in Figure 3-7: the calculations are for the $\langle c_{O_3} \rangle / \langle c_{O_3} \rangle^{\text{env}}$ ratio, as those in Figure 3-5, with measured values also shown, and the two curves correspond to the minimum and maximum measured value of I_s^c. The analogous calculation is shown in Figure 3-8 for the dissipation factor A_1 varying within its entire range of values, as reported in the literature for various flows, i.e. between 1.5 and 3.0. (The calculations of Figure 3-5 were performed with $A_1 = 3p = 2.72$). Another point that is worthy of mentioning is that calculations with the complete TRPM are less sensitive to random variations of the chemical rate coefficients, due e.g. to random variations in temperature or in light intensity, than calculations employing conventional kinetics. This of course is to be expected, since, in the case of turbulent kinetics, chemistry has to "share" the control of the system with the mixing processes. Figures 3-9a and 3-9b show the effect of varying k_3 on both turbulent and conventional kinetics calculations.

Finally, in order to provide a more general perspective, the theoretical predictions of the $\langle c_{O_3} \rangle / \langle c_{O_3} \rangle^{\text{env}}$ ratio for the reaction $O_3 + NO \rightarrow NO_2 + O_2$, again from numerical solution of the reaction–diffusion equation for both turbulent and conventional kinetics, are compared with results that incorporate the reverse reaction (with a constant average k_1), with all other parameters identical,

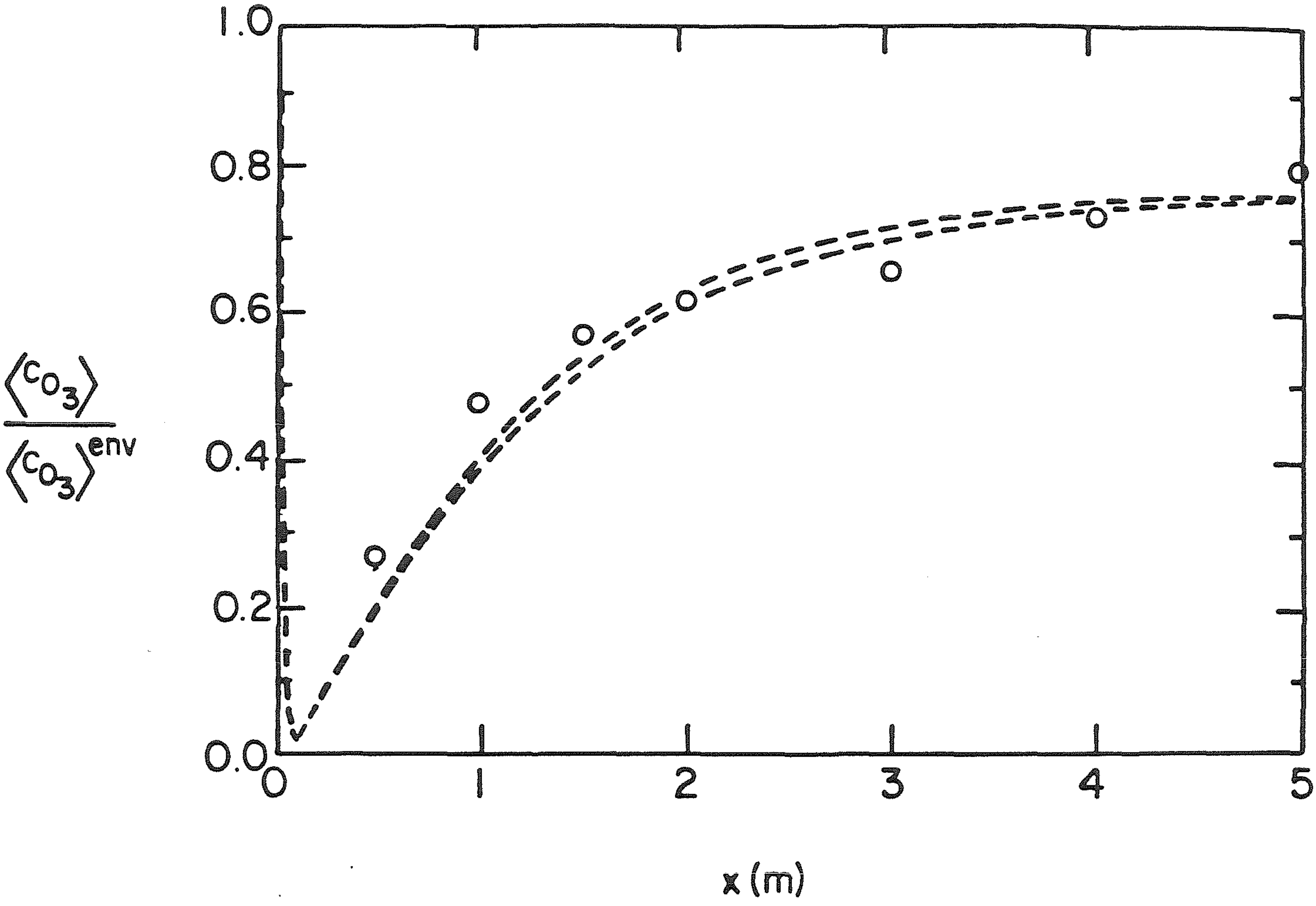

Figure 3-7

Sensitivity of TRPM Calculations to the Intensity of Plume Segregation:

Calculations of the Ratio

of O_3 Concentration (under reactive conditions)

to the Corresponding Background Value ($\langle c_{O_3}\rangle^{env}$)

along the Plume Centerline

for $\sqrt{I_s^c} = 0.65$ (upper curve) and for $\sqrt{I_s^c} = 0.35$ (lower curve)

(Data of Builtjes (1981))

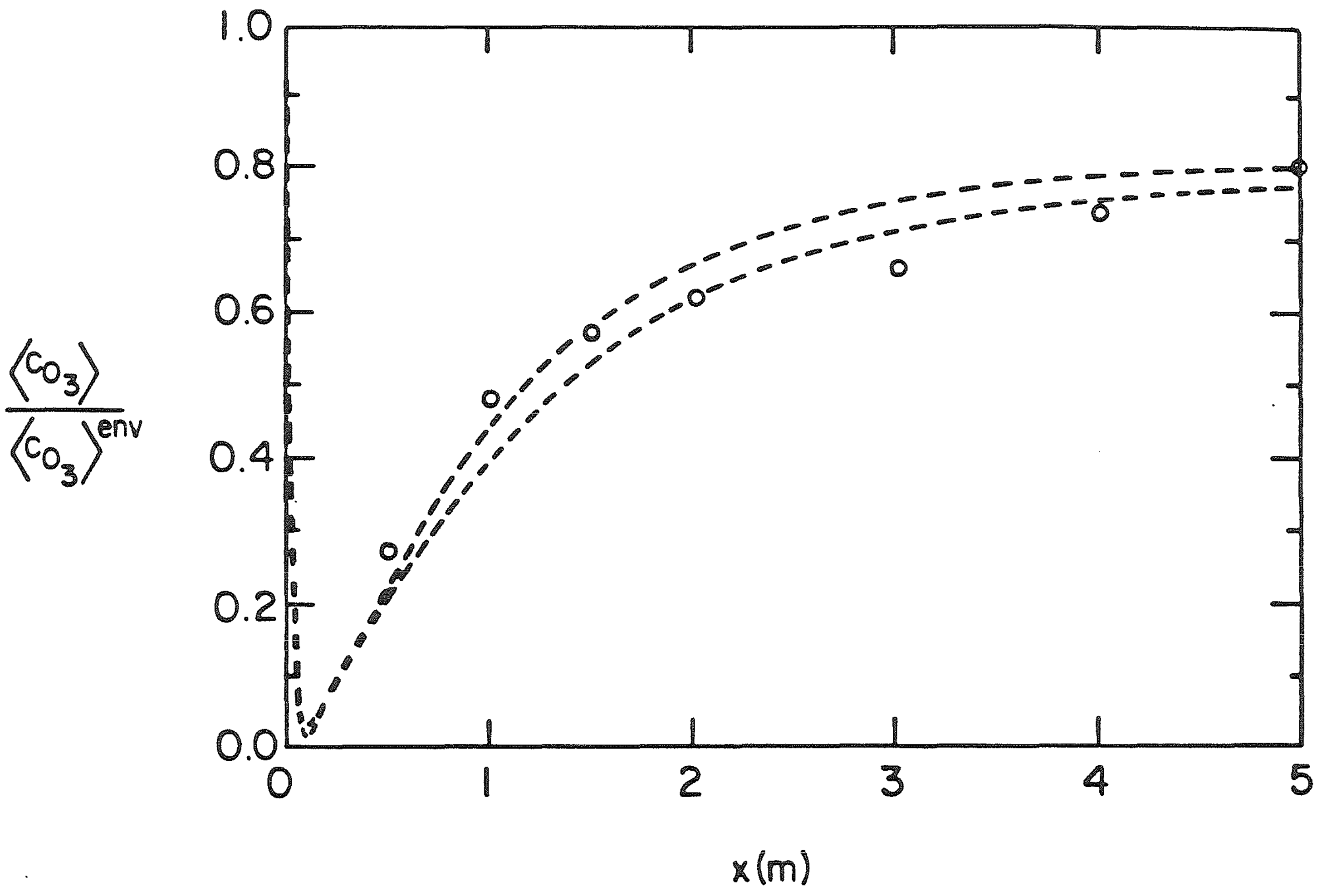

Figure 3-8

Sensitivity of TRPM Calculations to the Dissipation of Fluctuations Scale Factor:
Calculations of the Ratio
of O_3 Concentration (under reactive conditions)
to the Corresponding Background Value ($\langle c_{O_3}\rangle^{env}$)
along the Plume Centerline
for $A_1 = 1.5$ (upper curve) and for $A_1 = 3.0$ (lower curve)
(Data of Builtjes (1981))

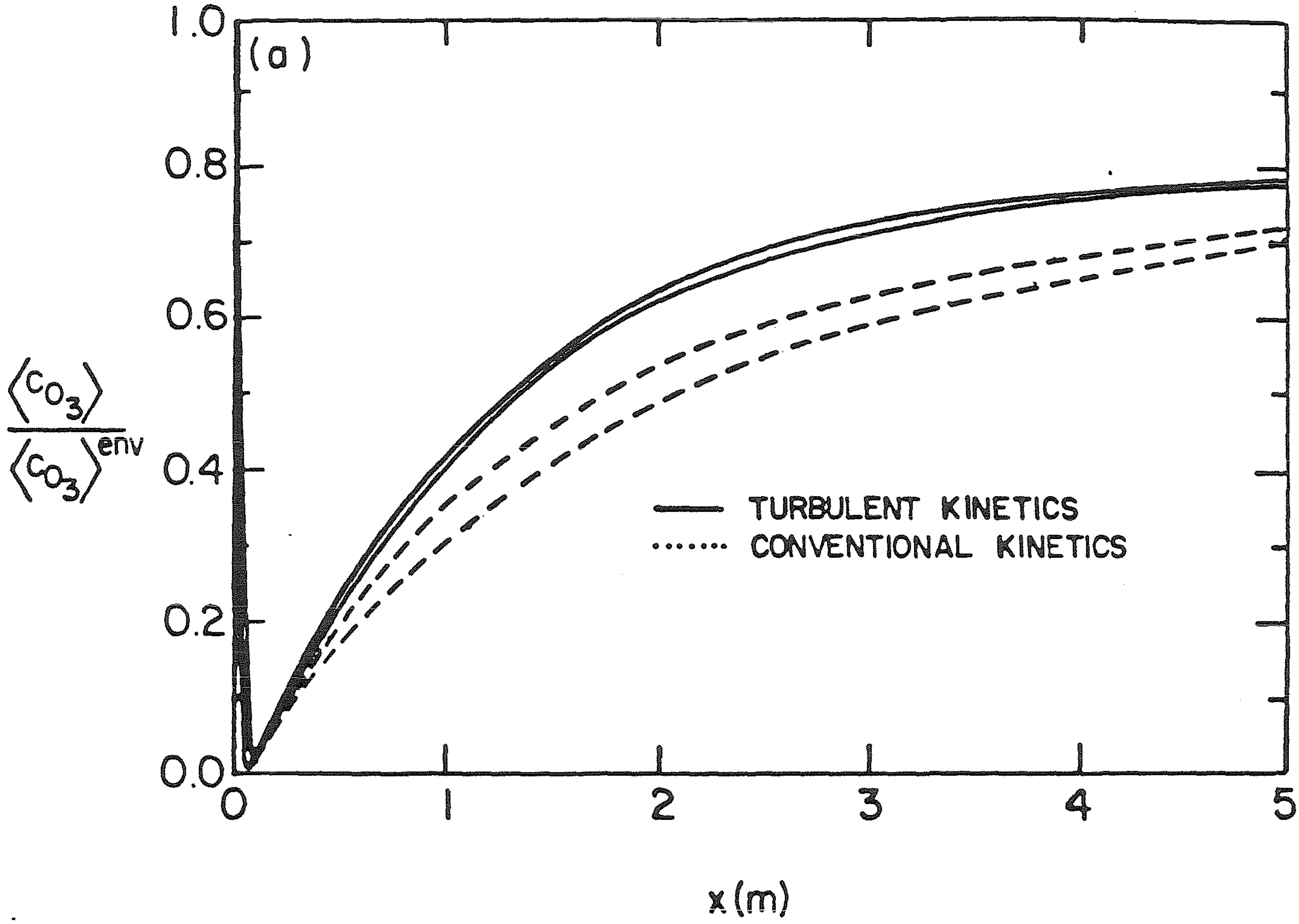

Figure 3-9a

Sensitivity of Turbulent and Conventional Kinetics Calculations
to the Reaction Rate Constant:
Calculations of the Ratio of O_3 Concentration (under reactive conditions)
to the Corresponding Background Value ($\langle c_{O_3} \rangle^{env}$)
along the Plume Centerline
for $k_3 = 0.36$ ppm^{-1} s^{-1} (upper solid and dashed curves)
and for $k_3 = 0.44$ ppm^{-1} s^{-1} (lower solid and dashed curves)

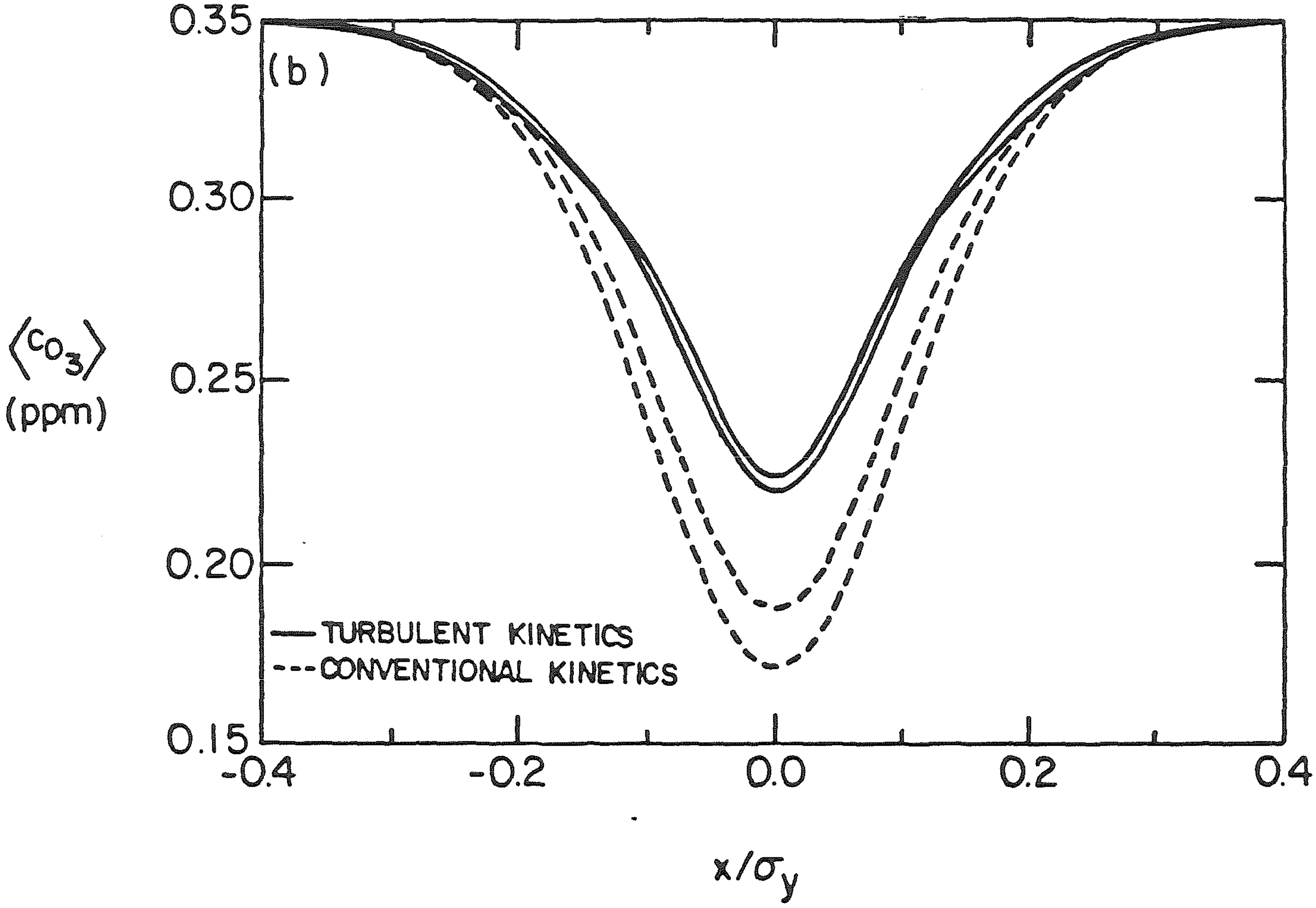

Figure 3-9b

Sensitivity of Turbulent and Conventional Kinetics Calculations to
the Reaction Rate Constant:
Calculations of the Ratio of O_3 Concentration (under reactive conditions)
to the Corresponding Background Value ($\langle c_{O_3} \rangle^{\mathrm{env}}$),
Horizontally at Source Height and at $x = 2$ m,
for $k_3 = 0.36$ ppm^{-1} s^{-1} (upper solid and dashed curves)
and for $k_3 = 0.44$ ppm^{-1} s^{-1} (lower solid and dashed curves).

(a) from solution of the reaction–diffusion equations exactly as before but incorporating the new kinetic term, and,

(b) from assuming photostationary equilibrium and applying $\tilde{R} = 0$ (Figure 3-10).

These calculations show that, under conditions such as those prevailing in the reactive plume experiments of Builtjes, photostationary equilibrium is an acceptable approximation only after travel times of about 15 s at the wind tunnel scale (at which time micromixing effects also become negligible). Close to the source, where the concentration of NO is 4 or 5 orders of magnitude higher than that of the background O_3, a requirement for equilibrium induces a significant increase of the reaction rate. However, this increase cannot be observed in reality, because the rate of mixing would then constitute a much slower step and would control the overall process. The (hypothetical) variation of the photostationary state parameter along the plume centerline under the assumption of local equilibrium with turbulent kinetics is shown in Figure 3-11.

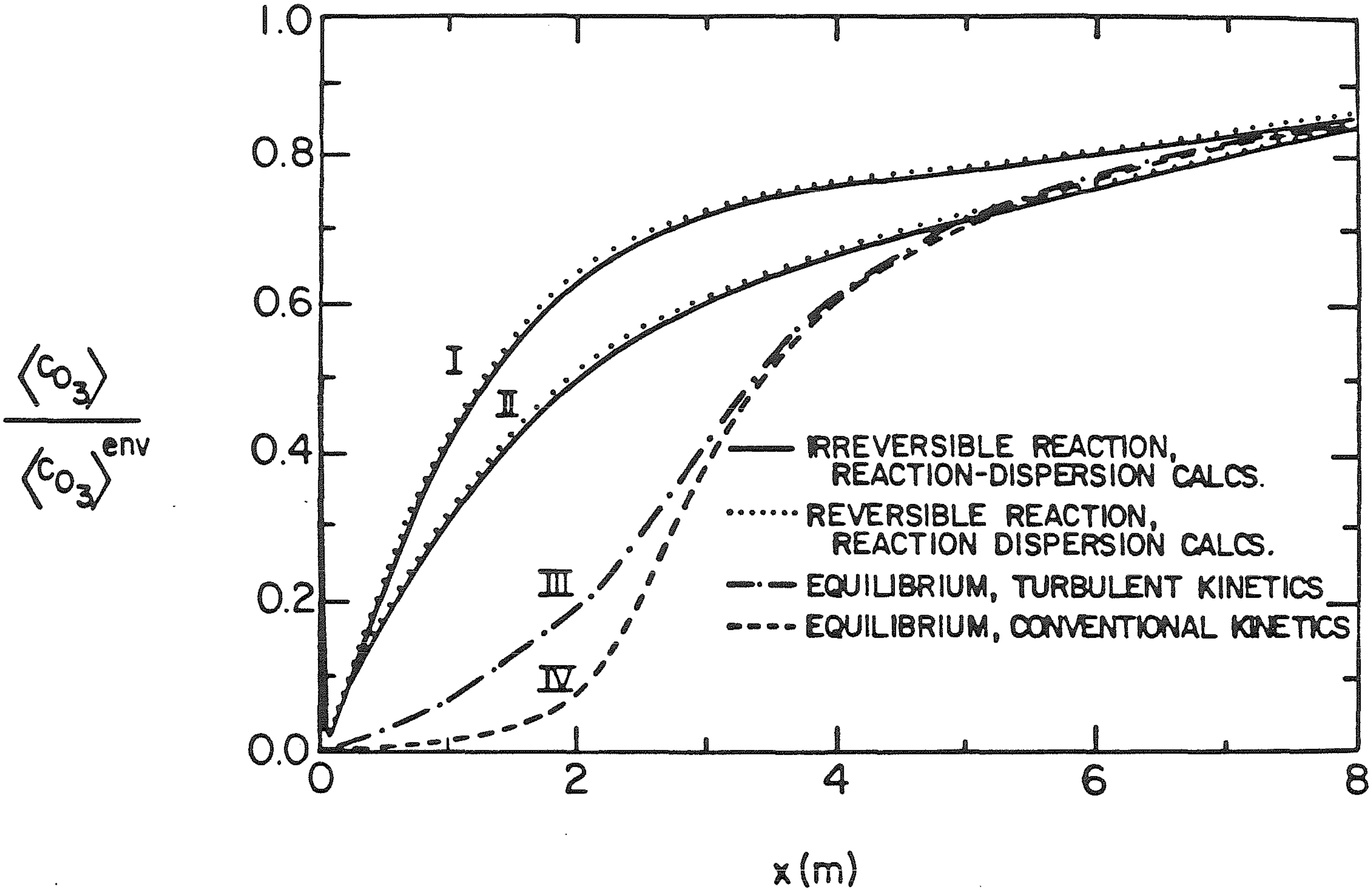

Figure 3-10

Effect of the Reverse Reaction $NO_2 \rightarrow NO+O_3$

on the Calculations of Figure 3-5:

(I) Turbulent Kinetics Reaction–Dispersion calculations

(II) Conventional Kinetics Reaction–Dispersion Calculations

(III) Photostationary Equilibrium Approximation with Turbulent Kinetics

(IV) Photostationary Equilibrium Approximation with Conventional Kinetics ($\lambda = 1$)

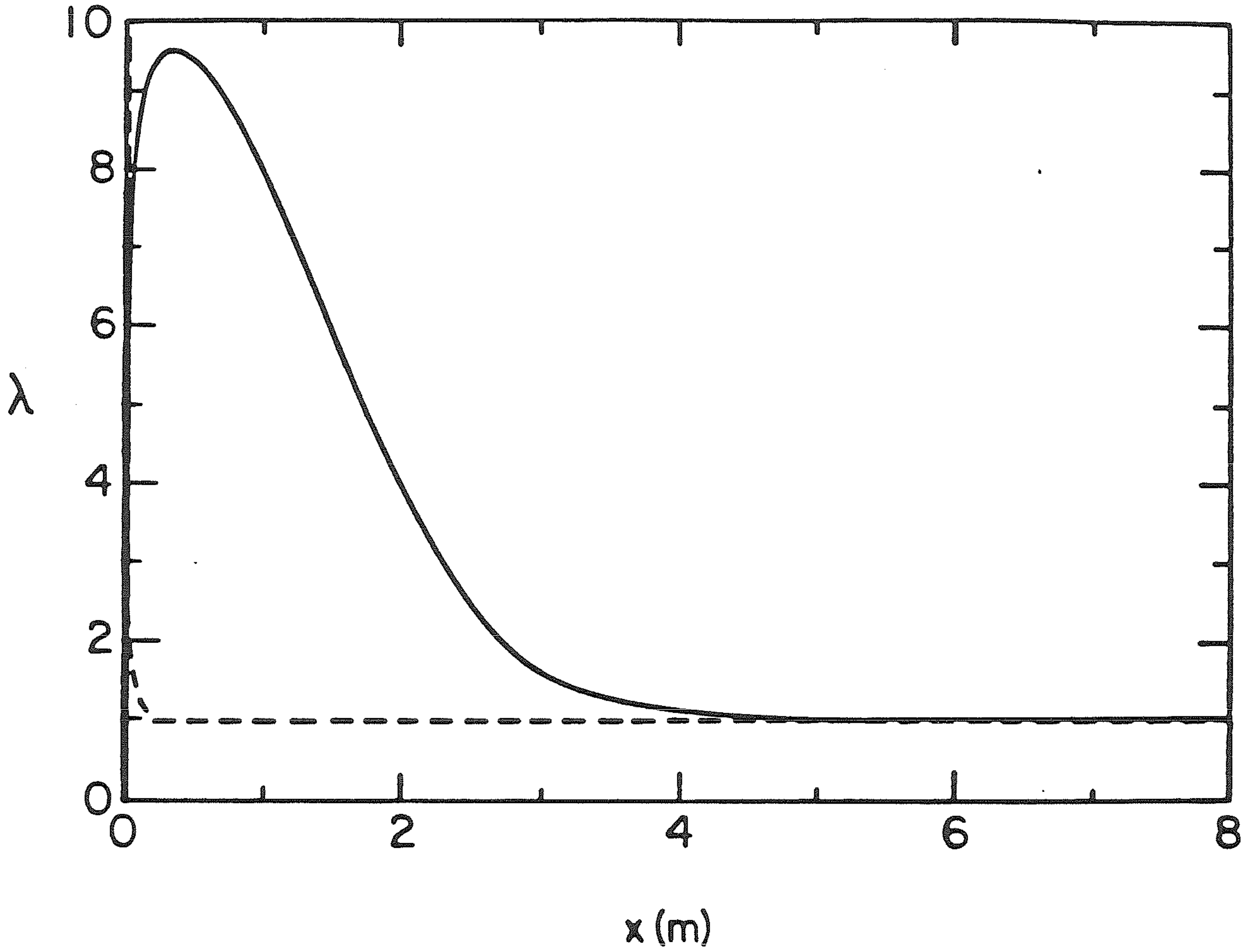

Figure 3-11

Variation of the Photostationary State Parameter λ along the Plume Centerline (under the assumption of photostationary equilibrium with turbulent kinetics) for Emission Conditions as in Builtjes (1981) Experiments

3.5 CONCLUSIONS

Comparisons with experimental data indicate that the TRPM (described in Chapter 2) represents the processes of simultaneous plume dispersion and reaction in a satisfactory manner. In particular it is worthy to note that the calculations show a definite lack of sensitivity with respect to the exact values of the physical parameters involved in the description of the effects of incomplete micromixing. Hence it seems possible that the TRPM could provide adequate estimates of these effects even with approximate values of these parameters.

Extension of the predictive capability of the model to much more complex situations, for example involving profound irregularities of the flow field (that cannot be treated as fluctuations of quantities with well behaved means), is in principle possible but will require use of more elaborate and computationally intensive versions of the TRPM than the one used for the calculations presented here, and, furthermore, will also demand inputs that are more complex and difficult to estimate.

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APPENDIX A3.1

Alternating Direction Implicit Finite Difference Form of (3.3-3)

The results presented in Chapter 3 in comparison with the experimental data of Builtjes (1981) were obtained from numerical solution of (3.3-3) through an Alternating Direction Implicit (ADI) finite difference scheme which is the standard choice for solving the basic TRPM equations in its master module (the alternative is the iterative solution of the integral equation that is equivalent to the problem described by (3.3-3) and the associated side conditions).

The finite-difference grid spans the vertical plume cross-section and calculations are performed in alternative (vertical and horizontal) directions at each time step The basic features of the ADI method are described in several standard referenes (see, e.g., Richtmyer and Morton, 1967; Ames, 1977; Lapidus and Pinder, 1982). The choice of this method for the solution of (3.3-3) is natural because the nonlinearity appears only in the chemical kinetics term and therefore can be handled easily in the calculations by introducing in the r.h.s. the value of $\langle \xi \rangle$ estimated in the iteration that is performed in the alternative direction. Furthermore, the special nature of the r.h.s. term in (3.3-3), which "spreads" the forcing function ("disturbance") in the entire three dimensional space makes the solution procedure less sensitive with respect to the discretization (and thus allows use of rather large steps in both space and time).

In the calculations the plume is assumed symmetric with respect to the vertical plane passing through the centerline; this allows reduction of the calculations to the half cross-section of the plume while imposing an artificial boundary condition on the vertical axis. (Moreover, in the very early stages of the atmospheric dispersion phase – see Chapter 7 – where the effects of the ground are negligible, the plume cross-section can also be assumed symmetric with respect to the horizontal plane passing through its center of mass. Then calculations can be performed in only a quadrant of the cross-section by imposing an artificial boundary condition on the horizontal axis as well.) The initial source concentration is assumed Gaussian (with maximum equal to the source concentration); this profile is used for the calculation of the starting $\tilde{R}_i$'s. At each time step these "turbulent kinetics functions" are estimated using the analytical expressions for the mean and variance of NO_x provided by the Gaussian and the LPF formulas respectively.

Let us for convenience set

$$a^k_{i,j} = \langle \xi \left(x = \overline{u} k \Delta t, y = i \Delta y, z = j \Delta z \right) \rangle$$

(and similarly use subscripts and superscripts to denote the values of $\tilde{R}_i$ at each node of the plume cross-section and at each time step.

Further let

$$r_y = \frac{\Delta t\, K_y\left(x\right)}{\left(\Delta y\right)^2}, \quad r_y = \frac{\Delta t\, K_z\left(x\right)}{\left(\Delta z\right)^2}$$

and

$$\hat{r}_y = \frac{\left(\Delta y\right)^2}{K_y\left(x\right)}, \quad \hat{r}_z = \frac{\left(\Delta z\right)^2}{K_z\left(x\right)}$$

Then, the finite difference equations corresponding to the *specific* problem described by (3.3-3) and (3.3-7), (3.3-8) are:

Plume Interior

Odd Traverses

$$\begin{aligned} & a^{k+1}_{i,j}\left(\frac{1}{r_z} + 2\right) - a^{k+1}_{i,j+1} - a^{k+1}_{i,j-1} = \\ & = \left(\frac{1}{r_z} - 2\frac{r_y}{r_z}\right) a^k_{i,j} + r_y a^k_{i+1,j} + r_y a^k_{i-1,j} + \\ & + \hat{r}_z \left[\left(\tilde{R}_1\right)^k_{i,j} \left(a^k_{i,j}\right)^2 + \left(\tilde{R}_2\right)^k_{i,j} a^k_{i,j} + \left(\tilde{R}_3\right)^k_{i,j} \right] \end{aligned} \qquad (A3.1-1)$$

Even Traverses

$$\begin{aligned} & a^{k+2}_{i,j}\left(\frac{1}{r_y} + 2\right) - a^{k+2}_{i+1,j} - a^{k+2}_{i-1,j} = \\ & = \left(\frac{1}{r_y} - 2\frac{r_z}{r_y}\right) a^{k+1}_{i,j} + r_z a^{k+1}_{i,j+1} + r_z a^{k+1}_{i,j-1} + \\ & + \hat{r}_y \left[\left(\tilde{R}_1\right)^{k+1}_{i,j} \left(a^{k+1}_{i,j}\right)^2 + \left(\tilde{R}_2\right)^{k+1}_{i,j} a^{k+1}_{i,j} + \left(\tilde{R}_3\right)^{k+1}_{i,j} \right] \end{aligned} \qquad (A3.1-2)$$

Boundaries

Free Boundary – Odd and Even Traverses

$$a^{\text{bound}}_{i,j} = 0 \qquad (A3.1-3)$$

Vertical Plane at $y = 0$

Odd Traverses

$$a_{0,j}^{k+1}\left(\frac{1}{r_z}+2\right)-a_{0,j+1}^{k+1}-a_{0,j-1}^{k+1}=$$

$$=\left(\frac{1}{r_z}-2\frac{r_y}{r_z}\right)a_{0,j}^{k}+2r_y a_{1,j}^{k}$$

$$+\hat{r}_z\left[\left(\tilde{R}_1\right)_{0,j}^{k}\left(a_{0,j}^{k}\right)^2+\left(\tilde{R}_2\right)_{0,j}^{k}a_{0,j}^{k}+\left(\tilde{R}_3\right)_{0,j}^{k}\right] \qquad (A3.1-4)$$

Even Traverses

$$a_{0,j}^{k+2}\left(\frac{1}{r_y}+2\right)-2a_{1,j}^{k+2}=$$

$$=\left(\frac{1}{r_y}-2\frac{r_z}{r_y}\right)a_{0,j}^{k+1}+r_z a_{0,j+1}^{k+1}+r_z a_{0,j-1}^{k}+$$

$$\hat{r}_y\left[\left(\tilde{R}_1\right)_{0,j}^{k+1}\left(a_{0,j}^{k+1}\right)^2+\left(\tilde{R}_2\right)_{0,j}^{k+1}a_{0,j}^{k+1}+\left(\tilde{R}_3\right)_{0,j}^{k+1}\right] \qquad (A3.1-5)$$

Horizontal Axis - Odd Traverses

$$a_{i,0}^{k+1}\left(\frac{1}{r_z}+2\right)-2a_{i,1}^{k+1}=$$

$$=\left(\frac{1}{r_z}-2\frac{r_y}{r_z}\right)a_{i,0}^{k}+r_y a_{i+1,0}^{k}+r_y a_{i-1,0}^{k}+$$

$$+\hat{r}_z\left[\left(\tilde{R}_1\right)_{i,0}^{k}\left(a_{i,0}^{k}\right)^2+\left(\tilde{R}_2\right)_{i,0}^{k}a_{i,0}^{k}+\left(\tilde{R}_3\right)_{i,0}^{k}\right] \qquad (A3.1-6)$$

Horizontal Axis – Even Traverses

$$a_{i,0}^{k+2}\left(\frac{1}{r_y}+2\right)-a_{i+1,0}^{k+2}-a_{i-1,0}^{k+2}=$$

$$=\left(\frac{1}{r_y}-2\frac{r_z}{r_y}\right)a_{i,0}^{k+1}+2r_z a_{i,0}^{k+1}+$$

$$+\hat{r}_y\left[\left(\tilde{R}_1\right)_{i,0}^{k+1}\left(a_{i,0}^{k+1}\right)^2+\left(\tilde{R}_2\right)_{i,0}^{k+1}a_{i,0}^{k+1}+\left(\tilde{R}_3\right)_{i,0}^{k+1}\right] \qquad (A3.1-7)$$

Initial Node – Odd Traverses

$$
\begin{aligned}
& a^{k+1}_{0,0}\left(\frac{1}{r_z}+2\right)-2a^{k+1}_{0,1}= \\
&=\left(\frac{1}{r_z}-2\frac{r_y}{r_z}\right)a^{k}_{0,0}+2r_y a^{k}_{1,0}+ \\
&+\hat{r}_z\left[\left(\tilde{R}_1\right)^{k}_{0,0}\left(a^{k}_{0,0}\right)^2+\left(\tilde{R}_2\right)^{k}_{0,0}a^{k}_{0,0}+\left(\tilde{R}_3\right)^{k}_{0,0}\right]
\end{aligned}
\qquad (A3.1-8)
$$

Initial Node – Even Traverses

$$
\begin{aligned}
& a^{k+2}_{0,0}\left(\frac{1}{r_y}+2\right)-2a^{k+2}_{1,0}= \\
&=\left(\frac{1}{r_y}-2\frac{r_z}{r_y}\right)a^{k+1}_{0,0}+2r_z a^{k+1}_{0,1}+ \\
&+\hat{r}_y\left[\left(\tilde{R}_1\right)^{k+1}_{0,0}\left(a^{k+1}_{0,0}\right)^2+\left(\tilde{R}_2\right)^{k+1}_{0,0}a^{k+1}_{0,0}+\left(\tilde{R}_3\right)^{k+1}_{0,0}\right]
\end{aligned}
\qquad (A3.1-9)
$$

In the problem (3.3-3), (3.3-7), (3.3-8) the horizontal axis is on the ground; however the equations (A3.1-1) to (A3.1-9) remain the same in the frame attached to the plume centerline (with obvious transformations in the $\tilde{R}$-terms).

When analytical solutions for the inert surrogate concentration and/or the internal plume variance are not available these quantities must be calculated numerically in order to be introduced in the $\tilde{R}$-terms of the equations for $\langle\xi\rangle$; the relevant partial differential equations are solved by a finite difference system that is similar to equations (A3.1-1) to (A3.1-9) but with the term containing the $\tilde{R}$'s equal to zero (for the mean concentration calculations) or replaced by the appropriate discrete form of the r.h.s. terms of equation (2.6-4) (for the variance calculations; the ground boundary condition changes also in this case). Reformulation of the numerical scheme for non-symmetric plumes is obvious.

Finally, we note that the reader interested in the underlying theoretical fundamentals of the iterative computational scheme of equation (3.3-11) can find relevant information in the monographs of Kubicek and Hlavacek (1982) and Ortega and Rheinboldt (1970).

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for Appendix A3.1

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APPENDIX A3.2

Contribution of Thermal NO Oxidation to the Formation of NO_2

In emission inventories nitrogen oxides (NO_x) are often reported as equivalent emissions of nitrogen dioxide (NO_2) even though the exhaust NO_x is composed primarily of nitric oxide (NO). Unless the initial NO_2/NO_x ratio is specified from stack measurements it is necessary to establish appropriate fractions for reconstructing the actual emission levels of NO and NO_2 (McRae et al., 1982). Depending on the source, and the characteristics of the combustion process involved, the above fraction can vary from approximately 1 to 10%. In addition to the NO_2 formed during combustion, some small quantities can be formed in the exhaust gasses by the third order reaction

$$NO + NO + O_2 \xrightarrow{k_4} 2NO_2$$

This reaction step is normally ignored in photochemical reaction mechanisms because of the low ambient levels of nitric oxide. The dependence of $k_4(T)$ on temperature is given by (Baulch et al., 1978)

$$k_4(T) = \frac{1.0666 \times 10^{-5}}{T^2} \exp\left(\frac{530}{T}\right)$$

with T in degrees K. The units of $k_4(T)$ are $ppm^{-2}\ min^{-2}$.

McRae et al. (1982) presented a very simple model for the estimation of the fraction of NO which is converted to NO_2 in the vicinity of the source. (Their objective was to develop a simple approach for augmenting the emission inventory of nitrogen oxides). The approach adopted in this simple model is essentially the same with the one described in Appendix A1.1 for the photochemical reaction cycle of nitrogen oxides and ozon. However in the present case plume expansion is determined by the inherent plume dynamics and not by the ambient turbulence.

When the plume is considered to be well mixed across each transverse section in the near field the nitric oxide decay rate is

$$\frac{dc_{NO}}{dt} = -2k_4(T)\, c_{NO_2}^2 c_{O_2} + \frac{1}{dt}\frac{\mathrm{D}(t)}{dt}\left(c_{NO} - c_{NO}^b\right) \qquad (A3.2-1)$$

where $\mathrm{D}(t)$ is the plume dilution (see Appendix A1.1) and c_{NO}^b is the background concentration of nitric oxide. The nitrogen mass constraint enables the direct calculation of NO_2 from

$$c_{NO_2} = \mathrm{D}(t)\, c_{NO_x}(0) + [1 - \mathrm{D}(t)]\, c_{NO}^b - c_{NO}(t) \qquad (A3.2-2)$$

Some comments are useful at this point regarding the NO concentration dynamics downwind from the stack: Entrainment of cool ambient air into the plume causes an increase in the magnitude of $k_4(T)$ (Figure A3.2-1), the plume dilution also results in a reduction of NO. The combined effect of cooling and dilution can be described by integrating the species rate equation. If the background contribution in (A3.2-1) is ignored then the NO concentration decay is given by

$$c_{NO}(t) = \frac{c_{NO}(0)\,\mathrm{D}(t)}{1 + 2c_{NO}(0)\int_0^t k_4(T)\left\{\mathrm{D}(t)\,c_{O_2} + [1-\mathrm{D}(t)]\,c^b_{O_2}\right\}\mathrm{D}(t)\,dt} \qquad (A3.2-3)$$

Within the plume, the oxygen and temperature distributions are given by

$$c_{O_2}(t) = c^b_{O_2} + \mathrm{D}(t)\left[c_{O_2}(0) - c^b_{O_2}\right] \qquad (A3.2-4)$$

$$T(t) = T^b + \mathrm{D}(t)\left[T(0) - T^b\right] \qquad (A3.2-5)$$

To describe initial plume dilution McRae et al. used the expression

$$\mathrm{D}(t) = \exp(-0.15t) \quad (t < 30\mathrm{s}) \qquad (A3.2-6)$$

Given the initial and background conditions for NO_x, T and O_2 the system of equations (A3.2-1 to A3.2-6) can be solved to give the conversion fractions for short travel times. Figure A3.2-2 (from McRae et al., 1982) presents the results of one such calculation where the initial $NO_2(0)/NO_x$ ratio was 5.0%, $c_{O_2}(0) = 30000$ ppmV, and the instack NO varied from 200 to 2000 ppmV. (A comparison between the pure dilution cases and those in which the chemistry was included indicated that between 2 and 12% of the increase in NO_2 concentration at any travel time can be explained by thermal oxidation.)

This analysis led McRae et al. (1982) to the following conclusions: The first was that, close to the source, thermal oxidation can be significant, which in turn implies that more attention needs to be given to characterizing the stack exhaust gas concentration and temperature distributions when assembling emission inventory information. However since the effects of thermal oxidation are minimal when the dilution is high, there is no need to include this reaction in models dealing with the atmospheric dispersion phase (see Chapter 7) of plume evolution: the incremental conversion can be incorporated by simply increasing the initial NO_2/NO_x emission ratio.

References
for Appendix A3.2

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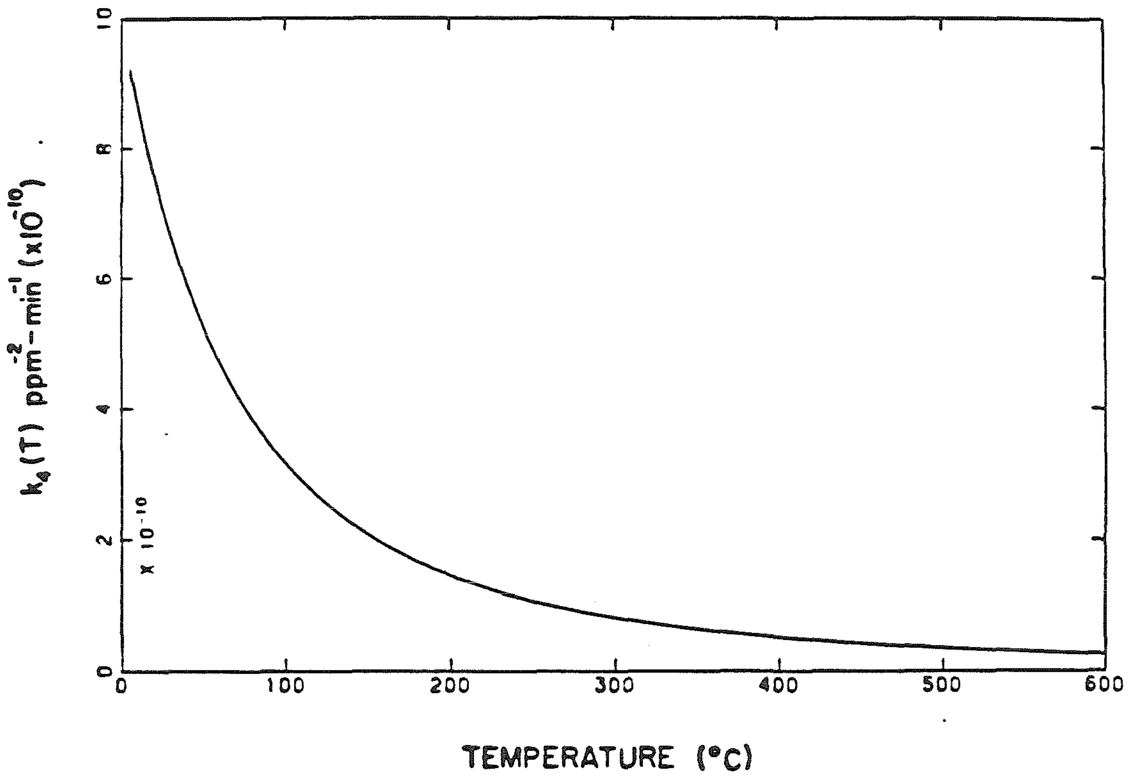

Figure A3.2-1

Variation of the NO + NO + $O_2 \rightarrow 2NO_2$ Reaction Rate Constant with Temperature

(Source: McRae et al., 1982)

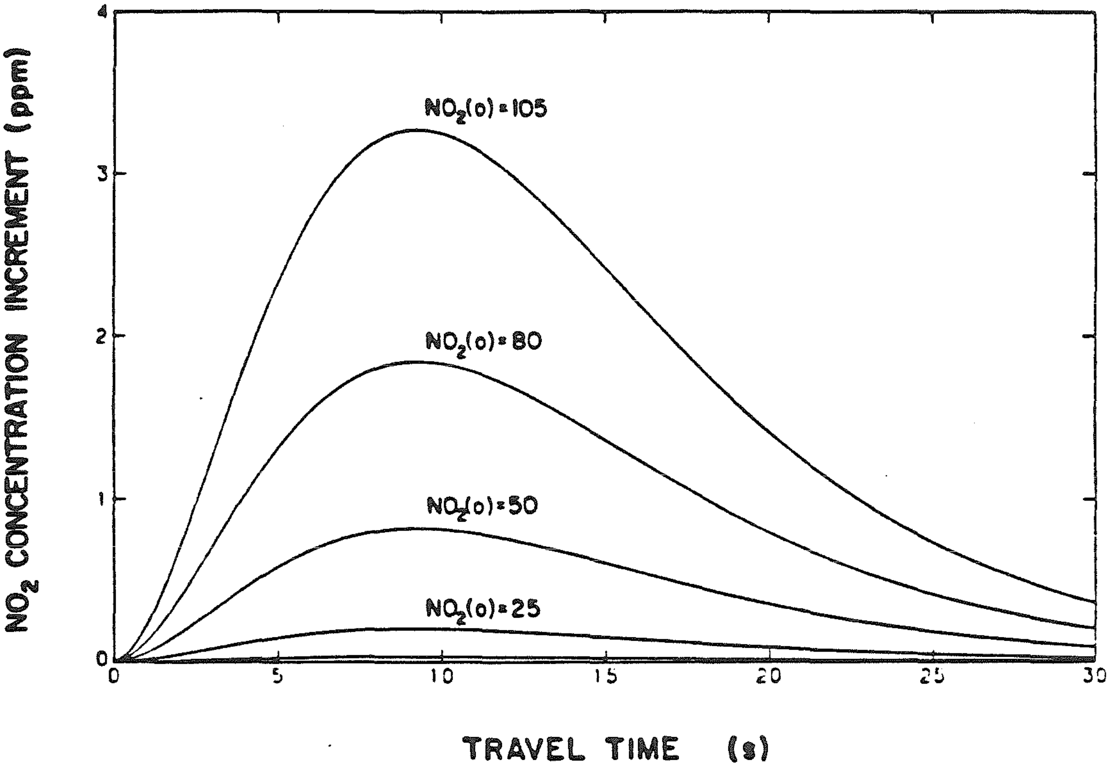

Figure A3.2-2

NO_2 Concentrations as a Function of Travel Time

(Stack Conditions $T = 250^0 C$, O_2=3%, $NO_2(0)/NO_x$=0.05, NO_2^b=0.02

(Source: McRae et al., 1982)

APPENDIX A3.3

The Effect of Temperature Fluctuations on the Formation of NO_2

(based on Kewley, 1978)

A simplified approach towards assessing the effect of temperature fluctuations on atmospheric reaction rates is to assume that the interaction between the random concentration and temperature fields (the latter being either homogeneous, that is uniform-in-the-mean or, not) takes place only through the dependence of the chemical kinetics on temperature, while all other temperature and flow field interactions are negligible (see also Chapter 4).

In this approach all effects of gradients and turbulent fluctuations of the temperature (or even the radiation) field are incorporated in fluctuating chemical kinetic coefficients. Kewley (1978) employed such a technique to study of the effect of temperature fluctuation on the value of the photostationary state parameter (see Chapter 1) in the atmospheric ozone-nitrogen oxides photolytic cycle. Indeed, if the kinetic coefficients, k_3, k_1 fluctuate randomly because of their dependence on the temperature which varies randomly inside a plume, one can write

$$k_3 = \langle k_3 \rangle + k'_3$$

$$k_1 = \langle k_1 \rangle + k'_1$$

and thus the relation

$$k_3\, c_{NO}\, c_{O_3} = k_1\, c_{NO_2}$$

leads after substitution of Reynolds decomposed quantities, and further ensemble averaging to

$$\langle k_3 \rangle \langle c_{NO} \rangle \langle c_{O_3} \rangle + \langle k'_3 c'_{NO} \rangle \langle c_{O_3} \rangle + \langle k'_3 c_{O_3} \rangle \langle c_{NO} \rangle + \langle k_3 \rangle \langle c'_{NO} c'_{O_3} \rangle + \langle k'_3 c'_{NO} c' O_3 \rangle =$$

$$= \langle k_1 \rangle \langle c_{NO_2} \rangle + \langle k'_1 c'_{NO_2} \rangle$$

Then, the photostationary state parameter defined through

$$\lambda = \frac{\langle k_3 \rangle}{\langle k_1 \rangle} \frac{\langle c_{NO} \rangle \langle c_{O_3} \rangle}{\langle c_{NO_2} \rangle}$$

will be given by the relation

$$\lambda = 1 - \frac{1}{\langle k_1 \rangle \langle c_{NO_2} \rangle} \left(\langle k'_3 c'_{NO} \rangle \langle c_{O_3} \rangle + \langle k'_3 c_{O_3} \rangle \langle c_{NO} \rangle + \langle k_3 \rangle \langle c'_{NO} c'_{O_3} \rangle + \langle k'_3 c'_{NO} c' O_3 \rangle - \langle k'_1 c'_{NO_2} \rangle \right)$$

Actually Kewley in his calculations assumed k_1 constant because of its less strong dependence on temperature (see Chapter 3). Despite the inherent deficiencies of Kewley's modeling approach regarding the description of dispersion processes (discussed already in Chapter 1), and the further assumption that temperature fluctuations are distributed in exactly an identical manner as concentration fluctuations (a claim for which there is no sufficient experimental support in the case of atmospheric plumes), it is worthwhile to note that these approximate calculations show in general that the effect of the randomness of the temperature field on the overall evolution of the reactive system becomes negligible very soon after the release of the effluents. Typical distances at which λ is estimated to be affected at an observable degree (and for typically strong initial temperature differences) were calculated to be of the order of 100 m downwind the stack and for points close to the plume centerline. It is reasonable therefore to conclude that, under conditions at which temperature variations will not be extremely strong as to induce large density and pressure variations, (and their action is felt only through the dependence of the kinetic coefficients on them), their effect can be neglected, at least at a first approximation, for the NO_x-O_3 system.

References
for Appendix A3.3

Kewley, D.J. (1978) "Atmospheric Dispersion of a Chemically Reacting Plume," *Atmos. Environ., 12,* 1895-1900.

PART IB

MATHEMATICAL MODELING OF TURBULENT REACTING PLUMES

Underlying Concepts

CHAPTER 4

Chapter 4 contains

- *an introduction to the problem of modeling nonlinear chemical reactions in turbulent flows, including a general literature survey and classification of existing methods,*
- *an exposition of the fundamentals of the Eulerian Statistical Approach for both direct and indirect chemical closure methods,*
- *a detailed presentation of the "concentration field splitting method," that is the particular indirect closure technique employed in the formulation of the TRPM*

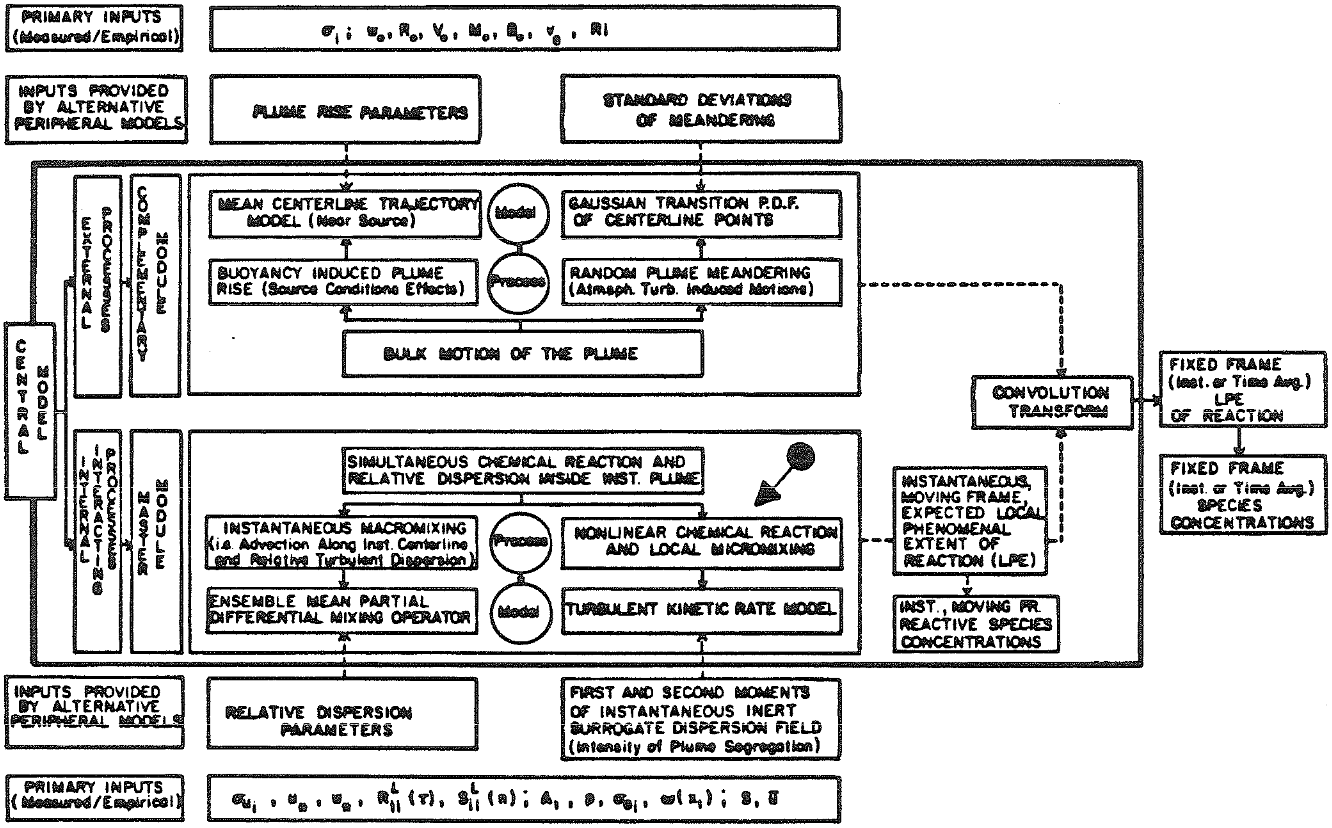

Figure 2-1a

TRPM Components Discussed in Chapter 4

CHAPTER 4

CHEMICAL REACTIONS IN TURBULENT FIELDS

4.1 INTRODUCTION

Many chemical reactions, either single-phase (on which we focus attention here) or multi-phase, of importance in both natural (environmental) and industrial systems, take place in turbulent flow fields. In general both the properties of the flow field in which the reaction occurs and the way the reactants are introduced in it will affect the spatial and temporal evolution of these systems. Further, the state of a particular system will be determined by the nature of the reaction kinetics involved (monomolecular or multimolecular) and by the relative rates of the simultaneously occurring chemical and dispersion processes.

The state of environmental systems (e.g. atmospheres and oceans) is turbulent for almost all common circumstances; on the other hand industrial flow and reaction systems are also deliberately, in most cases, in a turbulent state, in order to utilize the enhanced rates of heat and mass transfer resulting from turbulent motions (commonly called "turbulent mixing").(*) As a consequence, the problem of simultaneous

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(*) One should keep in mind that the term (turbulent) mixing is used in somewhat different context by different authors. Thus, for example, in some works turbulent mixing processes are assumed to involve just turbulent diffusion due to small scale turbulent eddies and in others to involve both this turbulent diffusion and "bulk convection" due to eddies of larger scales. It is therefore necessary to always specifically define terms like "mixing" in the analysis of systems where multiscale dispersion processes occur simultaneously.

turbulent mixing and chemical reaction is commonly encountered in a vast variety of different situations. Table 4-1 gives a typical list of cases of engineering interest where this problem has been realized and research is active towards its analysis. Although the selection of subjects in this list is far from being exhaustive, it is at least indicative of the broad range of areas in which significant interaction between turbulence and chemistry appears. The relevant research studies problems arising in fields such as chemical and environmental engineering, combustion and propulsion aerodynamics, laser and plasma chemistry etc. The major interest today appears in the area of combustion research (see, e.g., Libby and Williams, 1980; Chigier, 1981; Williams, 1985, and the proceedings of the Symposia (International) on Turbulent Combustion – the proceedings of the 20th published in 1985) where the problem of interaction between reaction and turbulent mixing seems to assume its most complex levels.(*) Increasing interest has also been arising recently in various other fields, especially in environmental applications. More specifically, Donaldson and Hilst (1972) and Lamb (1973) (see also Lamb and Seinfeld, 1974; Seinfeld, 1977) recognized the importance of incomplete turbulent mixing phenomena in the processes of photochemical smog formation and a number of related works have appeared since then (e.g. Bilger, 1978; Kewley and Post, 1978; Kewley and Bilger, 1979; Kewley, 1980; see also Chapter 1).

Due to both the variety of the problems in which the problem of rective turbulence is encountered and the wide range of approaches through which this problem is attacked (not to mention the differences, in both method and terminology, that appear in the treatment of equivalent problems in different scientific disciplines), an attempt to get familiar with the essentials of the entire spectrum of modeling tech-

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(*) The complexity of the problem in the field of combustion is basically associated with the large heat releases accompanying combustion reactions and the resulting intense variation of temperatures, densities and pressures. This leads to a complicated multidirectional coupling among the processes of heat, momentum and mass transport and the chemistry. On the contrary, in many typical environmental applications the transport processes can be assumed decoupled. The complexity of the mixing–reaction problem in environmental systems is thus associated more with the complexity and the peculiarities of the turbulent environmental flow per se (temporal and spatial variation of turbulence characteristics, many scales, unknown parameters, etc.).

niques in the field would constitute a most difficult task. Basic aspects of such techniques are covered in standard textbooks in chemical engineering (see, e.g., Froment and Bischoff, 1979) and in combustion theory (see, e.g., Williams, 1985). However the interested reader will eventually have to confront a plethora of specialized articles and publications; some comprehensive reviews (usually focusing on a specific topic) and compilations of works dealing with particular applications are available to help in his quest. In particular the collections edited by Murthy (1975), Brodkey (1975) and Libby and Williams (1980), contain a wide range of applications from various fields and some excellent reviews of specific approaches. Among the review papers with a more general perspective, those of of Hill (1976), which covers mainly the "fluid mechanical" approach to the mixing–reaction problem (together with some discussion on spectral and "micro-structural" techniques – see the analysis that follows) and of Pratt (1979), which contains a brief summary of modern chemical reactor theory on the basis of population balance approaches, can serve as tutorial introductions to the subject of reactive turbulence. Some more recent developments not contained in the above works can be found in the reviews of Villermaux (1983) and Pope (1985). (*)

It would be beyond the scope of the present work to attempt a detailed exposition of the various modeling methodologies and techniques which have appeared in the vast literature that deals with turbulence and chemistry interactions. However, the importance of these phenomena in atmospheric applications – and in particular in relevance to moderately fast reactions in point source plumes (see Chapter 1) – is a subject that merits further study and development of procedures for proper modeling

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(*) Three other comprehensive review articles, (published together), that give an overview of the reactive turbulence field from a "chemical engineering viewpoint" are those of Brodkey (1981), Nauman (1981) and Patterson (1981). One must also note that, even in order to deal exclusively with single-phase reactions (homogeneous at equilibrium systems), it is very useful to realize the analogy of the behavior of these systems with the behavior of reactive dispersions in turbulence (see, e.g., Rietema, 1964; Olson and Stout, 1967; Tavlarides and Stamatoudis, 1981). Structural methods now commonly used to model small scale turbulence effects on reaction originated in the analysis of dispersions (e.g., Curl's "coalescence-redispersion" approach); in fact one should keep in mind that before complete mixing is achieved the reactive mixture is essentially a multiphase system.

in order to improve current atmospheric dispersion and reaction models. This fact, together with the lack of an exposition of the fundamentals of the simultaneous mixing and reaction problems covering specifically the spectrum of methods that can be used in environmental applications, dictates the necessity for a concise and coherent presentation of the subject. So, in this chapter after discussing briefly some basic concepts and terms, we attempt to show the range and interrelationship of the various approaches to the mixing–reaction problem by classifying them according to a general organizational scheme.

Thus we distinguish between

- *Eulerian Statistical* (or *global "fluid mechanical"* or *"mechanistic"*) approaches, and
- *Structural* approaches (not to be confused with the structural approaches employed in the modeling of turbulence in recent years), that include
  - (a) *Lagrangian trajectory methods*,
  - (b) distributed and lumped *Population Balance methods*, which encompass classical chemical reactor theories (e.g., the residence time distribution approach), and
  - (c) *"micro-structural"* (or *"micro-mechanistic"* or *"local fluid mechanical"*) modeling techniques, that focus on the description of the local concentration structure in small control volumes ("reacting laminae") at scales below the microscale of turbulence, and then attempt to deduce global properties of the turbulent system by viewing it as a random collection of such control volumes.

Naturally, a specific modeling application may contain elements from more than one of the above approaches.

In this chapter Sections 4.2 and 4.3 are devoted to an exposition of the fundamentals of the reactive turbulence problem. Basic terminology is reviewed and clarified, and important concepts are introduced. Then a comprehensive overview of the different modeling methods available, compactly organized in figures and tables completes this exposition. The following sections deal with the systematic development of Eulerian models that are appropriate for spatially varying environmental systems. The focus is on methods that can be employed in the modeling of turbulent atmospheric plumes, the criteria being scientific validity and computational simplicity. In particular, pure and mixed conserved scalar closure approximations, including the "concentration field splitting method" that is adopted in this work, are developed to directly usable forms.

Presentation of details not directly related to the framework of atmospheric plume modeling that was described in Chapter 1 will be avoided in this chapter. Instead, references to original works and, more often, to reviews of particular problems or approaches will be given.

In conclusion, the scope of this chapter is to provide both a comprehensive introduction to the relevant literature and at the same time present a concise but structured exposition of the fundamental principles and methods underlying approaches for modeling reactions in turbulent fields.

Table 4-1

Examples of Applications
with Significant Interaction of Turbulence and Chemistry

APPLICATION	EXAMPLE
• *Continuous Flow Stirred Tank Reactors*	Kattan and Adler (1972)
• *Tubular Flow Reactors*	Pratt (1979)
• *Jet Stirred Reactors*	Clegg and Coates (1967)
• *Turbulent Jets*	Shea (1977)
• *Turbojet Plumes*	Borghi (1974)
• *Turbulent Shear Layers*	Broadwell and Breidenthal (1982)
• *Pollutant Dispersion from Stacks*	Builtjes (1983)
• *Photochemical Smog Formation*	Kewley and Bilger (1979)
• *Biological Flow Reactors and Waste Treatment*	Fan et al. (1971)
• *Combustors and Combustion Processes*	Williams (1985)
• *Turbulent Flames*	Chigier (1981)
• *Weakly Ionised Plasmas*	Shkarofsky (1974)
• *Hypersonic Ballistic Wakes*	Proudian (1969)
• *Reacting Gas Coolants for Heat Exchangers*	Richardson and Getz (1968)
• *Chemical Lasers*	Hayday and Chung (1979)

4.2 SIMULTANEOUS TURBULENT MIXING AND REACTION: BASIC CONCEPTS AND TERMINOLOGY

The evolution of a system of reacting species in a turbulent field is determined by the combined action of three processes: turbulent dispersion (or random local advection), molecular diffusion and chemical reaction.

Turbulent dispersion transfers the species through the action of the fluctuating random velocity. It reduces gradients of the mean concentration field and at the same time creates local inhomogeneities at the molecular level which, in a continuum description manifest themselves as random concentration fluctuations. These inhomogeneities are dissipated by the action of molecular diffusion. Chemical reactions take place at the same time and will in general be affected by the spatial distribution of species concentrations at both macroscopic and local (molecular) levels to a degree that depends upon the reaction order and rate as well as on the initial mixing state of the reactants.

Consider, for example, the process of turbulent mixing of two "feeds" – or portions of fluid in general – which at equilibrium (that is after a long enough time period) (*) can be mixed down to the molecular level and constitute a single phase-system; we call this a homogeneous-at-equilibrium system. Each feed is assumed to be perfectly mixed down to the molecular level at the inception of the mixing process; it may contain one or more species that may react with species of the same or of the other feed. Various situations are possible with two fluid feeds, e.g.:

(a) mixing of finite amounts of two fluids in a process vessel, or in general in a confined space

(b) mixing of a finite amount of one fluid with an "infinite" amount of another, as in the dispersion of an instant release of material – or "puff" – in the atmosphere,

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(*) Such an equilibrium can be reached either in time, e.g., for a batch mixing process taking place in a vessel, or in space as for, e.g., a steady atmospheric plume where complete mixing is obtained only far enough downwind the source.

(c) mixing of a continuous feed with an "infinite" fluid, as in the dispersion of a continuous plume in the atmosphere,

(d) mixing of two continuous feeds,

(e) mixing of a continuous feed with a mass of fluid which retains constant composition via chemical reaction, as in the ideal continuous flow stirred tank reactor, etc.

In cases (a) and (b) the mixing process evolves in time whereas in (c) and (d) it evolves in space. In case (e) the mixing process is in a steady state (possibly non-equilibrium) after an initial start-up phase has passed.

4.2.1 Stream and Age Mixing

The terms *stream mixing* (or *cross-stream mixing* or *reactant mixing* or simply *mixing*) and *age mixing* (or *self mixing* or *backmixing*) have been employed, respectively, to characterize the extreme cases of mixing between two "fresh" separate fluid feeds and of mixing of one or more feeds with fluid that achieved its current identity (different from its initial) through the action of processes (such as mixing and reaction) that take place in the flow system under consideration. Some authors go as far as to stress that stream and self mixing are completely different physical processes (e.g. Brodkey, 1967); in general these processes usually coexist but in certain cases one is dominant. Thus, stream mixing is more important in flows that show a dominant upstream-to-downstream character and are described by parabolic transport equations, whereas age mixing is more important in flows where convective recirculation is dominant; transport in such situations is described adequately by elliptic equations. As far as chemical reactions are concerned, stream mixing is more important in situations of parabolic type transport for the cases of both premixed and unpremixed reactants. In situations of elliptic type transport age mixing is the important process when the reactants are premixed but both stream and age mixing affect critically the evolution of the reaction system when the reactants are unpremixed. These qualitative notions are summarized in Table 4-2. Pratt (1979) presents some simple models for the quantification of the description of pure as well as combined stream and age mixing processes. Other, more specific or technical terms such as *channeling, by-passing, dead-space flow* etc. are also used to describe special patterns of mixing, usually in process vessels, but they will not concern us here. (See, e.g., Himmelblau and Bischoff, 1968; Wen and Fan, 1975; Oldshue, 1983, for relevant discussions and details.)

4.2.2 Micromechanics of Mixing: Relevant Scales

Let us now return to the mechanics of the mixing process of two fluid portions. Whether stream or age mixing is dominant (or are combined), portions of fluid of different chemical composition are first brought in contact – by the action of the turbulent velocity field and – then give origin to regions of fluid ("mixed zones") of new chemical identity through the processes of molecular diffusion and perhaps chemical reaction. Assume for simplicity that molecular diffusivities of all species as well as kinematic viscosities of the two, initially separate but individually uniformly mixed, feeds are of the same order of magnitude, D and ν respectively. The turbulent energy of the flow field is dissipated at a rate ϵ . Then at scales large compared to the *Kolmogorov micro-length scale* ℓ_K, where

$$\ell_K \equiv \left(\frac{\nu^3}{\epsilon}\right)^{1/4} \qquad (4.2-1)$$

turbulent velocity fluctuation distort the initial portions of different feeds by breaking, carrying, pulling and squeezing them into convoluted sheets and ribbons of decreasing thickness. The stretching, squeezing and breaking would continue indefinitely in the absence of molecular diffusion effects, that is if the Schmidt number

$$\mathrm{Sc} \equiv \frac{\nu}{D}$$

was infinite ($D \to 0$). In reality molecular diffusion acts from the start of the mixing process and slowly – in comparison to turbulent phenomena – creates regions of fluid

Table 4-2

Dominant Type of Mixing Process
in Relation to the Initial State of Reactants
and the Type of Flow

INITIAL CONDITION OF REACTANTS	GOVERNING PDE FOR THE CONCENTRATION FIELD	DOMINANT TYPE OF MIXING
premixed or un-premixed	parabolic for flows with a dominant upstream-to-downstream character	stream-mixing
premixed	elliptic	age-mixing
un-premixed	elliptic	combined

that are mixed down to the molecular scale at the interphases of portions of different feeds. In fact, if Sc is of order unity or larger, Batchelor (1959) showed that when the patches of fluid approach a thickness of order $O(\ell_B)$, where

$$\ell_B = \left(\frac{\nu D^2}{\epsilon}\right)^{1/4} = \ell_K \mathrm{Sc}^{-1/2} \qquad (4.2-2)$$

is the *Batchelor micro-length scale*, concentration gradients normal to the patch are sufficiently large that the molecular fluxes balance the compression of the patch by the straining motion, and the creation of fluid zones mixed at the molecular level is the dominant physical process. If Sc is much smaller than unity,i.e $\nu \ll D$, then the relevant microscale is the *Corrsin-Obukhov microscale* ℓ_C defined as

$$\ell_C = \left(\frac{D^3}{\epsilon}\right)^{1/4} = \ell_K \mathrm{Sc}^{-3/4} \qquad (4.2-2a)$$

(This is not to be confused with "Corrsin's dissipation scale" that is defined as the counterpart of Taylor's microscale for scalar diffusion and is discussed in Section 4.4 and in Chapter 5).

For diffusion of gases like CO, NO, NO_2, SO_2, etc., in the atmosphere, Sc is of order 1 and ℓ_K, ℓ_B assume approximately equal values; thus either scale is relevant.

Other microscales, of similar nature, have also been introduced in various models of local diffusion and reaction; among them the *"striation thickness"*, first defined by Mohr (1957) as a measure of the thickness of "patches" of completely mixed material, has been very popular in the modeling of "lamellar microstructures" (see Section 4.3.2) in turbulent reacting flows (see, e.g., Ranz, 1979; Ou and Ranz, 1983ab).

Another quantity of interest in detailed descriptions of reaction-diffusion phenomena at the local level of laminar conditions is the rate at which the thickness of perfectly mixed "patches" diminishes with time. A simplified analysis assuming a uniform local (laminar) velocity gradient gives for the thickness $\ell(t)$ of the mixed zone (Middleman, 1977)

$$\ell(t) = \ell(0)\left(1 + \gamma^2 t^2\right)^{-1/2}$$

where γ is the constant strain rate of the laminar shear, approximately given by (see, e.g., Bourne, 1982; Baldyga and Bourne, 1984)

$$\gamma \simeq 0.5 \left(\frac{\epsilon}{\nu}\right)^{1/2}$$

4.2.3 Macro-fluids versus Micro-fluids

Macro-mixing versus Micro-mixing

So, before final equilibrium is achieved, any mixture will have some of the characteristics of a two-phase (or multi-phase) system, as for a certain period of time portions of the different feeds will be intermixed by turbulent motion down to a rather fine but still macroscopic level of very small *"fluid elements"* or *"fluid particles"* which preserve their different identity defined by chemical composition. A fluid which can be viewed in this way, i.e. as consisting of elements of different identity, is often called a *macro-fluid* in contrast to a *micro-fluid* (*) in which all different species are mixed down to the molecular level (see, e.g., Levenspiel, 1972). The small "structural elements" of a macro-fluid (which, when it corresponds to a homogeneous-at-equilibrium system is of course always in a transition state) are not always identified in the same way but we will not discuss this subject in detail here. Use of the term "fluid particle" dictates however a few comments. The concept of a fluid particle is widely used in Lagrangian descriptions of turbulent diffusion (see, e.g., Monin and Yaglom, 1971, 1975; Hinze, 1975; Seinfeld, 1975) as well as in population balance methods for modeling both single and multi-phase flow and reaction systems (see, e.g., Himmelblau and Bischoff, 1968). The identity of a fluid particle in such treatments is not necessarily determined by its composition; other properties such as, e.g., its temperature or its "age" (time it has spent in the flow field) are often used instead. Many other terms like "fluid element," "material point of fluid", "fluid lump", "fluid clump", "continuum element of fluid", "fluid molecule", have also been employed in

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(*) Sometimes the terms macromixed and micromixed fluid (or reactor) are used instead (see, e.g., Pratt 1979).

the literature; however the context in which these terms are used is not always the same. For some authors a fluid particle (or element) has completely uniform "internal properties" (concentrations, pressure) and is so small (smaller than the appropriate microscale of turbulence) that its structure cannot be affected (e.g. distorted) by the turbulent motions. In this way it corresponds to a "point" of the *fluid continuum.* For others it can have larger dimensions, non-uniform internal structure and can be distorted by the action of the turbulent motions. In this way it corresponds simply to a Lagrangian *material volume* of fluid. Hinze (1975) discriminates between a *fluid particle* (which can only be advected by turbulence) and larger *fluid lumps* (which can be distorted and separated into smaller lumps or fluid particles). According to such a definition the only interaction of a fluid particle with its environment can only be purely molecular in nature (but of course can be approximately modeled as a larger scale random process, i.e. a coalescence and redispersion model of fluid particles can be used to simulate a "spreading" of properties actually due to molecular diffusion). Hinze (1975, §5.1) further distinguishes between *volume particles* and *property* or *substance particles.* A volume-particle is defined as a small constant volume of fluid following the (random or not) flow, whereas a property-particle is defined in terms of some property of the material constituting it and thus can be viewed as a collection of marked (by their chemical identity or age, etc.) molecules. If molecular effects are negligible the volume and property particle remain identical during any dispersion processes; otherwise the motion of the centroid of the property particle deviates from that of the original volume particle. A point worthy of noting here is that in fact the dispersion of a property due to molecular diffusion is *not* statistically independent of that due to macroscopic random turbulent velocities; see, e.g., Hinze (1975, §5.5).

The way in which fluid particles of different identities are distributed spatially in the flow field determines the *state* or *degree* of *macromixing* of the system (or *"the system's macrostate"*). Mean continuum properties, (that is first means of stochastic continuum quantities defined over "points" which are of the size of fluid particles), reveal and characterize this macrostate. Thus, if fluid particles from two feeds of different chemical composition are uniformly distributed over a volume or area of the flow field, the mean concentration of any conserved species of the mixture will also appear to be uniform there.(*) As time passes compositions of individual volume fluid particles may change through the process of molecular diffusion until all such particles are identical and molecular uniformity has been achieved, but mean concentrations of the of the conserved species will remain the same. Thus, the degree of macromixing is determined (locally for a spatially varying system) by the "gross" characteristics of the flow i.e. *first moments* of random variables and characterizes uniformity of mixing at the level of fluid particles. Further, it is *insensitive* to the *degree* or *state* of *micromixing* (or *"system's microstate"*) which refers to the finer structure of the flow field, at scales smaller than those of the fluid particles, down to the molecular level. For a given macrostate the instantaneous degree of micromixing of a system may vary from *complete segregation*, in which no observable zones of microscopically mixed fluid have been created and the fluid particles retain unaltered their initial identities (the mixture is a macro-fluid), to *maximum mixedness*, in which molecular diffusion has brought intimate mixing of individual molecules in the entire system (the mixture is a micro-fluid). This however does not necessarily imply that concentrations are also uniform in the mixture. In terms of continuum variables of the flow field, micromixing is revealed by their fluctuations and the variation of their higher order moments and correlations.

The distinction between these two different kinds or levels of mixing in a given system is of crucial importance, as far as the evolution of chemical reactions is concerned, for both premixed and unpremixed reactants. This was recognized in the 1950's by Danckwerts (1953, 1958) who introduced this distinction of mixing con-

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(*) Some authors (e.g., Patterson, 1975) use the term macromixing in a different context, that is to describe a mixture is in a state of complete segregation (which in our terminology is one extreme state of micromixing) and the term micromixing to describe the state of maximum mixedness. This use of a term in very different contexts is unfortunately very common in the field and unavoidably causes confusion to anyone not familiar with the terminology of different authors.

cepts in chemical reactor theory (*) with ideas that were soon extended by Zwietering (1958) and Van Krevelen (1958). Danckwerts also introduced quantitative measures for the description of macrostates and microstates which since then have been used in chemical engineering literature almost exclusively to describe premixed reactants systems where age mixing is the dominant process.

Thus the *residence time distribution* (RTD), defined as the time response at the exit of a reactor for an instantaneous concentration pulse of inert tracer acting as input at time $t = 0$ at its entrance, where all properties are considered uniform over the exit and entrance, characterizes the state of macromixing of the reactor as a whole (see, e.g., Himmelblau and Bischoff, 1968; Levenspiel, 1972). Another *equivalent* definition, more closely related to the concept of *age mixing*, views the RTD as the probability density that a fluid particle which enters the reactor at time $t = 0$ will leave at time t.

RTD models defined in this way represent a method of modeling through macroscopic averaging and treat the reaction-flow field as a *lumped system* with a single entrance and a single exit (a "global concept"). Hence they are not appropriate to describe systems where stream mixing is dominant (since stream mixing is a process that basically evolves in space and not in time) and in general distributed systems that do not have a single entrance and exit and the complete distribution of properties in their "interior" is of interest. Although such an approach is not common in the literature one can generalize the classical lumped-system RTD concept to such distributed systems by defining it as a function of both time and *two* sets of spatial coordinates – one for a "source" and one for a "receptor" – again as the response (concentration) at the receptor for an instantaneous release of inert tracer at the source (i.e. a Green's function for the inert mixing – i.e. advection-diffusion – boundary value problem). In general the spatial distribution of mean concentrations (steady or not) in a flow system gives a complete characterization of its macrostate.

(*) Actually Danckwerts wrote of "scales of mixing and segregation" and of "mixing at the molecular level"; the prefixes "micro" and "macro" were introduced by Van Krevelen (1958).

4.2.4 Scale and Intensity of Segregation

According to Danckwerts the degree of micromixing of a system needs *two* parameters for a *local* description. These parameters are usually called the *scale* L_s and the *intensity*, I, *of segregation.* A variety of other names is also used for the concept of I such as *mixing effectiveness* (Pratt 1979), simply *segregation* (Brodkey 1966, 1967) and *unmixedness* (Hawthorne et al.,1948). Also the term *mixing parameter* is used for $-I$ and the term *contact index* for $(1 - I)$ (see Hill, 1976; Donaldson and Hilst, 1972).

Often the intensity of stream segregation is distinguished from the intensity of age segregation and different symbols such as I_s and I_α respectively are used (see, e.g., Brodkey 1967, 1975, 1981; Pratt, 1979).

The scale of segregation describes the degree to which the dispersing material has been "spread out" by the action of turbulence. In the case of stream mixing it is a measure of some typical average size of unmixed lumps of different feeds. As these lumps are pulled, contorted and break into smaller ones the scale of segregation is reduced. Quantitative definitions of L_s can be constructed in terms of spatial correlations of concentration fluctuations. Thus, if c' is the fluctuation of the instantaneous concentration of an inert species about its ensemble mean value $\langle c \rangle$, Brodkey (1967, 1981), for example, defines for the case of *uniform* $\left\langle c'^2 \right\rangle$ the scale L_s by

$$L_s = \int g_c(\mathrm{r})\, d\mathrm{r} \qquad (4.2-3)$$

where

$$g_c(\mathrm{r}) = \frac{\langle c'(\mathrm{x})\, c'(\mathrm{x}+\mathrm{r})\rangle}{\langle c'^2 \rangle}$$

L_s is an average over relatively large distances and thus it is a measure of the "large scale breakup process", "but not of the small scale diffusional process" (Brodkey, 1981). Quantities like g_c and L_s are in general difficult to be calculated and various methods have been proposed for their estimation (see, e.g., Brodkey, 1967; Patterson, 1981, 1983).

The intensity of segregation describes the effect of molecular diffusion on the mixing process. For the case of stream mixing it is basically a measure of the difference in concentration between neighboring lumps of fluid particles of the mixture; for age mixing it is defined as a measure of the difference in age of such lumps. Quantitative definitions of I appear in the literature in a variety of different forms (some of which are appropriate only for stream mixing and others only for age mixing). In the perspective of the present work particularly useful is the definition of I as the local intensity of fluctuations of an inert scalar

$$I = \frac{\left\langle c'^2 \right\rangle}{\langle c \rangle^2} \tag{4.2-4}$$

where $\left\langle c'^2 \right\rangle$ and $\langle c \rangle$ refer to the same space-time point. The intensity I as defined in (4.2-4) describes the quality of micromixing of an inert species with the background environment, the latter seen as a single component. Such a definition is useful mainly for cases of dominant *stream mixing*.(*) This quantity is a basic parameter of the Turbulent Reactive Plume Model described in Chapter 2 and we devote Chapter 5 to its estimation in the case of steady atmospheric point source plumes.

If stream mixing is complete on a molecular scale (maximum mixedness micromixing), or if only inert tracer is present for all ensemble realizations, then $\left\langle c'^2 \right\rangle = I = 0$. For steady state cases time averages are usually used as estimates of theoretical (ensemble) means. According to the definition (4.2-4) I will be equal to unity in the particular case of complete segregation with equal probabilities of tracer existing or not existing at the point and instant of measurement (in other words in cases with local concentration *intermittency* equal to 1/2; see Chapter 5). A major disadvantage of the definition (4.2-4) is the behavior of I for tracer concentrations tending to zero. Thus in the plume case both nominator and denominator of (4.2-4) go to zero as the plume boundaries are approached but the denominator decreases faster with I tending to infinite values.

(*) Pratt (1979) defines the intensity of segregation through (4.2-4) exclusively for stream mixing.

Other definitions of I attempt to express the state of mixing of two particular species A and B and thus use two stochastic concentration fields instead of the one employed in definition (4.2-4), e.g.,

$$I = -\frac{\langle c'_A\, c'_B \rangle}{\langle c_A \rangle \langle c_B \rangle} = 1 - \frac{\langle c_A\, c_B \rangle}{\langle c_A \rangle \langle c_B \rangle} \qquad (4.2-5)$$

In this case I varies from zero, for a uniformly micromixed solution, to one, when A and B do not coexist anywhere. If non reacting A and B are mixed, and B is defined as *not* – A then $c'_A = -c'_B$, and (4.2-5) gives

$$I = \frac{\left\langle {c'_A}^2 \right\rangle}{\langle c_A \rangle \langle c_B \rangle} = \frac{\left\langle {c'_B}^2 \right\rangle}{\langle c_A \rangle \langle c_B \rangle} \qquad (4.2-6)$$

which is very similar to (4.2-4). A possible advantage of (4.2-6) over (4.2-4) is that the denominator now does not go to zero as fast as in (4.2-4), since $\langle c_A \rangle$ and $\langle c_B \rangle$ cannot both be simultaneously zero, and thus its change is more easily compensated by changes in the nominator. For complete segregation $I = 1$ and

$$\left\langle {c'_A}^2 \right\rangle = \left\langle {c'_B}^2 \right\rangle = \langle c_A \rangle \langle c_B \rangle$$

Hence, for unpremixed reactants – where their initial variances of fluctuations

$$\left\langle {c'_A}^2 \right\rangle_0, \left\langle {c'_B}^2 \right\rangle_0,$$

correspond necessarily to complete segregation – we can write

$$I = I_s = \frac{\left\langle {c'_A}^2 \right\rangle}{\left\langle {c'_A}^2 \right\rangle_0} = \frac{\left\langle {c'_B}^2 \right\rangle}{\left\langle {c'_B}^2 \right\rangle_0} = -\frac{\langle c'_A\, c'_B \rangle}{\langle c_A \rangle_0 \langle c_B \rangle_0} \qquad (4.2-7)$$

which is another definition of I, holding *only* for stream mixing.

For the definition of intensity of segregation in cases of dominant age mixing concentrations are viewed as functions of the species ages, that is the elapsed time $\alpha = t - t_0$ since the species molecule was introduced in the flow field. So let $c(\alpha)$ be the instantaneous concentration at a point of tracer molecules that have age α. The mean of this variable at a point and instant can be expressed only as an ensemble average and any estimate would be the average over, say, N realizations of the dispersion phenomenon, in each of which the random variable $c(\alpha)$ takes the value $c_i(\alpha), i = 1, \ldots, N$:

$$\langle c_A(\alpha) \rangle = \frac{1}{N} \sum_{i=1}^{N} c_i(\alpha)$$

(Time averages are meaningless in this case.) The mean age of molecules at the point of measurement will be

$$\alpha_p = \frac{\int_0^\infty \alpha \langle c(\alpha) \rangle \, d\alpha}{\int_0^\infty \langle c(\alpha) \rangle \, d\alpha}$$

Then, the intensity of age segregation at a point is defined (see, e.g., Pratt, 1979) as the ensemble average of variances of the $c_i(\alpha)$'s about $\langle c(\alpha) \rangle$ at that point:

$$I_\alpha = \frac{\frac{1}{N} \sum_{i=1}^{N} \int_{\alpha^-}^{\alpha^+} \left[c_i(\alpha) - \langle c(\alpha) \rangle \right]^2 d\alpha}{\left[\int_0^\infty \langle c(\alpha) \rangle \, d\alpha \right]^2} \tag{4.2 – 8}$$

The limits of the integral in the summation of (4.2-8) are the lower and upper values of α for which $\langle c(\alpha) \rangle$ is non-zero.

Danckwerts (1958) defined a measure of age segregation for the reactor as a whole, i.e. the ratio of the variance of point ages to the variance of molecule ages throughout the reaction field

$$J = \frac{\mathrm{var}\alpha_p}{\mathrm{var}\alpha} \tag{4.2 – 9}$$

where

$$\mathrm{var}\alpha = \overline{(\alpha - \langle \alpha \rangle)^2} \tag{4.2 – 10}$$

is the variance of the ages of all the molecules in the system ($\langle \alpha \rangle$ is the mean age of all molecules which are at some particular instant in the system), and

$$\mathrm{var}\alpha_p = \overline{(\alpha_p - \langle \alpha \rangle)^2} \tag{4.2 – 11}$$

is the variance of mean ages at a point. In (4.2-10) averaging is meant over all molecules of the system whereas in (4.2-11) is meant over all continuum points of the system.

J is a global measure of the degree of molecular homogeneity in a system whereas I (for both stream and age mixing) is a local measure. J and I_α are measures only of atom ages and do not consider the chemical identify of atoms; thus they have no utility as measures of stream mixing effectiveness.

Another point that needs to be stressed here is that I (or I_α) as well as L_s are *expected* local properties of the field; obviously in an actual random realization of the field the mixing at a "point" will always correspond either to complete segregation or to maximum mixedness.

4.2.5 Mixing in Atmospheric Plumes

In the *dispersion of an atmospheric plume* it is typically assumed that axial diffusion is negligible and that recirculative convection phenomena do not take place. In such a case, where advection by the mean wind field and lateral dispersion are the only significant physical processes, the mixing of effluents with the background air down to the molecular scale is accompanied by a decrease of I (for stream segregation) from 1 to 0 in the downwind direction but I_α and J will always be equal to 1. They will be reduced from this value only if diffusion mixes effluent molecules of different ages; however as long as there are advection effects they will assume non-zero values.

4.2.6 Interaction of Mixing and Chemical Reaction

The effect of the mixing state on the evolution of reactions taking place in the flow field has already been stressed in the introduction of this chapter as well as in Chapter 1. Monomolecular reactions (that is with intrinsic linear kinetics) are affected only by the macrostate and their temporal and spatial evolution depends only on the mean concentration field of the reacting species. Thus, for lumped systems, the RTD alone is adequate to describe the macroscopically averaged evolution of linearly reactive networks.

(a) The Effect of Rate Order

Reactions of order different from unity are in general affected by both the macro- and micro- state of the system as well as by the initial state of the reactants (premixed or unpremixed) and the nature of the dominant mixing process (stream or age mixing). It must also be clarified here that controlling macro- and micro- states of evolving flow and reaction systems must always be identified for a stage of their evolution that is relevant to the reactions of interest. Thus, if a reaction is very slow and occurs in a flow system that evolves quickly towards equilibrium with respect to the mixing processes, it will not be practically affected by the early mixing states – since they correspond to times for which conversions are very close to zero. Hence, when slow reactions take place in a homogeneous-at-equilibrium flow system it is usually assumed that the latter has achieved its maximum mixedness microstate before the chemical processes have advanced significantly. On the other hand instantaneous or fast reactions are affected to a varying degree by the early mixing states of the system since the intrinsic kinetics of the reactions, under conditions of equilibrium mixing, would have produced non-negligible conversions at short times corresponding to these states. The comparison of the different rates at which the chemical and mixing processes evolve in a particular system and the subsequent characterization of a reaction as slow or fast should be done on the basis of appropriate characteristic time scales for the various processes. Such scales as well as nondimensional characteristic groups were used in Chapter 1 and will be further discussed in section 4.4.1 of this chapter.

(b) The Effects of Initial Conditions

The different effects of *molecular dispersion* processes on reaction evolution and their dependence on the *initial condition* of the reactants should also be mentioned here. Thus, in the case of *unpremixed* reactants, molecular diffusion is necessary to bring the reactants together at the molecular level so that reaction occurs. In this way it enhances the effective kinetic rate, for reactions of order greater than unity, by homogenizing the mixture. The action of the same phenomenon, i.e. molecular diffusion, has opposite effects on the case of *premixed* reactants. Its action homogenizes the reactive mixture with inert dilutant (in the case of stream mixing) or with older, converted, mixture (in the case of age mixing). As a result it lowers the levels of concentration that determine the local kinetic rates and consequently the effective rate of reactions of order greater than unity decreases too.

Similarly, *random flow field* (turbulent dispersion) effects also depend on the initial state of the reactants. Although the action of both molecular and turbulent diffusion typically results in "spreading" of material this is done at different levels, that is at the molecular and the fluid particle level respectively. At the local fine scale level they are actually *antagonizing* processes. Indeed, turbulence creates local random concentration gradients and fluctuations which are dissipated by the action of the molecular diffusion. The correlations of fluctuating concentrations will be positive for premixed and negative for unpremixed species and therefore opposite effects on the observed ("phenomenal") rates are to be expected for these two cases.

In Table 4-3 we have summarized the different effects of molecular and turbulent dispersion phenomena on single-phase reactions of order greater than unity for both premixed and unpremixed reactants. (For reactions of order less than unity the various effects mentioned are generally reversed).

Table 4-3

Effect of Mixing on Reaction:
Dependence on Initial State of Reactants
(for Reaction Order Greater than Unity)

DISPERSION PHENOMENON	SINGLE/PREMIXED SPECIES	UN-PREMIXED SPECIES
Molecular Diffusion	Depresses the overall rate; it homogenizes the reactive mixture with the diluent	Enhances the overall rate by dissipating concentration fluctuations; its rates are more critical than for premixed species since it is necessary to bring the reactants together
Turbulence (and stochastic initial conditions)	Creates positive correlations of concentration fluctuations and enhances the overall rate because at non-diluted spots reaction takes place at faster rates	Creates negative correlations of concentration fluctuations and depresses the overall rate

4.3 METHODOLOGIES FOR THE DESCRIPTION OF TURBULENT REACTIVE SYSTEMS

As it was stated in Section 4.1, modeling methods for turbulent reacting systems can be classified as

(a) *Eulerian Statistical* (or Global Fluid Mechanical or Mechanistic), and

(b) *Structural*, including Lagrangian Trajectory Schemes, Population Balance Methods and/or Models of Local Laminar Micro-structures.

Elements of both approaches can be present in a particular model formulation at different organizational levels (Figure 4-1).

The choice and application of a particular method depends mainly on the *dimensionality* of the model that is assumed to describe satisfactorily the system under study. (e.g., lumped in space or in time etc.).

4.3.1 Fundamental Concepts of the (Global) Eulerian Statistical Approach

The Global Eulerian Approach is presented in relative detail in Sections 4.4 to 4.6, with emphasis on formulations and results that are simple and directly applicable to situations of interest in the present study. This systematic presentation also contains a survey of methods that have appeared in the literature. In the present sub-section we introduce this approach through a brief overview which, in combination with the brief survey of Structural Approaches of the next sub-section, reveal the range, complexity and diversity as well as the relationships of methods that have been used to attack the problem of reactions in turbulent fields.

Global Eulerian Statistical Approaches are based on the Eulerian local and instantaneous species transport equations, which incorporate reaction terms, perhaps in combination with the respective equations for momentum and energy transport (Section 4.4.1). These equations are assumed to describe globally (everywhere) the

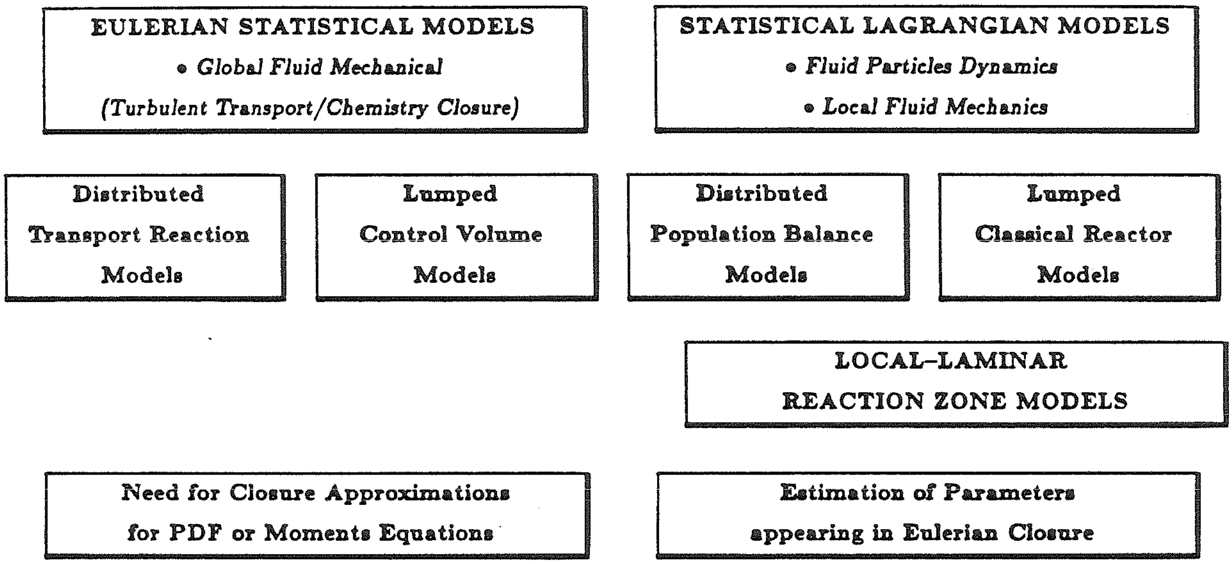

Figure 4-1

Modeling Approaches
for Chemical Reactions in Turbulent Fields

turbulent flow and reaction field, always at an instantaneous pointwise basis, and therefore, with the appropriate initial and boundary conditions constitute the starting point for model development. The stochastic nature of the flow field imposes the necessity for a statistical formulation that will provide information for the probabilistic characteristics of the unknown concentration (and perhaps temperature etc.) fields. The common procedure for constructing such a formulation is to derive, through ensemble averaging of the stochastic transport equations, equations for the first (or subsequently the higher order) moments of the unknown random quantities. As is well known, such an equation for the n-th moment will necessarily contain as new unknowns the correlations of fluctuations of stochastic variables of total order greater than n. Nonlinear chemical kinetic rates are responsible for the appearance of more such unknowns. Formulation of evolution equations for these new terms leads progressively to an infinite hierarchy which excludes the possibility of exact solutions (Closure Problem). An approximation scheme must be introduced at some level to account for the correlations of fluctuations. Such a scheme is called an *n-th order closure* if it is incorporated as a correlation approximation in the governing equations for the n-th moments. We shall further call *"chemical closure schemes"* the approximations of the correlations that arise because of nonlinear chemical rates to distinguish from *"transport closure schemes"* which account for the interaction of the random velocity and transferred quantity fields. Once estimates of moments (either joint or of a single random variable) are available, they can also be used as parameters in probability density functions of appropriate (assumed) form, a practice that has been extensively applied. In addition to moments or correlations modeling, a relatively limited range of reactive turbulence studies employing spectral schemes (for the reactive concentrations) has appeared in the literature (Section 4.5.3).

The alternative to deriving equations for the moments is to construct *functional evolution equations* for the entire joint probability density function of the unknown stochastic fields, starting again from the local instantaneous transport equations. The need of closure remains in these formulations too. Further, obtaining solutions for such equations is a very difficult task. Other, heuristic schemes for the construction of such pdf's assume a certain artificial random picture of the structure of the flow continuum and therefore actually belong in the Structural Approaches that are discussed later.

The main modeling effort has been focused on 2nd order reactions of either premixed or unpremixed species. Various schemes have been formulated starting from the basic Eulerian framework. Their complexity depends mainly on the relative rates of chemical and dispersion processes. Thus, if the reaction rate is *very slow* we have seen that complete micromixing is achieved before the reaction starts, and fluctuation effects are negligible. Also, if the rate is *much faster* than the diffusion (case of "infinite" reaction rate) the effect of turbulence is controlling but the analytical presentation of the problem can still be simplified greatly. Indeed, equilibrium (for reversible reactions), or a limiting stoichiometry (for irreversible reactions) are assumed to be achieved instantaneously and hold pointwise wherever the reactants are micromixed. So, an algebraic steady state relation between random concentrations is available to reduce the complexity of the mathematical description. If the reaction rate cannot be considered infinitely fast, but still is not slow enough for equilibrium to be assumed with respect to mixing processes, the local instantaneous kinetics are also in an evolving state which depends on both macro and micro-mixing conditions. In this case further evolution equations for appropriate reaction progress variables must be derived in the place of the stoichiometric or equilibrium relations.

For both the cases of finite and infinite rate chemistry the tasks of formulating chemical and transport closure schemes have been in general pursued on two different lines:

(a) The most tractable (and presently successful) approaches attempt a *decoupling of mixing and reaction processes* or *indirect closure* (Section 4.6). Thus some conserved quantitites ("coserved scalars"), such as stoichiometric invariants of the reactions or inert surrogate concentrations, are introduced to account separately for the transport effects. The probabilistic characteristics of the spatial and temporal distributions of the conserved quantities (which of course are also random variables) are determined with the use of appropriate Eulerian transport equations, incorporating closure schemes of first or higher order. The respective characteristics of reactive species concentrations are related to them *a posteriori.* This step involves approximations equivalent to chemical closure in an indirect way. The above technique is more natural and effective for infinite rate chemistry but certain extensions have appeared for finite rate cases.

(b) The alternative is to invoke *directly* a chemical closure approximation either using the moments or the joint pdf evolution equations formulations (Section 4.5). The usual approach, employing moment transport equations is to relate correlations resulting from nonlinear chemistry to lower order moments or correlations of the reactive species concentrations. This can be done in principle either at the level of governing equations for the first moments or at a higher level after forming first dynamic equations for the correlation and introducing estimates for the new unknowns.

The general organization of Eulerian methodologies is given schematically in Figure 4-2 which is supplemented by Table 4-4.

4.3.2 Fundamental Concepts of the Structural Approach

Under the general title of Structural Approaches we classify all those methodologies that instead of starting by developing governing equations for the entire distributed flow and reaction field, considering it as a continuum, they focus on small scale entities which are assumed to be "structural units" of the field. The average behavior of these entities then determines locally or globally the evolution of the overall system.

Many different theoretical treatments are based on the concept of structural units. Their variation depends mainly

(i) on how "complex" they assume this structural unit is, and

(ii) on whether they attempt a detailed (spatially distributed) description of the flow

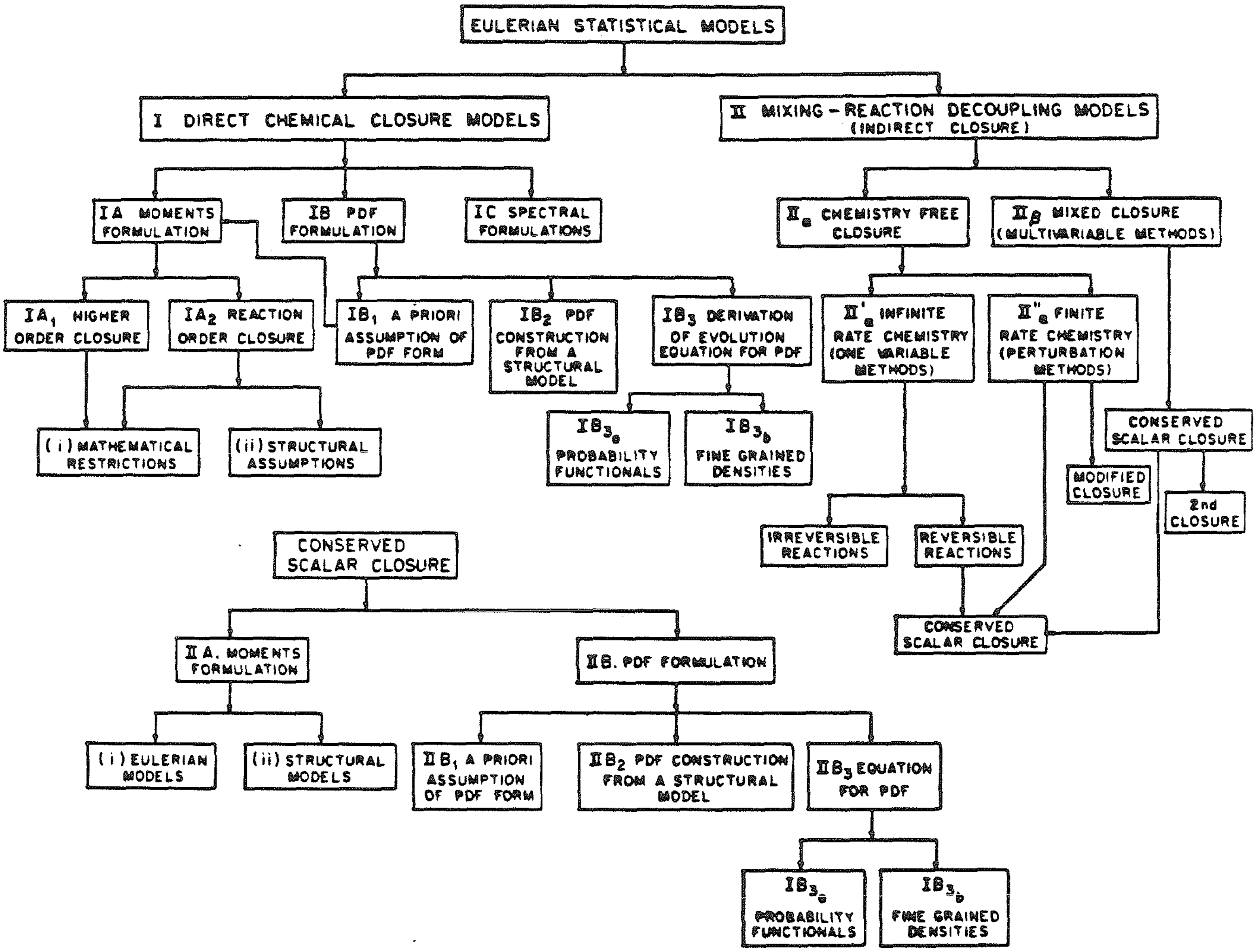

Figure 4-2

Eulerian Statistical Approaches

for the Treatment of Chemistry in Turbulent Fields

Table 4-4

Eulerian Statistical Approaches:

Selected References

TYPE OF MODEL	**EXAMPLE**
I Direct Chemical Closure	
IA Moments Formulation	
IA_1 Higher Order Closure	*McCarthy (1970)*
IA_2 Reaction Order Closure	*Patterson (1981)*
IB PDF Formulation	
IB_1 A priori Assumption of PDF Form	*Bilger (1980b)*
IB_2 Structural Model for PDF Construction	*Patterson (1973)*
IB_3 Evolution Equation for PDF	
(a) Probability Functionals	*Petty and Reed (1972)*
(b) Fine Grained Densities	*O'Brien (1980)*
IC Spectral Formulations	*Lundgren (1985)*
II Indirect Chemical Closure	
II_α Chemistry Free Closure	
II'_α Infinite Rate Chemistry	*Toor (1962)*
II''_α Finite Rate Chemistry	*Bilger (1980a)*
II_β Mixed Closure	*Lamb and Shu (1978)*

and reaction system or just develop estimates of macroscopic averages (a lumped picture of the system).

In some cases the structural entity can be viewed as a Lagrangian material volume following the flow which is large enough for the material fluxes through its boundaries (that are in general distorted by flow shear) to be caused not only by molecular diffusion but also by small eddies. In other cases this Lagrangian volume is considered smaller than the smallest eddies of the field and therefore it becomes equivalent to the (volume) fluid particle concept that was discussed in Section 4.2. Here we will use the term fluid particle (either volume or property particle) for the latter case and the term fluid lump or simply material volume for larger volumes. A fluid lump will in general have at any instant a non-uniform, random, internal structure. On the other hand a fluid particle is usually considered to possess completely uniform internal structure.

(a) First Structural Level Models

We shall call approaches that adopt the concept of fluid particles, as described above *1st structural level models.* The widest class of models relevant to arbitrary reaction and flow fields, the *Population Balance Models*, follows this line (see, e.g., Himmelblau and Bischoff, 1968; Froment and Bischoff, 1979, for introductions to the method). A set of properties is used to identify the various fluid particles. In a distributed description the properties include the three spatial coordinates of the particle ("external coordinates") plus properties that characterize the physicochemical state of the particle such as mass, volume, chemical composition, etc. ("internal coordinates"). If continuum properties, such as species concentration, density, pressure, temperature, etc., are to be used, they are taken to assume constant values over the internal continuum of the fluid particle. Distribution functions denoting how a population of fluid particles is distributed (or, more precisely, is expected to be distributed – see, e.g., Ramkrishna and Borwanker, 1973) in an extended coordinate or phase space that incorporates both internal and external coordinates can be defined.

Then evolution equations for these distribution functions in the extended space are constructed. The difficult part here is to devise appropriate models for terms in the equations that will account for mixing and reaction (that is molecular scale processes) among the constituent species of fluid particles. For premixed species each fluid particle behaves initially (that is at states of complete segregation of the reactive mixture and diluent system) as a batch reactor. Thus for very fast reactions the description is very simple. For moderately fast reactions the effects of stream mixing can be incorporated into dilution factors that will in general be proportional to the age of the particle. For unpremixed species however, some artificial mechanism of interaction between fluid particles must be invented.

(a1) *Lumped (1 dimensional) Systems*

Usually the Population Balance Equations are spatially averaged over control volumes with a single entrance and exit, or at least over control surfaces. When the only internal coordinate considered is the *age* of the fluid particles then these macroscopically averaged population distribution functions reduce to the well known *residence time distributions* or other similar concepts of the conventional chemical reactor theory which is based on lumped models formulations and considers mainly conditions of age mixing.

The original formulations of this method considered only extreme micromixing conditions, i.e. either complete segregation (Danckwerts, 1958; Zwietering, 1959), or maximum mixedness (Zwietering 1959), combined with arbitrary macromixing of the lumped system.

Different microstates of a system can also be modeled within the fluid particle framework. Thus one can assume that the fluid particles spend successive intervals of their residence time in the field under conditions of different but definite degree of segregation (e.g. they are completely segregated for an initial period and then they spend the rest of their residence time under conditions of maximum mixedness); these are the *Many-Environments models* (abbreviated as ME models). Two-Environment (see, e.g., Goto and Matsubara, 1975), Three-Environment, as well as Four-Environment Models have appeared in the literature (see Mechta and Tarbell, 1983, for references). Typically thse models are formulated for arbitrary macromixing (RTD) of the lumped system.

Alternatively, the evolution of microstates, which takes place through the action of molecular scale effects, can be approximated by processes of coalescence of fluid particles with initial different composition which form fluid lumps that immediately redisperse into new fluid particles of common composition. These are the *Coalescence and Redispersion models*, often referred to as "c–r" or "c–d" models, that provide an artificial but often useful model of molecular mixing that was originated in the work of Curl (1963) (for examples see, e.g., Kattan and Adler, 1967; Evangelista et al., 1969; Flagan and Appleton, 1974). (The analyses contained in these works are formulated for macromixing corresponding to either cstr or pfr conditions; Kattan and Adler (1972) presented a study for arbitrary macromixing).

Combinations of the ME and "c–r" approaches have also appeared in the literature. (see, e.g., Richie, 1980).

It must be stressed again that the main body of work that utilizes these approaches refers to systems that are at least partially lumped.

(a2) *Multidimensional Models*

Another approach, still at the 1st structural level, in principle appropriate to describe spatially distributed systems, is to develop schemes for the prediction of *random Lagrangian trajectories* of fluid particles. Such an approach would require the estimation of joint particle transition probability density functions. Reaction between unpremixed species will occur if two particles of the different feeds "collide". Of course in a formal Lagrangian description, individual particle trajectories cannot cross each other at a given time instant because of continuity constraints and thus a "collision" is interpreted as the approach of two trajectories at a micro-distance small enough to permit molecular interaction. This methodology is in principle an extension of the Lagrangian theories for turbulent diffusion to nonlinearly reactive systems; however it seems too complicated to be of practical use in the near future (see also Shu, 1976; Lamb 1976)

(b) Second Structural Level Models

Models that consider as structural entities *fluid lumps* that have a non-uniform internal structure and can also be distorted or broken by the action of turbulence can be named *2nd structural level models.* In such approaches the focus is on the progress of reaction and molecular diffusion phenomena in a control volume small enough so that all fluid motions inside it can be described in a deterministic manner. The major interest in such approaches concerns unpremixed species reactions.

The simplest approaches in this area confine their control volume around the "interface" of two fluid particles or fluid "patches" (or "slabs" or "drops" etc.) of different feeds and try to develop estimates and evolution patterns for the *mixing and reaction zone* that is created at this interface based solely on the relative rates of diffusion and reaction. In this category we can classify models such as Mao and Toor's (1970) "slab diffusion model," Nauman's (1975) "droplet diffusion model," David and Villermaux' (1975) "interaction by exchange with the mean model," Klein et al.'s (1980) "droplet diffusion and erosion model," etc. These approaches in general assume that the macroscopic configuration of the system is simple enough so that conclusions concerning conversions etc. for the entire system can be deduced from the local results.

More complicated models consider effects of turbulent shear on local fluid volume deformation on the evolution of the reaction zone. Some formulations try to model *"lamellar structures"* of many reaction zones separated by unmixed material (see, e.g. Ottino, 1980, 1982; Ou and Ranz 1983ab). A similar approach is examined in a series of papers of both theoretical and experimental content by Bourne and coworkers under the general title "Mixing and Fast Chemical Reaction" (see, e.g., Angst et al., 1984 – see also Baldyga and Bourne, 1984). All these models use Eulerian molecular diffusion– reaction equations at the local scale where flow is laminar.

4.3.3 Comments on the Interrelationships of the Models

An overall view of the range, diversity, and interrelationships of Eulerian and Structural Approaches is given schematically in Figures 4-1, 4-2 and 4-3. These Figures are supplemented by Tables 4-4 and 4-5 which contain selective lists of references arranged according to the general organizational scheme presented in these figures. It should be clear that a particular model intended for practical application may contain aspects of both methodologies at different levels of its structure. The various levels of description of the mixing processes that are commom in chemical reactor theory and their connection are shown schematically in Figure 4-4.

The Eulerian Approach is more straightforward (although it provides less insight on the local evolution of mixing) than the Structural Approaches (which, nevertheless, make extensive use of ad hoc assumptions and have been limited mainly to turbulent fields of very simple average macroscopic configuration). Thus the Eulerian methodology seems more appropriate for describing complex, spatially varying, systems that occur in environmental applications. For such studies the role of the structural approach can be supportive by providing estimation of certain parameters arising from closure approximations.

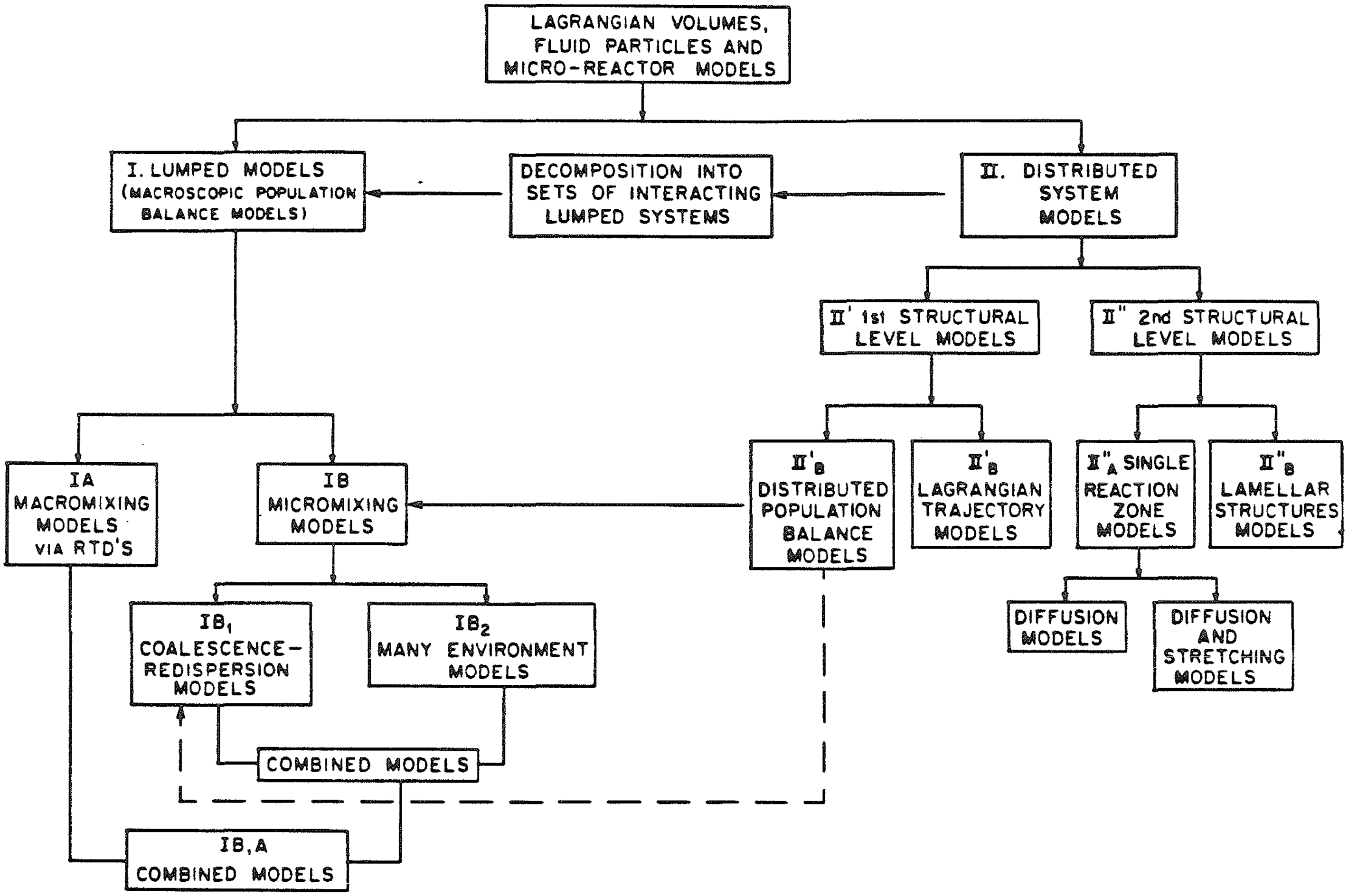

Figure 4-3

Lagrangian Statistical Approaches

for the Treatment of Chemistry in Turbulent Fields

Table 4-5

Lagrangian Statistical Approaches:
Selected References

TYPE OF MODEL	EXAMPLE
I Lumped Models	
IA Macromixing via RTD's	*Naumann (1981)*
IB Micromixing Models	
IB_1 Coalescence-Redispersion	*Kattan and Adler (1967)*
IB_2 Many Environments	*Mechta and Tarbell (1983)*
$\mathrm{IB}_{1,2}$ Combined M-E/C-R Models	*Richie (1980)*
IAB Combined Macro- and Micro-Mixing	*Kattan and Adler (1972)*
II Distributed Systems	
II' 1st Structural Level	
II'_A Distributed Population Balances	*Himmelblau and Bischoff (1968)*
II'_B Lagrangian Trajectories	*Lamb (1976)*
II'' 2nd Structural Level	
II''_A Single Reaction Zone	*Bourne (1982)*
II''_B Lamellar Structures	*Ou and Ranz (1983ab)*

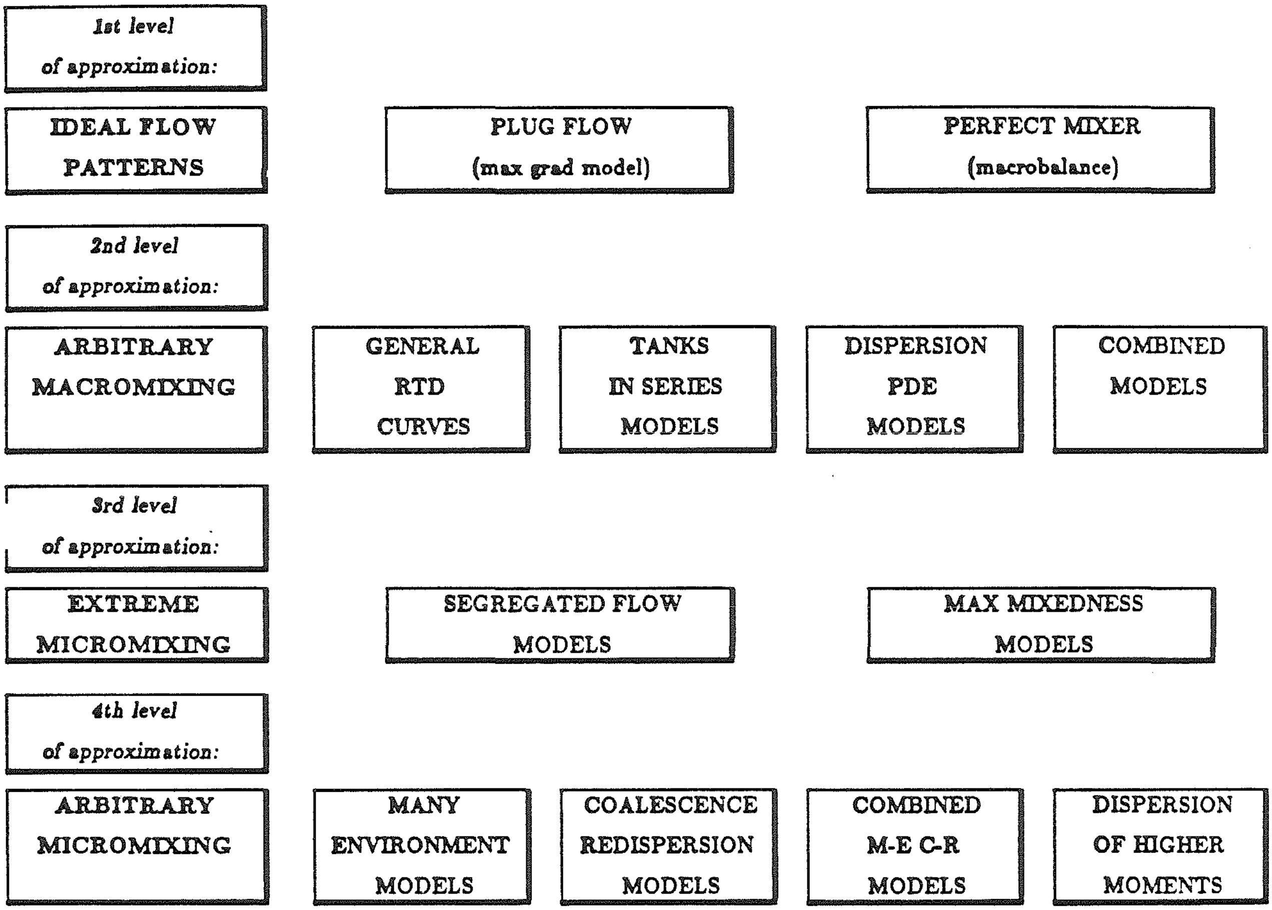

Figure 4-4

Levels of Description of Mixing
in Reactive Systems

4.4 THE EULERIAN STATISTICAL APPROACH: MODEL DEVELOPMENT

4.4.1 General Considerations

The starting point of the Eulerian Statistical or Global Fluid Mechanical Approach to turbulent reacting flows is the continuity equation for each of the species of the reacting and diffusing mixture. This equation is assumed to hold instantaneously and pointwise in the field. A general form for it is (see, e.g., Bird et al., 1960; Slattery, 1972) in the case of a binary mixture

$$\frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A \mathbf{u}) = -\nabla \cdot \mathbf{j}_A + \tilde{r}_A \qquad (4.4-1)$$

where $\mathbf{u}$ is the instantaneous mass average velocity of the mixture, ρ_A is the mass density (or mass concentration) of the species A, $\mathbf{j}_A$ is the rate of molecular diffusion of A (diffusive flux) with respect to $\mathbf{u}$, and $\tilde{r}_A$ in the rate of production (or dissipation) of A by chemical reaction per unit volume expressed in terms of the mass densities of A and of the species that participate in reaction with it. Equation (4.4-1) can of course be written for the instantaneous value of molar concentration c_A; however, in this case the molar average velocity must be used instead of the mass average velocity and such an approach is not very convenient for systems of variable density (Hill, 1976). The way it is stated in (4.4-1) species transport describes equally well both compressible and incompressible flows. With the use of the mass fraction Y_A and assuming that Fick's law for a binary mixture is valid

$$\mathbf{j}_A = -\rho D_A \nabla Y_A$$

where Y_A is the mass fraction of A, ρ is the mixture density and D_A is the molecular diffusion coefficient of the species A with respect to the mixture (usually a strong function of concentration), and if

(a) either $Y_A \ll 1$, or

(b) the mass density ρ is uniform and constant in time

then we can write (4.4-1) as

$$\frac{\partial c_A}{\partial t} + \mathbf{u} \cdot \nabla c_A - \nabla \cdot (D_A \nabla c_A) = r_A \tag{4.4 – 2}$$

where the reaction rate r_A is expressed in terms of the molar concentration of the reacting species. When D_A can be assumed constant (4.4-2) becomes

$$\frac{\partial c_A}{\partial t} + \mathbf{u} \cdot \nabla c_A - D_A \nabla^2 c_A = r_A \tag{4.4 – 2a}$$

This form of species transport equation is strictly applicable to isothermal, constant-pressure, binary mixtures of uncharged substances. For multicomponent mixtures $\mathbf{j}_A$ will depend upon the gradients of chemical potential of all species in the mixture as well as on the temperature gradients.

For atmospheric applications one can usually assume that the overall mass density of the air and pollutant mixture is uniform and constant and that this mixture is sufficiently dilute with respect to the relative species so that (4.4-2) is valid. Further the heat of reaction and reaction induced density changes in these situations are small enough so that the velocity $\mathbf{u}(\mathbf{x}, t)$ and the temperature $T(\mathbf{x}, t)$ fields can be considered independent of the reaction, the latter field being practically uniform for not very large spatial scales. Under such conditions the species transport equation is uncoupled from the simultaneous momentum and energy transport dynamics and is adequately approximated by (4.4-2), always on a stochastic instantaneous-pointwise basis (see, e.g., Seinfeld, 1975, Section 6.1.1). One can then proceed to develop equations for the moments of concentration by ensemble averaging this equation (traditional approach) or follow statistical-mechanical approaches (see Sections 4.5.2, 4.5.3) to formulate functional equations for the probability density functions of concentrations.

In a rather simplifying approach – which is more directly related to the perspective of environmental systems analysis and the present work — one can assume that the interaction between the random concentration and temperature fields takes place only through the dependence of the chemical reaction rate term on the temperature and the system is insensitive to other temperature and flow field interactions which can be considered negligible. Such an approach can also be extended to treat effects of fluctuations of solar radiation on the evolution of photochemical reactions. The key modeling assumption is that all effects of gradients and turbulent fluctuations of the temperature or the radiation field can be incorporated completely in spatially varying and fluctuating chemical kinetic coefficients. Kewley (1978) employed such a technique for a simplified study of the effect of temperature fluctuation on the value of the photostationary state parameter in the ozone-nitrogen oxides photolytic cycle in the atmosphere (see Chapter 3 and Appendix A3.3). His conclusion, specifically for the NO_x - O_3 system, was that, when the action of temperature variations is felt only through the dependence of the kinetic coefficients on them, their effect can be neglected, at least at a first approximation.

Thus, here we focus attention mainly on equation (4.4-2) for stochastic transport and reaction with reaction terms depending practically only on concentrations of the species. A set of equations of this type, with one corresponding to each reactive species, together with the appropriate initial and boundary conditions, and given the appropriate statistical characteristics of the independently varying velocity field $\mathbf{u}(\mathbf{x}, t)$, is assumed to describe completely the evolution of the system of concentrations. The reaction term appearing in (4.4-2), $r_A(\mathbf{x}, t)$, will be a *local* function of the reactive species concentration where the latter are assumed instantaneous, random point variables. The kinetic rate forms that have been most extensively studied up to now are

$$r_A = -kc_A^n \tag{4.4-3}$$

for a single-species reaction with $n = 1$ (linear kinetics) or $n = 2$, and

$$r_A = -kc_Ac_B \tag{4.4-4}$$

for 2nd order reactions between two species A and B:

$$A + B \longrightarrow P$$

Extension to reversible reactions with the reverse reaction also obeying one of the above laws are straightforward and on the same lines as the irreversible reactions. (*)

The stochastic nature of equation (3.4-2) and therefore of the dependent variable c is due to the stochastic nature of the turbulent velocity field. Another possible source for randomness in c may be due to the presence of statistical initial conditions; however, we will not be concerned with this possibility here (see, however, Section 3.5.1 for some relevant references).

The stochastic nature of the governing Eulerian transport equations for dispersion with reaction leads to the same fundamental problems of analytical description as inert dispersion. Thus a complete description of the random concentration fields is possible only through the knowledge of the probability density functions of concentrations at each point in space and time. The standard alternative to seeking these pdf's is a description through equations for moments of the stochastic fields. Such a procedure starts typically by introducing Reynolds type decomposition of the random variables, that is $\mathbf{u} = \langle \mathbf{u} \rangle + \mathbf{u}', c = \langle c \rangle + c'$, in the equations and of course leads to a moments closure problem, typical and unavoidable in turbulence theory. (Eulerian formulations for evolution equations of the entire pdf have analogous closure problems). A major difference between describing inert and reactive species

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(*) One must keep in mind that relations like (4.4-3) and (4.4-4) do not necessarily reveal the kinetic mechanism of the chemistry at the molecular level (see, e.g., Laidler, 1965; Emmanuel and Knorre, 1973). They are phenomenological approximations of molecular processes at the continuum level – exactly as the common transport equations of mass, momentum and energy – and must always be interpreted in this way. Certain approximations may have been incorporated in such laws; thus, for example a bimolecular reaction is often approximated by a linear (or pseudo-linear) kinetic law by use of the assumption that the concentration of one of the reacting species is so large that is not practically affected by the evolution of the reaction. However, despite this assumption the effects of turbulent mixing on such a reaction will be similar to those for a higher order (nonlinear reaction) since, e.g., from unpremixed reactants dispersion processes are necessary to bring the two species together in order to react although formally the rate seems to depend on one reactant only.

dispersion occurs however in the case of nonlinear chemical kinetic rates as it was discussed earlier in this chapter as well as in Chapter 1. Such a reaction rate produces *self-interaction*, as in the Navier-Stokes equations, which leads to the appearance of higher order correlation terms between the fluctuating parts of concentrations. This makes the closure problem more complicated because of the presence of more and higher order unknowns than in the case of inert dispersion.

Thus, for example, the rate $r_A = -kc_Ac_B$ will induce, after ensemble averaging, a second order correlation appearing in the dynamic equation for the first moment of c_A:

$$\langle r_A \rangle = -k \langle c_A \rangle \langle c_B \rangle - k \langle c'_A c'_B \rangle$$

The magnitude, and hence the importance, of these higher order correlations which describe the local homogeneity, or completeness of mixing, in the reaction field depends in general on the relative intensity of all three phenomena that take place simultaneously, that is the mixing processes (molecular and turbulent diffusion) and the chemical reaction .

In order to estimate the relative importance of these phenomena one can proceed directly from (4.4-2a) by transforming it into dimensionless form (see Hill, 1976)

$$\frac{\partial C}{\partial t_*} + N_T \mathrm{U} \cdot \nabla_* C - N_D \nabla_*^2 C = N_R \qquad (4.4-5)$$

Here

$$t_* = \frac{t}{\tau} \ , \ \nabla_* = L_0 \nabla \ , \ C = \frac{c}{c_0} \ , \ U = \frac{u}{u_0}$$

where L_0, τ, u_0, c_0, are characteristic length, time, turbulent velocity, and concentration scales. A reaction rate scale r_0 is used to non-dimensionalize the chemistry. Here N_T, N_D, N_R are dimensionless time ratios

$$N_T = \frac{\tau}{t_T} \qquad (4.4-6a)$$

$$N_D = \frac{\tau}{t_D} \qquad (4.4-6b)$$

$$N_R = \frac{\tau}{t_R} \qquad (4.4-6c)$$

with t_T, t_D, t_R characteristic times scales of the turbulent dispersion, molecular diffusion and chemical reaction processes. τ must be set equal to one of them; then the above time ratios become either equal to unity or to typical dimensionless groups which are in use in reaction and dispersion analyses (Peclet and Damköhler numbers). From the non-dimensionalization procedure the time scales have to be

$$t_T = \frac{L_0}{u_0} \tag{4.4-8a}$$

$$t_D = \frac{L_0^2}{D} \tag{4.4-8b}$$

$$t_R = \frac{c_0}{|r_0|} \tag{4.4-8c}$$

However, special care is needed in interpreting the significance of this direct approach, mainly as far as the choice of an appropriate L_0 is concerned. This is due to the fact that molecular and turbulent dispersion processes do not actually "compete" regarding how fast they will reduce gradients of concentration over the same *macroscopic* distance, say L_0. From that perspective one would expect that $t_D \gg t_T$ in general, and of course, as is well known, molecular dispersion is usually neglected in inert scalar turbulent transport studies. The importance of molecular diffusion is in producing micromixed spots where reaction can occur; thus its rate seems to be relevant mainly with respect to distances corresponding to neighboring random concentration differences maxima that occur in volumes locally macromixed but incompletely micromixed.(*)

Considering these facts some researchers (see, e.g., Brodkey, 1975) assume that it is more reasonable to define t_T in terms of some macroscopic turbulent length scale L_0 which is characteristic of the spatial persistence of mean gradients, and t_D in terms of another length scale ℓ_0 typical of the spatial scales at which the effect of

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(*) For the problems of interest in this study it is the comparison between this particular rate and the reaction rate that is most important. In the closure "solution" adopted by the TRPM the effects of molecular diffusion are actually incorporated in the phenomenal conversion rate term of the governing equation and not in the transport term.

molecular processes is felt directly (see, e.g., Bourne, 1982). Thus

$$t_T = \frac{L_0}{u_0} \tag{4.4 – 7'a}$$

$$t_D = \frac{\ell_0^2}{D} \tag{4.4 – 7'b}$$

$$t_R = \frac{c_0}{|r_0|} \tag{4.4 – 7'c}$$

Thus a global description, as provided by (4.4-5) is essentially abandoned and the analysis proceeds separately at two different scale levels, the local scale being viewed in the spirit of the second level structural models of Section 4.3.2. However, even in this approach, it is still in general difficult to decide which is the most appropriate choice for the characteristic scales. A first problem is the selection of a proper turbulent macro-length scale, especially in cases like the atmospheric plume where turbulence of different scales interacts in different ways with the other processes. (See also Builtjes, 1983; Libby and Williams, 1980 - Section 1.16; Bilger, 1980, for relevant discussions). A second problem is what the most appropriate scale ℓ_0 should be. Typically one of the microscales discussed in Section 4.2.2 (depending on the value of Sc) is assumed to be a good choice. If we set, e.g., $\ell_0 = \ell_K$, the Kolmogorov length microscale given by (4.2-1), we obtain $t_D = t_K$ where $t_K = (\nu/\epsilon)^{1/2}$ is the Kolmogoroff time scale.

The three characteristic time scales introduced here are measures of the time needed for

(i) achieving *mean* uniformity by turbulent mixing (t_T),

(ii) achieving detailed local uniformity (i.e. complete micromixing) by molecular diffusion, thus being a characteristic time for the decay of fluctuations of a scalar field (t_D), and

(iii) of reaching chemical equilibrium or some limiting stoichiometry (t_R).

The magnitude of the ratios of these time scales, given by the dimensionless groups N_T, N_D, N_R after a choice of τ has been made, characterizes the relative rates of the processes corresponding to the nominator and denominator of the group. Traditionally, the ratios of turbulent and molecular dispersion to chemical rates are named first and second type Damköhler groups respectively and denoted as $\mathrm{Da_I}$, $\mathrm{Da_{II}}$.

When there are *no* gradients in the mean concentration field then the single dimensionless ratio N_R defined for $\tau = t_D$ – in which case it is a second type Damköhler group $\mathrm{Da_{II}}$, (*) also called *mixing modulus* by some authors (e.g., Bourne, 1982) – is sufficient to determine the relative importance of the terms $\langle c_A \rangle \langle c_B \rangle$ and $\langle c'_A c'_B \rangle$ in the kinetic rate term (when we consider the reaction $A + B \rightarrow$ Products) and the degree at which the evolution of the reactive system is determined by the intrinsic kinetics or the rate of molecular diffusion. This was discussed in Chapter 1 where, for small to moderate intensities of segregation, and for species that have molecular diffusion coefficients of approximately the same magnitude D, it was shown how

$$N_R = \mathrm{Da_{II}} = \frac{t_D}{t_R} = \frac{k\left[\langle c_A^* \rangle + \langle c_B^* \rangle\right] \ell_d^2}{2D}$$

can be suggested as a local estimate of the second Damköhler group when appropriate values of the concentration scales $\langle c_A^* \rangle$ and $\langle c_B^* \rangle$ are used.

Finally, if we want to characterize a chemical reaction as slow or fast in an arbitrary turbulent concentration field we must take into account the relative magnitude of both the first and second Damköhler groups. If for example we assume that $t_T > t_D$, then $\mathrm{Da_I} > \mathrm{Da_{II}}$ and the various regimes of chemical rates can be identified as follows:

(a) $\mathrm{Da_{II}} \ll 1$: (infinitely) fast chemistry, mixing limited conversions,

(b) $\mathrm{Da_{II}} < 1 < \mathrm{Da_I}$: moderately fast chemistry, interaction of turbulence and chemical reaction,

(c) $\mathrm{Da_I} \ll 1$: slow chemistry, no effects of turbulence on reaction rate.

4.4.3 Chemical Closure

As it has been already mentioned, Chemical Closure can be obtained by either "direct" or "indirect" (i.e. mixing–reaction decoupling) methods; the different routes

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(*) It is very interesting to note that the Damköhler group is analogous to the Thiele modulus in heterogeneous catalysis and to the Hatta number that appears in modeling absorption with simultaneous reaction.

followed by these approaches as well as their interrelationships were also briefly presented there. In the following sections we consider a more detailed development of these methods, following basically the moments formulation and providing information and references for the pdf formulation. The focus is on the methods that seem more promising for applications from the viewpoint of justification, generality and computational simplicity. The presentation here is confined mainly to practically isothermal–constant density conditions, relevant to those of typical atmospheric systems. For discussions of the problems related to non-isothermal cases see, e.g., Libby and Williams (1980), Williams (1985).

4.5 DIRECT CHEMICAL CLOSURE

4.5.1 Moments Formulation

Direct closure methods that employ moments approximations attempt to express correlations of the type appearing in the last term of the r.h.s. of (1.3-8) in terms of more tractable (i.e. more easily estimated) variables.

As introductory attempts towards a better understanding of the problem there have been several studies of the most simple nonlinear rate case, i.e. that of a single species–2nd order reaction evolving in a monodimensional system (e.g. a macroscopically mixed volume or a pfr). The governing (stochastic) equation will be

$$\frac{dc_A}{dt} = -kc_A^2 \tag{4.5-1}$$

The initial conditions may also be assumed stochastic.

O'Brien (1966) compared expressions for $\langle c_A(t)\rangle$ and $\left\langle {c'_A}^2 \right\rangle$ obtained by averaging the exact solutions of this equation for Gaussian initial conditions with the predictions for these quantities computed using the third moment discard, quasinormal, and direct interaction (DIA) approximations.(*) None of the approximations behaved satisfactorily when the relative amplitude of initial fluctuations was large. Later O'Brien (1968) recognized that since c_A is a nonnegative random variable, its moments must satisfy Liapounov's inequality (Uspensky, 1937):

$$\langle c_A^b\rangle^{a-c} \leq \langle c_A^c\rangle^{a-b} \langle c_A^a\rangle^{b-c}, \quad a > b > c \geq 0 \tag{4.5-2}$$

where a, b, c are constants. As an illustration, the third central moment of c_A must satisfy

$$\left\langle {c'_A}^3 \right\rangle \geq \langle c_A\rangle \left\langle {c'_A}^2 \right\rangle \left(\frac{\left\langle {c'_A}^2 \right\rangle}{\langle c_A\rangle^2} - 1 \right)$$

(*) See, e.g., Leslie (1973) for details on the quasinormality assumption and the DIA.

It is obvious that if one adopts, say, the third moment discard approximation, $\left\langle {c'_A}^2 \right\rangle / \langle c_A \rangle^2$ must be ≤ 1 at all times. To avoid unrealistic restrictions on the initial fluctuations, O'Brien (1968) proposed a so–called "inequality preserving closure approximation" (IPCA) so that Liapunov's inequality is always satisfied. O'Brien again compared the predictions of his ICPA with the exact solutions of (4.5-1) and found satisfactory agreement. O'Brien and Eng (1970) generalized the closure for reaction order one to three, and O'Brien and Lin (1972) used a different ICPA for two-species reaction with spatial dependence. Lee (1973) presented a "generalized direct interaction approximation". All of these approximations appeared to behave satisfactorily when tested against (4.5-1). However, since each of these closure schemes was developed and tested mainly on a simple system, namely (4.5-1), there is no assurance that they will hold when appllied to the full continuity equations.

There are relatively few direct closure schemes that have been applied to either single- or multi-species reactions using the full continuity equations for reactive scalars (i.e.(4.4-2)). A "brute force" approach was that of McCarthy (1970). By discarding fifth order cumulants, he developed a hierarchy of (seventy eight) differential equations for single-point concentration moments and microscales.

Later Lin and O'Brien (1972) presented a closure theory which incorporates Lin's (1971) third order ICPA for the reaction terms and Lee's (1966) modification of the quasinormal approximation for the convective terms. Computations of the decay of moments and spectra of A were carried out for various conditions. The decay of $\langle c_A \rangle$ and $\left\langle {c'_A}^2 \right\rangle$ was found to depend primarily on the second Damköhler number (see Section 4.4).

Hilst et al. (1973) combined a third order ICPA (different from that of Lin, 1971) for the reaction term $c'_A c'_B$ with an "invariant model" (Donaldson and Rosenbaum, 1969) for the convection term. Hilst et al. then applied the model to the reaction of O_3 and NO emanating from four cross-wind freeway line sources and solved the resulting 12 coupled differential equations numerically. Borghi (1974, 1979) has also investigated the probability of higher order direct closure; he addresed non–isothermal problems with all the consequent complications.

Donaldson and Varma (1976) discussed second-order techniques for both transport and chemical closure and applied them to idealized dispersion-reaction problems (among which there was the case of point source dispersion-2nd order reactions with the background). They further discussed issues related to more realistic situations.

Due to their mathematical complexity and the lack of experimental support, none of the closure schemes mentioned above appears to be useful at this time in applications to chemical and enviromental engineering (in particular atmospheric pollution) problems.

Some steps towards a more simple approach have been proposed by Patterson (1981, 1983) whose closure suggestion is based on a "quasi-equilibrium" hypothesis (*) that assumes irreversible chemistry so fast that segregation is complete everywhere, all the time ($I = 1$), but the mixing rate still affects chemical conversions (obviously through dilution of the reactants concentrations in their segregated volumes caused by the diffusion of product and/or inert material).Consider the reaction $A + B \longrightarrow P$ of unpremixed A and B, which is so fast that A and B remain totally segregated from one another. Hence (from Section 4.2.4),

$$\left\langle {c'_A}^2 \right\rangle = \left\langle {c'_B}^2 \right\rangle = \langle c_A \rangle \langle c_B \rangle$$

The rate of decrease of $\langle c_A \rangle \langle c_B \rangle$ due to reaction may be expressed as follows:

$$-\left(\frac{\partial \left(\langle c_A \rangle \langle c_B \rangle \right)}{\partial t} \right)_r = -\left(\langle c_A \rangle \langle c_B \rangle \right) \left(\frac{\partial \langle c_A \rangle}{\partial t} \right)_r \qquad (4.5-3)$$

because

$$\left(\frac{\partial \langle c_A \rangle}{\partial t} \right)_r = \left(\frac{\partial \langle c_B \rangle}{\partial t} \right)_r \qquad (4.5-4)$$

when they are due only to chemistry.

(*) Unfortunately Patterson's assumptions are not always stated explicitly; he just proposes the formulation we discuss here for "infinite rate irreversible kinetics." However in such a case mixing and reaction are naturally uncoupled and the closure problem is trivial (see Section 4.6).

We also have

$$-\left(\frac{\partial\left(\langle c_A\rangle\langle c_B\rangle\right)}{\partial t}\right)_r=\left(\frac{\partial\left\langle {c'_A}^2\right\rangle}{\partial t}\right)_r \tag{4.5 – 5}$$

Patterson (1981, 1983) now sets

$$\left(\frac{\partial\left\langle {c'_A}^2\right\rangle}{\partial t}\right)_r=\left(\frac{\partial\left\langle {c'_A}^2\right\rangle}{\partial t}\right)_m \tag{4.5 – 6}$$

This means that the rate of dissipation of fluctuations of the reactive species due to chemical processes alone is exactly the rate of dissipation caused by molecular diffusion effects. This assumption expresses the fact that all reactive material coming to a state of complete micromixing through molecular diffusion is immediately consumed by chemical reaction. Hence, now in the place of the chemical rates expressions one can put

$$r_A=r_B=\left(\frac{\partial\langle c_A\rangle}{\partial t}\right)_r=\left(\frac{\partial\langle c_B\rangle}{\partial t}\right)_r=$$

$$=\frac{1}{\langle c_A\rangle+\langle c_B\rangle}\left(\frac{\partial\left\langle {c'_A}^2\right\rangle}{\partial t}\right)_m \tag{4.5 – 7}$$

The dissipation term can subsequently be modeled as in the case of inert scalars; this subject is examined in detail in Chapter 5. In particular, Patterson (1981) uses Corrsin's (1964a) relations (see Chapter 5) for isotropic turbulent mixers, adopting a scalar segregation length scale equal to that of the turbulence macroscale. This last assumption is not justified in the cases of localized sources since the concentration field cannot be assumed locally isotropic. This is a major limitation in Patterson's modeling schemes. Nevertheless, in spite of the various deficiencies of the complete approach, we believe that the approximation just described is useful in showing how one can introduce significant simplifications into a turbulent kinetic model, at least for rather extreme conditions like those of "quasi-equilibrium". Approximations at a similar level, usually for very simple (1-dimensional) systems like the multijet plug flow reactor etc., have been proposed by various investigators; see, e.g., Brodkey

(1975) and Murthy (1975) for relevant references. One such approximation results from Patterson's (1973) simple "interdiffusion model" (essentially a simple microstructural model; see also Section 4.5.2 and Figure 4-5) which gives

$$\langle c'_A c'_B \rangle = -\left\langle {c'_A}^2 \right\rangle \frac{(1-\gamma)}{\beta(1+\gamma)} \qquad (4.5-8)$$

where

$$\beta = \frac{\langle c_A \rangle_0}{\langle c_B \rangle_0}$$

and

$$\gamma = \frac{\beta \langle c_A \rangle \langle c_B \rangle - \left\langle {c'_A}^2 \right\rangle}{\beta \langle c_A \rangle \langle c_B \rangle + \left\langle {c'_A}^2 \right\rangle}$$

(A relation for $\left\langle {c'_A}^2 c'_B \right\rangle$ can also be obtained but Patterson (1981) suggests setting these correlations equal to zero.)

It must be emphasized that extensions of the above equations to more complicated, 3-dimensional situations, localized sources e.t.c., common in environmental problems, would be questionable.

4.5.2 PDF Formulation

Probability density schemes use the joint probability density function, or a related quantity (like a moments generating functional) of reactive species concentrations, and possibly of other random variables such as velocities, to describe the reacting system. One-point or multi-point densities (or related functions) may be the object of study depending on the complexity of the case modeled and on the desired level of approximation. All statistical characteristics like first and higher order moments and correlations of all kinds are then derived directly from the pdf.

A "degenerate" type of pdf formulation is that in which the pdf form is chosen *a priori* on the basis of relevant experimental information (or just by guessing). Then the parameters of the pdf have to be estimated (this being an auxilliary "closure step"). After that, any other statistic of the random field is evaluated from the pdf. Hence, since the parameters of the pdf (usually two or more) are directly related to moments, this scheme actually reduces to moment closure (of appropriate order) plus the primary closure assumption involved in the selection of the pdf, which subsequently will determine higher order moments. Pdf's that are marginally (and jointly) Gaussian have been usually assumed in the past; see, e.g., Lockwood and Naguib (1975). However such an assumption might be highly unrealistic, especially for arbitrary types of mixing or localized injection of material (see, e.g., Hill, 1976).

Another type of pdf formulation is based on simple structural models that assume special, simple, random or pseudo-random structures of the concentration fields. This results in discrete ("spiked") pdf's for the reactive concentrations. For example Patterson's (1973) "interdiffusion model" assuming idealized concentration distributions of unpremixed species (Figure 4-5), produces a probability distribution that is nonzero only for three values of the concentration (i.e. for zero, for the unpremixed stream value and for a value corresponding to completely mixed feeds). Donaldson's (1975) "most typical eddy" model similarly postulated a joint pdf consisting of delta functions at fixed locations in the composition space. The strengths of these delta functions are parameters that require appropriate estimation. Much more elaborate models have also been constructed on the basis of structural (Lagrangian) assumptions. Kuznetsov and Frost (1973) assumed that both the turbulence and the scalar fields obey Langevin's equations and proceeded from there to model their statistics. Following a different line, Pope (1981) presented an approach that utilizes Monte Carlo schemes of dispersion. His method conceptually stands between older structural approaches and the Eulerian models to be discussed next.

Pdf models that are really Eulerian in nature proceed from the fundamental transport principles (e.g. equation (4.4-2)) to derive evolution equations not for the moments and correlations of the reactive species concentrations but for their (joint) probability density functions (possibly jointly with properties of the turbulence field). Typically enough, the problem of turbulence will lead again, as in the moments case, to an infinite hierarchy of equations and some kind of closure approximation will have

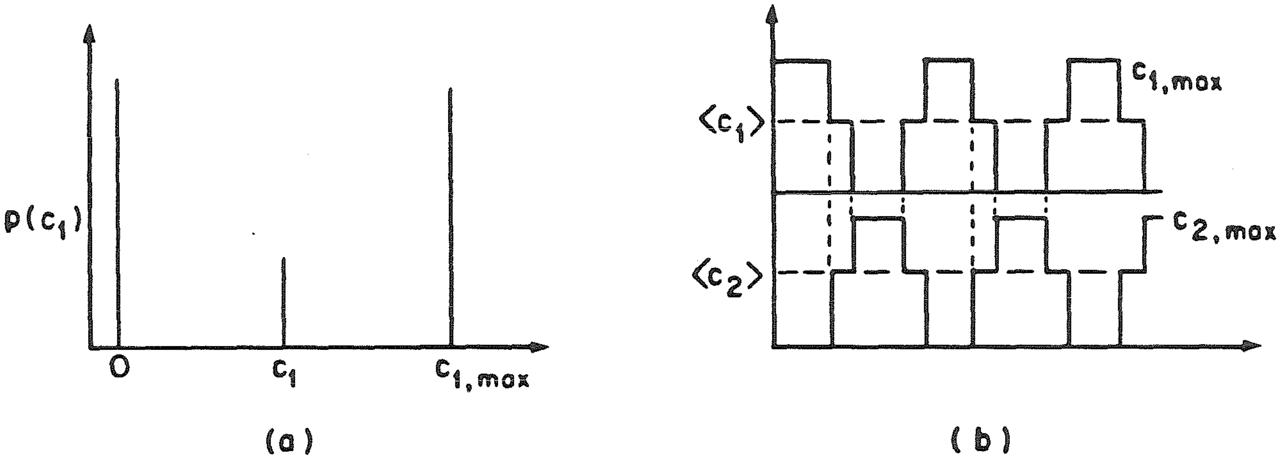

Figure 4-5

Local Concentration Profiles

(and the associated concentration probabilities)

assumed in Patterson's (1981, 1983) "Interdiffusion Model" to be invoked. The schemes for deriving the pdf evolution equations are provided by modern Statistical Mechanics. In particular two different methods have been used in the study of reactive turbulence.

The first is the *method of probability functionals.* Here, from an equation for the probability density functional (Hopf, 1952), which is linear and closed, one deduces an unclosed n-point pdf evolution equation. Lewis and Kraichnan (1962) first studied the probability functional of the turbulent velocity field; (see also Leslie, 1973; Monin and Yaglom 1975). Petty and Reed (1972), Ievlev (1973), Dopazo and O'Brien (1974) (see also Dopazo and O'Brien, 1975, 1976) studied the analogous equations for reacting species in turbulent flows. However, quoting O'Brien (1980), "there seems little prospect that a broad range of applicable results can be obtained at present by such a direct approach".

The second method was introduced by Lundgren (1967) in modeling turbulent velocity fields. It is sometimes called the *"fine grained probability densities method"* and is simpler and more efficient (although not as general and straightforward) than the previous one. It produces the pdf evolution equations directly from the partial differential equations which define the conservation laws of the system. The hierarchy of equations derived in this way is analogous to the BBGKY hierarchy in the kinetic theory of gases (see, e.g., Reichl, 1981). Hill (1970) used a similar scheme to study chemical reactions in turbulence and, after him, many researchers offered different versions of this approach. Dopazo and O'Brien have published a series of papers exploiting the method. Two of these publications are, at least formally, studies of the turbulent reacting plume problem (Dopazo, 1976; O'Brien et al., 1976 – see also Chapter 1). Relatively recently O'Brien (1980) reviewed the method and the closure approximations proposed by various authors; this review should be consulted for further information on the subject. For another recent comprehensive review (but with a more general perspective) on PDF methods for turbulent reactive flows see Pope (1985).

4.5.3 Spectral Formulations

Some researchers have tried to describe simple cases of reactive transport in turbulence by means of spectral models for the concentration fields. Such models have been developed exclusively for *single species reactions*, usually 1st order,and most computations have been limited to the use of spectral transfer theories for the universal equilibrium range. The second order irreversible reaction $A + A \longrightarrow P$ has been studied by Corrsin (1964b) and Dash (1973). They used the "Further Generalized Onsager Model" (Corrsin, 1964b) and the Corrsin–Pao "Unified Spectral Cascade Concept" (Pao, 1964).

Recently Lundgren (1985) constructed a model for the analytical estimation of the form of the concentration spectrum of the product of a fast bimolecular chemical reaction of the $A + B \longrightarrow P$ type for wavenumbers greater than the Kolmogorov wavenumber. This analysis considered unpremixed reactants in a stirred tank and assumed a vortical microscale structure for the turbulent fluid motion in the tank.(*) The Schmidt number was large and the volume of one of the reactants was small. Under these conditions Lundgren found that the spectra first decrease like k^{-1} (i.e. as for a passive scalar) and then increase linearly with wavenumber, peaking near the Batchelor wave number from which it drops off like k^{-4} for large wavenumbers, to finally decay exponentially.

As far as relevant experimental information is concerned, Kewley et al. (1978) have measured co-spectra of O_3-NO_2 in photochemical smog.

Nevertheless, spectral methods do not seem at the moment very promising for describing reactions under conditions relevant to environmental flows (although some information from the spectral approaches can be useful in other modeling schemes). For more information and references one may consult the reviews by Hill (1976) and Bilger (1980) and Lundgren's (1985) paper.

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[*] The whole development of this model is based on an advanced microstructural approach of the 2nd level (Section 4.3.2). However, since its major results concern concentration spectra, we mention it here.

4.6 INDIRECT CHEMICAL CLOSURE

4.6.1 Methods of Decoupling Mixing and Chemistry

Among the methods that use Equations (4.4-1) or (4.4-2) as a starting point, the ones that have led up to now to more tractable final working schemes, at least for not very complex physical situations, are based on techniques which decouple and in some way "isolate" the analytical description of the phenomena of mixing and chemical reaction. The underlying concept is rather old and early applications appeared in theories of turbulent combustion (Burke and Schumann, 1928; Hawthorne et al., 1949). The recent interest in the method originated mainly from the work of Toor (1962) and his coworkers who considered infinitely fast reactions of nonpremixed species in tubular flow reactors. A rather recent review of the approach for the case of nonpremixed reactants, containing many details and references, is given by Bilger (1980b); however some of the existing techniques are not discussed and thus certain aspects and capabilities of the method are not revealed.

Consider for simplicity the case of an isothermal reaction system where all the dependent (unknown) variables are members of the random concentration vector $\mathbf{c} = (c_1, c_2, \ldots, c_n)$. (In case of non-isothermal systems more unknowns such as the temperature, density etc., must also be included in the treatment.) Then the general idea of the method, expressed in rather crude terms, consists of the two following steps:

- First, introduce a set (vector) of quantities,

  $$\mathbf{c}_s = (c_{s_1}, c_{s_2}, \ldots, c_{s_n})$$

  such that

  $$\mathcal{L}^M c_{s_i} = 0 \qquad (4.6-1)$$

  holds for all i with the appropriate boundary and initial conditions. Here $\mathcal{L}^M$ is the overall mixing operator defined in in Chapter 1 [equation (1.3-4)]. The quantities c_{s_i} are thus conserved scalars. They are random quantities and their evolution is governed by stochastic equations like (4.6-1).

- Second, construct a general relation of the form

$$\Psi\left(\langle \mathbf{c}\rangle, \langle \mathbf{c}^*\rangle, \mathbf{f}(\mathbf{c}_s)\right) = 0 \qquad (4.6-2)$$

which will connect the expected values of the members of the unknown reactive species concentration vector $\mathbf{c}$ to *deterministic* functions $f_i(\mathbf{c}_s)$ of the random vector of conserved scalars $\mathbf{c}_s$. The vector function $\mathbf{f}$ will usually be a vector of moments or pdf's of the c_{s_i}'s. A vector of *auxilliary variables* with expected value $\langle \mathbf{c}^*\rangle$ may also have to be introduced in this step and appear in the general relation (4.6-2) depending on the complexity of the particular problem and the details of the formulation. Construction of (4.6-2) will unavoidably (except in the simplest case of irreversible infinite rate reaction) require *closure hypotheses* regarding either higher order moments or pdf's. If such hypotheses involve functions of the conserved scalar only they will be referred to as *pure conserved scalar closure models.* If the approximations involve functions of the conseved scalar and reacting species they will be referred to as *mixed indirect closure models.*

In this way the f_i's, which in general will be estimated by a procedure that starts from equations (4.6-1), describe analytically the mixing state of the system, with chemistry effects having been "removed" from it. Then relation (4.6-2) supplements the description with the a posteriori consideration of these effects.

Both steps of the modeling procedure pose various questions. The obvious problems in the first step is how may conserved scalars must be introduced and how are they chosen. The answers to these depend on basic characteristics of the system like number and uniformity of feeds etc. The second step raises more difficult questions directly connected to the complexity of the given problem and the level at which it is wished to be modeled.

4.6.2 Number and Forms of the Conserved Scalars

There has been a great variation in the choice of conserved scalars in the literature (see, e.g., Bilger, 1980b, for a review and relevant references). There is also a certain confusion with respect to the merits of various choices. In many circumstances the conserved scalars are all linearly related so that solution for one yields all of the others. The choice is then arbitrary up to a point, depending perhaps on requirements arising from other points of the modeling procedure. Under other circumstances there may be factors that directly favor the choice of one or more relative to the others. Such factors include nonequal molecular diffusivity effects, the number and uniformity of the reactant feeds and the complexity of the chemical mechanism.

A complete analysis of a general situation with an arbitrary number of feeds and reactions is not available, neither it seems to be very useful, so we limit the present discussion mainly to the case of two "feeds", under conditions of dominant stream mixing *which is the situation relevant to the atmospheric plume problem.*

A condition particularly useful for practical purposes, is that of equal (in practice of the same order of magnitude) molecular diffusivities for all the species of the system. In fact these molecular diffusivities are usually and considered negligible in magnitude in comparison to turbulent dispersion and the above condition is satisfied for almost all cases.(*) Then, since the transport properties are characteristic of the flow field and not of the species that are present there, the number of conserved scalars needed to describe the mixing state of the system is minimum. Thus, for two feeds or streams of distinct but *constant initial chemical identity* the state of mixing is uniquely determined by one conserved scalar variable. In general for n feeds $n-1$ conserved scalar variables will be adequate to determine this state (Bilger, 1980b). This results from the fact that all differentiation of different feeds arises from chemical

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(*) Significant differences in molecular diffusivities of importance in practical applications appear when light gases, as for example molecular hydrogen, are present. These species have very high diffusivities relative to other species as, e.g., oxygen, nitrogen, etc. and therefore rather strong differential diffusion source terms will appear in transport equations for linear combinations of concentrations incorporating them.

identity only and not from difference in transport properties. Any more conserved scalars that could be defined will be necessarily linearly dependent with the initial ones under the condition that each feed is initially perfectly mixed. (If a feed is not perfectly mixed then it can further be seen as composed by other, perfectly mixed feeds). Bilger (1980b) states this condition as a requirement for uniformity, that is "spatial and temporal constancy" of each feed, with respect to elemental composition only, whereas, "each feed may be in several streams each of which may have any state of chemical aggregation, e.g. it may be partially reacted or pyrolyzed".

In general, conserved scalars can be chosen either from the stoichiometric invariants of the reaction under consideration or they can be "artificially conserved" quantities like fictitious inert surrogate concentrations of the actual reactive species. When they correspond to a stoichiometric invariant of the system they actually correspond to a conserved quantity; the term conserved scalar in the literature has been used almost exclusively for choices of this type.

In principle any quantity that is conserved during the reaction process can be adopted as a conserved scalar. The "fundamental" conserved scalars are naturally the atomic mass fractions Z_i or the gram-atomic concentrations $\hat{c}_i$ of the different *elements* in the reactive system. If the number of elements is M then, since the total mass in the system is constant, there are in general $M-1$ independent variables. Solution of the $M-1$ equations of the type (4.6-1) yields the instantaneous and mean (after ensemble averaging of the equations) elemental composition throughout the field and this may be looked upon as a description of the mixing of the system. Constancy of the composition of the feeds provides further relations between the fundamental conserved scalars when differences in the molecular diffusivities of the species are assumed negligible. Then the required number of equations of the type (4.6-1) is reduced significantly.

In practice other conserved scalars have been used in both chemical engineering and combustion applications and have already appeared in the modeling of photochemical pollution and plume dispersion processes (Bilger, 1978; Kewley, 1978, 1980).

In the case of a one-step reaction such as

$$A + mB \longrightarrow nP \tag{4.6 – 3}$$

where the (molar) formation rates of A,B and P are related through

$$r_A = \frac{r_B}{m} = -\frac{r_P}{n} \tag{4.6 – 4}$$

one can define the so-called *Shvab-Zeldovich coupling functions* (see, e.g., Williams, 1985).

$$\varsigma_{AB} = c_A - \frac{c_B}{m} \tag{4.6 – 5a}$$

$$\varsigma_{AP} = c_A + \frac{c_P}{n} \tag{4.6 – 5b}$$

$$\varsigma_{BP} = c_B + \frac{mc_P}{n} \tag{4.6 – 5c}$$

or

$$\hat{\varsigma}_{AB} = m\varsigma_{AB} = mc_A - c_B,$$

and so on, which are immediately seen to satisfy (4.6-1). Depending on the particular application *Favre averaged* (see, e.g., Hinze, 1975) concentrations or mass fractions can be used in the definitions (4.6-5) whereas other conserved scalars of the same type can be formed using the sensible specific enthalpies of the feeds in the case of highly exothermal reactions (see, e.g. Bilger, 1980b). Toor (1962, 1975) refers to the same technique, which he applies for conditions of equal molecular diffusivities, as the *Burke-Schumann transformation* of the reactive transport equation (see Burke and Schumann, 1928).

With the assumption of equal molecular diffusivities the balance equation for a conserved scalar becomes free of artificial source terms resulting from differential diffusion effects and is exactly the same for all conserved scalars. In two-feed problems the conserved scalars can be *normalized* in such a way that boundary conditions also become identical (see, e.g., Bilger, 1979a). A normalized conserved scalar which can alone describe the mixing state of the system is the *mixture fraction* χ which is defined through (see, e.g., Toor, 1975; Bilger, 1979a).

$$\chi = \frac{Z_i - Z_i^{(2)}}{Z_i^{(1)} - Z_i^{(2)}} = \frac{\varsigma - \varsigma^{(2)}}{\varsigma^{(1)} - \varsigma^{(2)}} \tag{4.6 – 6}$$

where superscripts (1) and (2) refer to the uniform composition of the two different feeds, Z_i is the mass fraction of any element and ς is any Shvab-Zeldovich function of the type defined in (4.6-5).

Then, in feed (1) we have

$$\chi = 1 \tag{4.6 – 7a}$$

and in feed (2)

$$\chi = 0 \tag{4.6 – 7b}$$

So, χ can be physically interpreted as the mass (or mass per volume) fraction of the material in the mixture at a given point and time instant which originated in feed (1) with $1 - \chi$ the fraction originating in feed (2). Thus the result of turbulent and molecular diffusion on the composition of the whole mixture at a point is the same as if we took a quantity of mass χ from feed (1) and mix it *thoroughly* with a quantity of mass $1 - \chi$ of feed (2) and *then let reaction occur.* Of course the instantaneous χ is a random quantity like the quantities in terms of which it is defined.

Any conserved scalar c_s is related to χ and its initial values in the two separate feeds denoted ny superscripts (1) and (2) through

$$c_s = \chi c_s^{(1)} + (1 - \chi) c_s^{(2)} \tag{4.6 – 8}$$

(Necessary condition for the validity of this relation is the equality of molecular diffusivities of all the reacting species of the system.)

Considering now the case where in feed (1)

$$c_A = c_{A_0},\ c_B = 0,\ \varsigma_{AB}^{(1)} = c_{A_0} \tag{4.6 – 9a}$$

and in feed (2)

$$c_A = 0,\ c_B = c_{B_0},\ \varsigma_{AB}^{(2)} = -\frac{c_{B_0}}{m} \tag{4.6-9b}$$

we obtain the following expression for χ

$$\chi = \frac{m\varsigma_{AB} + c_{B_0}}{mc_{A_0} + c_{B_0}} = \frac{\hat{\varsigma}_{AB} + c_{B_0}}{mc_{A_0} + c_{B_0}} \tag{4.6-10}$$

in terms of the "pure stream" concentrations c_{A_0}, c_{B_0}. There will be a special value of χ, χ_s at which the two feed materials coexist at a point in exact stoichiometric proportion. For the one step reaction (4.6-4), with conditions as in (4.6-9) we have

$$\chi_s = \frac{c_{B_0}}{mc_{A_0} + c_{B_0}} \tag{4.6-11}$$

This value of χ corresponds to $\varsigma_{AB} = 0$ and has a particular significance. For a one-step irreversible reaction with infinitely fast kinetics $\chi = \chi_s$ corresponds to the random instantaneous location of the surface (of infinitesimal thickness) on which chemical reaction is confined. For reversible multi-step reactions as well as for slower chemistry this location will be an approximate center for the instantaneous reaction zone. It is important to realize that, although all quantities in the r.h.s. of (4.6-11) are deterministic, the position at which $\varsigma_{AB} = 0$ and (4.6-10) reduces to (4.6-11) is random at any time instant.

Another point to be mentioned here is that, for the two feeds case, the most important of the quantities describing the degree of micromixing, that is the intensity of segregation, can be defined e.g. through (4.2-4), in terms of any conserved scalar, e.g.

$$I = \frac{\left\langle {\varsigma'_{AB}}^2 \right\rangle}{\left\langle \varsigma_{AB} \right\rangle^2} = \frac{\left\langle \chi'^2 \right\rangle}{\left\langle \chi \right\rangle^2}$$

The use of the concept of inert surrogates for conserved scalars is examined in more detail in section 4.6.3.

Now we proceed in examining the various possible model formulations in terms of conserved scalars for the two cases of infinite and finite rate chemical kinetics, as outlined in Figure 4-2.

4.6.3 Pure Conserved Scalar Closure

(a) The Case of Infinite Rate Chemical Kinetics

As it has already been mentioned, when chemical processes can be assumed much faster than the dispersion processes the problem of reactive turbulence modeling simplifies greatly. Indeed, if we focus on the problem of nonpremixed reactants(*) contained in two feeds of uniform composition and assume that all species have approximately equal molecular diffusivities it is easy to see that in the limit of infinitely fast chemistry all concentrations are instantaneously related to the value of an arbitrarily chosen conserved scalar. Actually in this case the statistics not only of concentrations but of all thermodynamic variables of the system should be obtainable from sufficient knowledge of the statistics of that scalar. This is the situation where *pure conserved scalar closure* is either not needed at all or is directly applicable and most useful.

(a1) *Irreversible Reaction*

In the case of one-step irreversible reactions (e.g. reaction (4.6-3) in the forward direction only) we will have $c_B = 0$ when $\chi > \chi_s$ and $c_A = 0$ when $\chi < \chi_s$ whereas both c_A and c_B will be zero when $\chi = \chi_s$. Thus the following functional relationships will hold:

$$\varsigma_{AB} \le 0, \;\; \chi \le \chi_s : c_A = 0$$

$$c_B = n\varsigma_{AB} = n\tilde{c}(\chi_s - \chi) \tag{4.6-12a}$$

$$c_P = m\tilde{c}\chi(1-\chi_s) \tag{4.6-12b}$$

$$\varsigma_{AB} \ge 0, \;\; \chi \ge \chi_s : c_A = \varsigma_{AB} = \tilde{c}\,(\chi_s - \chi)$$

$$c_B = 0 \tag{4.6-13a}$$

$$c_P = m\tilde{c}\chi_s\,(1-\chi) \tag{4.6-13b}$$

---

* Of course a case of premixed reactants which react with infinitely fast rate cannot exist.

where

$$\tilde{c} = c_{A_0} + \frac{c_{B_0}}{n} = \frac{c_{A_0}}{\chi_s} \tag{4.6 – 14}$$

So we see how, at a given point in the flow, the value of χ at any particular instant defines the complete composition of the reactive mixture. Hence the problem for the steady state actually reduces to solving

$$\mathcal{L}^M \chi = 0$$

with (known) appropriate boundary conditions.Since all the above relations for c_A, c_B, c_P are linear in χ, there is no difficulty in relating the expected values $\langle c_A \rangle$, $\langle c_B \rangle$, $\langle c_P \rangle$ to $\langle \chi \rangle$ which is obtained from the solution of

$$\left\langle \mathcal{L}^M \chi \right\rangle \simeq \mathcal{L}_*^M \langle \chi \rangle = 0 \tag{4.6 – 15}$$

where $\mathcal{L}_*^M$ is an approximation of $\left\langle \mathcal{L}^M \right\rangle$ resulting from a closure approximation.

(a2) *Reversible Reaction*

If the infinitely fast reaction is reversible (with both forward and backward rates being very fast compared to the mixing processes) c_A and c_B will both have nonzero values not only for $\chi = \chi_s$ but for a range of values from χ^- to χ^+ where

$$1 \geq \chi^+ > \chi_s > \chi^- \geq 0$$

The values χ^+, χ^- define the local boundaries of the *reaction zone* . The reaction zone, for infinitely fast chemistry is exactly that local portion of the space of the entire system which is micromixed (not necessarily uniformly). This will be called the *mixed zone* . The composition of the mixture at any given point of the reaction zone, at any particular instant, will be the same as that if the mixture were isolated and allowed to come to chemical equilibrium. The species concentrations will again be unique functions of the conserved scalar. However, now the existing relations for chemical equilibrium replace limiting stoichiometry equations for the attainment of mathematical closure of the system of unknown concentrations. These equilibrium relations, in contrast to limiting stoichiometry, will be in general nonlinear and this creates a chemical closure problem as higher order statistical characteristics of the concerved scalar c_s (χ, ς_{AB}, or whatever else) are needed for the estimation of the expected values of species concentrations. Even for many species and multiple reactions the fast chemistry assumption implies that these will be effectively equilibrated. There will be sufficient equilibrium constants available to enable calculations of species concentrations in terms, e.g., of elemental composition which is directly related to any conserved scalar. Thus a set of relations of the form

$$c_i = c_i^e(c_s) \tag{4.6-16}$$

where the superscript e denotes equilibrium and c_s is the random conserved scalar will be available. (In general not only for concentration but also for other thermodynamic variables such as temperature and density). These c_i^e s are exactly the functions f_i that appear in the general equation (4.6-2). So now the problem is actually how, starting from (4.4-16), to relate the $\langle c_i \rangle$'s to the field $\langle c_s \rangle$, the latter being governed by $\mathcal{L}_*^M \langle c_s \rangle = 0$ with the appropriate boundary conditions. As an example let us consider again the reaction

$$A + B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} P \tag{4.6-17}$$

which obeys the kinetic law

$$R = k_f \, c_A \, c_B - k_b \, c_P \tag{4.6-18}$$

When equilibrium is assumed we have $R = 0$ and

$$\frac{c_A \, c_B}{c_P} = \frac{k_f}{k_b} = K \tag{4.6-19}$$

This equation can be combined with two relations of the type (4.6-5) and with (4.6-6) to give c_A, c_B, c_P in terms of K and χ. Indeed, in terms of the mixture fraction we have, for the conditions described in (4.4-23), and if there is no P in the feed streams, the following relations:

$$c_A - c_B = \left(c_{A_0} + c_{B_0}\right)\chi - c_{B_0} \qquad (4.6-20a)$$

$$c_A + c_P = c_{A_0}\chi \qquad (4.6-20b)$$

which, together with (4.6-19), provide a closed system for c_A, c_B, c_P. So, for this case we obtain

$$c_A = \frac{K}{2}\left(-B + \sqrt{D}\right) \qquad (4.6-21)$$

with

$$A = \frac{1}{K} \qquad (4.6-22a)$$

$$B = 1 + c_{B_0} - \left(c_{A_0} + c_{B_0}\right)\chi \qquad (4.6-22b)$$

$$D = B^2 - 4\frac{c_{A_0}}{K}\chi \qquad (4.6-22c)$$

The nonlinearity of these instantaneous relations between concentrations and the conserved scalar does not allow a direct connection of expected values of these quantities by ensemble averaging. Thus one has to invoke an appropriate closure scheme either

(a) by introducing the probability density function of the conserved scalar c_s, $p(c_s)$ in which case expected values of the c_i's will be obtained through

$$\langle c_i \rangle = \int_0^\infty c_i^e\left(c_s\right) p\left(c_s\right)\, dc_s \qquad (4.6-23)$$

("pdf closure")

or

(b) by ensemble averaging (4.6-16) (i.e.(4.6-21)) so that after some algebraic manipulations one has

$$\langle c_i \rangle = f\left(\langle c_s \rangle, \langle c_s^2 \rangle, \ldots\right) \qquad (4.6-24)$$

This is an equation involving only the first few moments of the conserved scalar. ("moment closure").

So, the chemical closure problem is reduced to the estimation of moments and/or pdf's of the conserved scalar; thus it has been "transferred" to the closure problem appearing in the governing equations for these quantities.

For the particular system under study, i.e. reaction (4.6-17), the function $c_A^e(c_s)$ is given directly by (4.6-21) with $\chi = c_s$. The function f can also be obtained from (4.6-21) after ensemble averaging of both sides, but this is not a trivial task. For this reason practically all models that have followed the methodology described in this sub-section adopt equation (4.6-23) for their calculations.

Now, when pdf closure is employed, the problem is very similar to that of pdf modeling for reactive species (Section 4.5.2). However there is a definite advantage in dealing with pdf's of conserved scalars because their form and properties are much more predictable for a great variety of flow geometries. Both experimental as well as theoretical information is much more extensive for pdf's of inert scalars than for reactive ones; the same is true for moments also, whose study, e.g., through Eulerian transport equations, is not complicated by chemical interaction terms.

The pdf of the conserved scalar can be studied theoretically exactly on the lines described in Section 4.5.2, i.e., either by formulation of pdf evolution equations (methods of probability functionally and of fine grained densities), or by employing some structural model that describes mixing in terms of processes that are experienced by the fluid particles (see, e.g., Bilger, 1979b; O'Brien, 1980; Pope, 1981; Kollmann and Janicka, 1982). However, the most common approach in applications is the a priori assumption of the probability density form.

In combustion applications (where the method of this sub-section has been applied most extensively in many variations) there has been a variety of choices for the conserved scalar pdf. Modelers have used more commonly "Clipped Gaussian" (or semi–Gaussian: see Chapter 5) pdf's (see, e.g., Bilger, 1980b) and Beta function distributions; other choices that have also appeared in the literature are the sinusoidal and the triangular pdf's (see Murthy, 1975, and Effersberg and Peters, 1983, for relevant references). In air pollution problems, where the method has been applied by Bilger (1978) and Kewley (1978, 1980), the semi-Gaussian pdf has been the only choice. In particular Kewley (1978) assumed a semi-Gaussian distribution for the plume concentration field; this also incorporates the effect of intermittency too (see Chapter 5). However, since only the "internal" concentration fluctuations, and not the ones caused by meandering, affect chemical reactions in plumes, it seems that such a distribution might not be the most appropriate choice. Actually, as it has been discussed in the previous chapters, it is needed to disengage instantaneous dispersion and meandering effects and to attempt statistical description of each process separately. A lognormal (or some other positively skewed distribution) seems to be a reasonable choice for the instantaneous concentrations when viewed in a frame that follows the random meandering of the centerline. This and related problems are discussed in more detail in Chapter 5 where the moment estimation problem (specifically: second moment estimation for atmospheric plumes) is studied extensively; hence the present section is complemented by Chapter 5.

(b) The Case of Finite Rate Chemical Kinetics

For moderately fast reactions pure conserved scalar closure is not directly possible, i.e. immediatelly from the equations (4.6-23), (4.6-24). Indeed now there are no algebraic equilibrium equations to relate in a simple fashion reactive species and conserved scalar concentrations. Hence mixed (or "multivariable") closure of the type to be described in the next subsection is more appropriate. However there have been attempts to extent pure conserved scalar closure to finite rate kinetics by viewing the actual solution of the problem as a "departure" (or perturbation) from the equilibrium solution that is obtained for infinite rate kinetics. Thus, perturbations of the conserved scalar are introduced as extra variables (Bilger 1979b, 1980ab). Until now, however, the method has been applied in a very limited number of situations.

4.6.3 Mixed Indirect Closure and the Concentration Field Splitting Technique

Application of the conserved scalar approach to finite rate chemistry requires the introduction of extra variables, besides the conserved scalars. These will be affected by the chemistry. One of the reactive species concentrations can be such a variable but it would be better if one could introduce other parameters easier to treat when closure complications appear. Indeed, closure assumptions now have to accommodate these "auxilliary" variables too. So, the underlying idea of the method is to define them in a way such that their correlations (or perhaps cross–correlations with the conserved scalar) are easily predictable for the given problem.

Bilger (1980) discusses these "Two–Variables" approaches. Another model that has implicitly followed this line is that of Shu (1976), Lamb (1976), and Lamb and Shu (1978). The fundamental idea of this model was chosen in the present Reacting Plume study to assess the effects of turbulent fluctuations on the kinetics because of its generality, its relative simplicity (especially for the plume case), and its significant potential for future improvement.

The formulation (and hence the subsequent application) of the model in the works of Shu and Lamb is limited (because of the restrictive use of spatial averaging over the mixed zone and other similarly defined volumes) to one-dimensional problems (where variation of mean concentrations takes place only in one, spatial or temporal, dimension). Furthermore, some results of their analysis, relevant to local microstructures, are not directly extendable to a global statistical picture of the flow. In Chapter 2 we presented a new, generalized, formulation of this model that holds for pointwise defined instantaneous concentrations in arbitrary, non uniform, fields, and formally deals with the global statistical equations. In the following we further discuss this formulation, presenting the proofs that were omitted in Chapter 2 and commenting on various points of the modeling procedure. The exposition of Chapter 2 is essentially repeated here to facilitate reading of the next paragraphs by avoiding repeated references to definitions and equations in Chapter 2; furthermore, in this way the present chapter provides a self-contained treatment of chemical closure modeling.

The "Concentration Field Splitting" Method

Let $c_A^I(\mathbf{x},t)$, $c_B^I(\mathbf{x},t)$ be the hypothetical concentrations of A and B that would exist at the space-time point $(\mathbf{x},t)$ if they did not react with each other but, still, were transported in the field by exactly the same molecular and convective mechanisms. (A point to note here is that the present analysis implicitly assumes that differences in the molecular diffusivities of the various species under consideration are negligible.) We can define these new variables as concentrations of fictitious *inert surrogates* A^I, B^I, of A and B. The quantities c_A, c_B, as well as c_A^I, c_B^I at any $(\mathbf{x},t)$ are random variables. The approach proposed in this work accounts for the possible states of mixing of the two species by viewing each of the above concentration fields not only as random functions of $(\mathbf{x},t)$ but also as *functionals* of the entire ensembles of realizations of the inert surrogate of their "mixing partners" at $(\mathbf{x},t)$. Indeed, the possible micromixing states of, say, A or A^I at any point depend on the probabilistic characteristics of the conentration of B^I at this point. Thus $c_A(\mathbf{x},t)$ and $c_A^I(\mathbf{x},t)$ are functionals of the ensemble of all possible values of $c_B^I(\mathbf{x},t)$. This dependence is expressed formally through the following integral representation of each random realization of, say, $c_A(\mathbf{x},t)$:

$$c_A\left(\mathbf{x},t;[c_B^I(\mathbf{x},t)=\gamma_B^I]\right)=\int c_A\left(\mathbf{x},t;[c_B^I]\right)\,\delta\left(\gamma_B^I-c_B^I(\mathbf{x},t)\right)\,dc_B^I \qquad (4.6-25a)$$

$$c_B\left(\mathbf{x},t;[c_A^I(\mathbf{x},t)=\gamma_A^I]\right)=\int c_B\left(\mathbf{x},t;[c_A^I]\right)\,\delta\left(\gamma_A^I-c_A^I(\mathbf{x},t)\right)\,dc_A^I \qquad (4.6-25b)$$

$$c_A^I\left(\mathbf{x},t;[c_B^I(\mathbf{x},t)=\gamma_B^I]\right)=\int c_A^I\left(\mathbf{x},t;[c_B^I]\right)\,\delta\left(\gamma_B^I-c_B^I(\mathbf{x},t)\right)\,dc_B^I \qquad (4.6-25c)$$

$$c_B^I\left(\mathbf{x},t;[c_A^I(\mathbf{x},t)=\gamma_A^I]\right)=\int c_B^I\left(\mathbf{x},t;[c_A^I]\right)\,\delta\left(\gamma_A^I-c_A^I(\mathbf{x},t)\right)\,dc_A^I \qquad (4.6-25d)$$

Then, defining

$$a=c_A\left(\mathbf{x},t;[c_B^I=0]\right),\quad \alpha=c_A\left(\mathbf{x},t;[c_B^I=\gamma_B^I\neq 0]\right) \qquad (4.6-26a)$$

$$b = c_B\left(\mathbf{x},t;[c_A^I = 0]\right), \quad \beta = c_B\left(\mathbf{x},t;[c_A^I = \gamma_A^I \neq 0]\right) \qquad (4.6-26b)$$

$$a^I = c_A^I\left(\mathbf{x},t;[c_B^I = 0]\right), \quad \alpha^I = c_A^I\left(\mathbf{x},t;[c_B^I = \gamma_B^I \neq 0]\right) \qquad (4.6-26c)$$

$$b^I = c_B^I\left(\mathbf{x},t;[c_A^I = 0]\right), \quad \beta^I = c_B^I\left(\mathbf{x},t;[c_A^I = \gamma_A^I \neq 0]\right) \qquad (4.6-26d)$$

one has

$$c_A(\mathbf{x},t) = a(\mathbf{x},t) + \alpha(\mathbf{x},t)$$
$$c_A^I(\mathbf{x},t) = a^I(\mathbf{x},t) + \alpha^I(\mathbf{x},t)$$
$$c_B(\mathbf{x},t) = b(\mathbf{x},t) + \beta(\mathbf{x},t)$$
$$c_B^I(\mathbf{x},t) = b^I(\mathbf{x},t) + \beta^I(\mathbf{x},t)$$

One advantage of this representation ("concentration field splitting") lies in the fact that the evolution of a, a^I, α, α^I, etc., or, more precisely, of their statistical moments and correlations, is more easily predictable than of the rectant concentrations themselves. Thus it should be is in general easier to make reasonable assumptions (based on physical insight and simplified pictures of the mixing process) involving these statistical quantities. Another advantage of the integral functional formulation, that will be used in the following, is that it allows a particularly useful interpretation of ensemble averages:

- Means and correlations of of c_A, c_A^I, a, a^I, α, α^I are the result of integration over the domain of γ_B^I (after the definitions (4.6-25) and (4.6-26) have been introduced).
- Means and correlations of of c_B, c_B^I, b, b^I, β, β^I are the result of integration over the domain of γ_A^I (after the definitions (4.6-25) and (4.6-26) have been introduced).
- Cross-correlations of c_A and c_B, a and b, etc., are obtained by simultaneous integration over the domains of both γ_A^I and γ_B^I.

Definitions (4.6-25abcd) and the ensemble averaged form of (1.3-3)

$$\mathcal{L}^M c_S = r_S \qquad (1.3-3)$$

(where S stands for A, B or P) can be used to deduce relations between correlations of c_A, c_B and a, α, b, β, a^I, α^I, b^I and β^I. Thus, when the forward reaction in (1.3-1)

$$A + B \rightleftharpoons P \qquad (4.6-1)$$

dominates the backward (a situation which is expected to be valid in the near field of plume dispersion), and therefore

$$\left\langle c_A^I(\mathbf{x},t)\right\rangle \geq \langle c_A(\mathbf{x},t)\rangle\,, \quad \left\langle c_B^I(\mathbf{x},t)\right\rangle \geq \langle c_B(\mathbf{x},t)\rangle$$

$$\left\langle c_A^I(\mathbf{x},t)c_B^I(\mathbf{x},t)\right\rangle \geq \langle c_A(\mathbf{x},t)c_B(\mathbf{x},t)\rangle$$

$$\left\langle c_A^I(\mathbf{x},t)c_B(\mathbf{x},t)\right\rangle \geq \langle c_A(\mathbf{x},t)c_B(\mathbf{x},t)\rangle$$

$$\left\langle c_A(\mathbf{x},t)c_B^I(\mathbf{x},t)\right\rangle \geq \langle c_A(\mathbf{x},t)c_B(\mathbf{x},t)\rangle$$

it can be shown that

$$\langle c_A c_B\rangle = \langle \alpha\beta\rangle\,, \quad \left\langle c_A^I c_B^I\right\rangle = \left\langle \alpha^I \beta^I\right\rangle \qquad (4.6-27)$$

and

$$\langle a(\mathbf{x},t)\rangle = \left\langle a^I(\mathbf{x},t)\right\rangle\,, \quad \langle b(\mathbf{x},t)\rangle = \left\langle b^I(\mathbf{x},t)\right\rangle \qquad (4.6-28)$$

Indeed (4.6-27) is a direct consequence of the definitions (4.6-26abcd) and the inequalities listed above, from which one can deduce the *independence relations*

$$\langle ab\rangle = \langle a\alpha\rangle = \langle a\beta\rangle = \langle b\alpha\rangle = \langle b\beta\rangle \qquad (4.6-27a)$$

$$\left\langle a^I b^I\right\rangle = \left\langle a^I \alpha^I\right\rangle = \left\langle a^I \beta^I\right\rangle = \left\langle b^I \alpha^I\right\rangle = \left\langle b^I \beta^I\right\rangle \qquad (4.6-27b)$$

Relations (4.6-28) are proved as follows: Consider the equations

$$\mathcal{L}^M\,(a+\alpha) = c_A\, c_B$$

$$\mathcal{L}^M\,\left(a^I+\alpha^I\right) = 0$$

Multiplying the first of these equations by a, the second by a^I and then using the definitions (4.4-25) and integrating both equations over the entire domain of γ_B^I, one finds that

$$\left\langle a\mathcal{L}^M\, a\right\rangle = -\left\langle a\mathcal{L}^M\, \alpha\right\rangle$$

$$\left\langle a^I\mathcal{L}^M\, a^I\right\rangle = -\left\langle a^I\mathcal{L}^M\, \alpha^I\right\rangle$$

Now since a and α and a^I and α^I are statistically independent (see relations (4.6-27ab), the same will be true for arbitrary linear transformations of these quantities. Thus the r.h.s. of both the above equations is zero and therefore (realizing also that initial conditions, which can actually be incorporated in the mixing operator anyway, are identical for a and a^I and for α and α^I) one has $\langle a(\mathbf{x},t)\rangle = \left\langle a^I(\mathbf{x},t)\right\rangle$, and similarly$\langle b(\mathbf{x},t)\rangle = \left\langle b^I(\mathbf{x},t)\right\rangle$

Now, we introduce the *mixing functions*

$$M_{c_1c_2} = \frac{\langle c_1 c_2\rangle}{\langle c_1\rangle\langle c_2\rangle},\quad M^I_{c_1c_2} = \frac{\left\langle c_1^I c_2^I\right\rangle}{\left\langle c_1^I\right\rangle\left\langle c_2^I\right\rangle} \tag{4.6 – 29}$$

which allow formulation of the expression:

$$\langle c_A c_B\rangle = \frac{\varphi}{\mu_A\mu_B} M^I_{AB}\left[\langle c_A\rangle - (1-\mu_A)\left\langle c_A^I\right\rangle\right]\left[\langle c_B\rangle - (1-\mu_B)\left\langle c_A^I\right\rangle\right] \tag{4.6 – 30}$$

where φ is the *reaction parameter* and μ_A, μ_B are the *mixing parameters* defined by

$$\varphi = \frac{M_{\alpha\beta}}{M^I_{\alpha\beta}} \tag{4.6 – 31}$$

and

$$\mu_A = \frac{\left\langle\alpha^I\right\rangle}{\left\langle c_A^I\right\rangle},\quad \mu_B = \frac{\left\langle\beta^I\right\rangle}{\left\langle c_B^I\right\rangle} \tag{4.6 – 32}$$

In the special case of macroscopically uniformly mixed fields μ_A and μ_B represent the fractions of the total quantities of the fictitious inert surrogates of A and B that coexist in completely micromixed volumes. For arbitrarily macromixed feeds these fractions can be interpreted as the probabilities for a structural unit of A or B respectively to be in a micromixed state at a given space-time point.

Equation (4.6-30) is an exact relation. It expresses the unknown correlation in terms of mean values of the unknowns and in terms of parameters all of which except one, namely φ, depend only on inert scalar mixing. The problem of course has been transformed in the problem of estimation of these parameters.

A substantial simplification of (4.6-30) can be obtained in the special case where $\langle c_B(\mathbf{x},0)\rangle$ is nonzero for all $\mathbf{x}$. This situation (which of course contains the case of an ideally point source of A in a background containing B) means that $\langle c_B^I(\mathbf{x},t)\rangle$ is also nonzero for all $\mathbf{x}$ and t and therefore $\langle a^I(\mathbf{x},t)\rangle \equiv 0$, $\langle \alpha^I(\mathbf{x},t)\rangle \equiv \langle c_A^I(\mathbf{x},t)\rangle$, which give $\mu_A = 1$ for all $(\mathbf{x},t)$ (notice, however, that $\mu_B \neq 1$ in general). As it was discussed in Chapter 2 this result can be utilized for a typical atmospheric plume where the emissions of A (e.g. NO) have near source concentrations that are orders of magnitude higher than those of B (e.g. O_3). The fact $\langle c_A\rangle \gg \langle c_B\rangle$ near source implies that it will make no observable difference to the conversions of A if it were assumed that B is perfectly mixed with the emissions at the source, at a concentration equal to that of the ambient (in agreement with the idealization of the point source). Indeed, in such a case it does not make an appreciable difference to the overall evolution of reaction and the observed conversions of A if A and B are initially premixed or unpremixed. This further means that fine scale segregation of A and B inside the plume is induced mainly by the chemical reaction. This simplifies the analysis considerably, especially if it is assumed that the reaction is not infinitely fast and a local steady state with microscopic coexistence of A and B prevails. It is then possible using intuitive arguments to suggest that

$$\mu_B \simeq \frac{1}{M_{AA}^I}, \text{ and } M_{AB}^I \simeq 1$$

are acceptable *closure assumptions*. It can further be shown, by examining the significance of the participating correlations under the aforementioned conditions, that φ should be of order one. This is corroborated by the analysis of Shu (1976) and Lamb and Shu (1978) the main results of which are summarized in Appendix A4.1.

Hence, to recapitulate, in the case of a point release of A into an initially uniform field of B, and under the assumption that the concentrations of A, at least near the plume axis, are much greater than the background concentration of B, we can approximate the term $\langle c_A c_B \rangle = \langle c_A \rangle \langle c_B \rangle + \langle c'_A c'_B \rangle$ by

$$\langle c_A c_B \rangle \simeq M^I_{AA} \langle c_A \rangle \langle c_B \rangle + \left(1 - M^I_{AA}\right) \langle c^I_B \rangle \langle c_A \rangle \qquad (4.6-33)$$

where M^I_{AA} is a function characteristic of the state of *inert* species mixing in the plume.

Alternatively,if we consider the fluctuations $c^{I\,\prime}_A$ about $\langle c^I_A \rangle$, M^I_{AA} can be written as $M^I_{AA} = 1 + I^I_A$ where

$$I^I_A = \frac{\left(\sigma^I_A\right)^2}{\langle c^I_A \rangle^2} \quad \text{where} \quad \left(\sigma^I_A\right)^2 = \left\langle (c^I_A)'^2 \right\rangle \qquad (4.6-34)$$

is the relative intensity of concentration fluctuations of an inert emitted species in a plume (i.e. the intensity of stream segregation).

Introducing I^I_A we can write (4.6-33) as

$$\langle c_A\, c_B \rangle \simeq \langle c_A \rangle \langle c_B \rangle + I^I_A \langle c_A \rangle \left(\langle c^I_B \rangle - \langle c_B \rangle\right) \qquad (4.6-35)$$

which of course is equivalent to

$$\langle c'_A\, c'_B \rangle \simeq I^I_A(\langle c^I_B \rangle - \langle c_B \rangle)$$

The overall mean rate of reaction (1.3-1) at a point will therefore be

$$\langle R \rangle \simeq \tilde{R} = k_f \langle c_A \rangle \langle c_B \rangle - k_f I^I_A \langle c_A \rangle \left(\langle c^I_B \rangle - \langle c_B \rangle\right) - k_b \langle c_P \rangle \qquad (4.6-36)$$

Hence, all the effects of turbulence (or incomplete mixing) on the chemical kinetics have been incorporated in the second term of (4.6-36) which involves

(i) the mean concentrations of the reactive species $\langle c_A \rangle$, $\langle c_B \rangle$ which are the actual unknown variables we want to estimate,

(ii) the mean concentrations of inert surrogate species $\langle c^I_A \rangle$, $\langle c^I_B \rangle$, and

(iii) the variance of fluctuations of an inert emitted species.

The form of the second term of (4.6-36) suggests that it can be interpreted as representing a *fictitious reverse reaction* that retards the overall kinetic scheme in comparison to perfectly mixed conditions. The kinetic constant $k_f I_A^I$ of this "reaction" will depend on position in the plume because I_A^I shows a strong dependence on axial and radial position. The "reactants" participating in this fictitious step are A and the portion of B at any point that has already undergone chemical reaction (and therefore it is not actually available at that point). Thus the term $\langle c_B^I \rangle - \langle c_B \rangle$ can be viewed as representing "occupied" or "de-activated" B molecules that participate in a backward reaction with A, with a kinetic constant that is determined by the intensity of turbulent fluctuations. The behavior of this term is determined by the relative magnitude of I_A^I, $\langle c_A \rangle$ and $\left(\langle c_B^I \rangle - \langle c_B \rangle \right)$.

4.7 CONCLUSIONS

The major conclusions arising from the preceding exposition of the nature of the reactive turbulence problem and of the methods used to study it, in connection to the interest of the present study in environmental systems, and, in particular, atmospheric plumes are:

(I) While the problem is extremely complex, it is sufficiently important to warrant a quantitative description.

(II) There is not currently a specific method available that is definitely superior to the others with respect to applicability in distributed parameters environmental systems.

The spectrum of methods dealing with simultaneous mixing and reaction is very wide, ranging from very simple, empirical or heuristic, models that simulate highly idealized systems, to very complex mathematical formulations that either require excessive computational effort to produce results, or, simply, cannot give results in usable form. Somewhere in the middle lie the schemes on which we focused here: Eulerian Statistical Formulations with approximations for transport closure that are as simple as possible to keep the number of required partial differential equations to a minimum.

As far as chemical closure is concerned we believe that indirect methods (Section 4.6) are presently at a better state of development (if there is a demand for simplicity) and seem to be able to utilize more extensive and reliable theoretical and experimental information (regarding behavior of inert scalars in turbulence) than that available for direct methods (regarding the respective behavior of reactive species). So they should be preferred in practical modeling procedures. Mixed closure methods are needed to treat finite rate kinetics; however it is not always clear when the chemistry (especially for reversible reactions) must be characterized not slow but also not "infinite". Future research should insist on identifying the importance of the differences in predictions between simple and well developed models for infinite rate chemistry and the more complex models formulated for finite rate chemistry.

Specifically for atmospheric plumes, and if the reaction rate is assumed finite, the Concentration Splitting model described in subsection 4.6.3 shold be considered an appropriate choice at the present time, in terms of generality and computational simplicity (especially when integrated with the concept of the *local phenomenal extent of reaction* defined in Chapter 2). Its disadvantage is the limited knowledge on the behavior of its parameters. From this perspective other models may be better supported for special conditions. For example, if the chemistry is infinitely fast, there might be more reliable information for a model utilizing equations (4.6-21), (4.6-23). In any case, current research promises substantial improvement of the prediction of scalar behavior in turbulence and in particular in atmospheric boundary layers. Closure schemes should be constructed in such a way as to utilize the most reliable information available regarding this behavior.

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APPENDIX A4.1

Discussion
of the Chemical Closure Assumptions
in the Concentration Field Splitting Method

Chemical closure through the Concentration Field Splitting Method reduces to the estimation of the mixing and reaction parameters μ_A, μ_B and φ which are defined as

$$\mu_A = \frac{\langle \alpha^I \rangle}{\langle c_A^I \rangle}, \quad \mu_B = \frac{\langle \beta^I \rangle}{\langle c_B^I \rangle} \tag{A4.1 - 1}$$

and

$$\varphi = \frac{M_{\alpha\beta}}{M_{\alpha\beta}^I} \tag{A4.1 - 2}$$

respectively. In the following we discuss these parameters.

The Mixing Parameters

Estimation of the mixing parameters in the case of a point source of A in a background containing B (or in the more realistic case of a finite-dimensions source of A emitting at concentrations much higher than those of the ambient concentrations of B) is particularly simple. The reason for this simplicity is that the point character of the source and the finite speed at which the dispersion process actually proceeds (despite the parabolic character of the approximate models that are used to describe the latter process) produce a situation in which A is always and everywhere perfectly mixed (locally) with B while B is not perfectly mixed with A. Thus

$$\langle a^I \rangle \equiv 0$$

everywhere, and

$$\langle \alpha^I \rangle = \langle c_A^I \rangle$$

which implies that

$$\mu_A = 1 \tag{A4.1 - 3}$$

everywhere. Furthermore, in typical environmental applications the ambient concentrations of the species (pollutants) under consideration have very small absolute magnitudes. Thus it is reasonable, for all practical situations, to assume that the local values of the concentration of the inert surrogate

B^I are not affected by the presence of A^I and, furthermore, that c_B^I is *almost deterministic*. This leads directly to the relations

$$M_{AB}^I = M_{\alpha\beta}^I = 1 \tag{A4.1-4a}$$

and

$$M_{BB}^I = M_{bb}^I = M_{\beta\beta}^I = 1 \tag{A4.1-4b}$$

On the other hand, straightforward calculations produce the following *general* expression for μ_B:

$$\mu_B = \frac{M_{AB}^I}{mAAi} \frac{\dfrac{\langle a^I \rangle}{\langle \alpha^I \rangle} \dfrac{M_{aa}^I}{M_{\alpha\alpha}^I} (1 - \mu_A) + \mu_A}{\dfrac{M_{\alpha\beta}^I}{M_{\alpha\alpha}^I}} \tag{A4.1-5}$$

(A similar expression holds for μ_A).

Introduction of equations (A4.1-3) and (A4.1-4ab) into (A4.1-5) gives

$$\mu_B = \frac{M_{\alpha\alpha}^I}{M_{AA}^I} \tag{A4.1-6}$$

In deriving the final operational turbulent kinetics equations for use with the TRPM (Chapters 2 and 4) it was assumed that

$$\mu_B \simeq \frac{1}{M_{AA}^I} \tag{A4.1-7}$$

that is, equivalently

$$M_{\alpha\alpha}^I \simeq 1 \tag{A4.1-8}$$

which is essentially the *closure approximation for the mixing parameters* (all previous approximations being derived directly from the idealized model of the system under consideration). Intuitively, (A4.1-7) can be justified by realizing that the probability of B^I "molecule" to be surrounded by A^I "molecules" at a given point is inversely proportional to the intensity of segregation of A^I at that point. This approximation is also consistent with the general closure assumption of Lamb and Shu (1978) for unpremixed reactants in a monodimensional (i.e. macroscopically homogeneous) system, which essentially states that

$$\mu_A = \frac{M_{AB}^I}{M_{BB}^I}, \quad \mu_B = \frac{M_{AB}^I}{M_{AA}^I}$$

(The above closure approximation is basically justified on the basis of the asymptotic behavior of an unpremixed system where $\mu_A, \mu_B \to 1$ as $t \to \infty$ and $\mu_A = \mu_B = 0$ at $t = 0$).

A more formal evaluation of (A4.1-8) can in principle be performed on the basis of a microstructural model that considers the local dynamics of a typical (laminar) mixing zone at a point (at a scale comparable to Batchelor's microscale ℓ_B–see Chapter 4), whose properties are assumed representative of the average properties of the entire ensemble of such mixing zones at this point. In this approach the macroscopic variations of the mean concentration field (as well as of the higher concentration moments) should be incorporated in the local model in the form of appropriate initial and boundary conditions. However, although sophisticated microstructural models, that examine in detail the mechanics of fluid mixing at the level of the microscale, have been appearing in recent years (see, e.g., Ou et al., 1985), incorporation of the aforementioned side conditions in these models to produce results relevant to the point source problem does not seem to be an easy task. Nevertheless, some insight can be gained by the simple analysis of Shu (1976, p.33) who considered a simple B - A - B configuration of "three adjacent layers" of unpremixed species (initially uniform), of total thickness $2\ell_B$, and approximated $M^I_{\alpha\alpha}$ at a given time instant by the "spatial" average of $c^I_A c^I_A$ over a single cross-section of thickness $2\ell_B$. In this extremely idealized situation c^I_A is governed by the one-dimensional molecular diffusion equation

$$\frac{\partial c^I_A}{\partial t} = D_A \frac{\partial^2 c^I_A}{\partial x^2}$$

with initial condition

$$c^I_A(x,0) = \begin{cases} \left(c^I_A\right)_0, & \text{if } -\frac{1}{2}\ell_B \le x \le \frac{1}{2}\ell_B; \\ 0, & \text{otherwise.} \end{cases}$$

Shu (1976) found $M^I_{\alpha\alpha}$ to increase from a value of 1.0 at $t = 0$ to a maximum value of about 2.0 at $t = 0.1\ell_B^2/D_A$, and then to decay to a final value of 1.0 within a period of about $10^4\ell_B^2/D_A$. These calculations, although steming from a very simplified picture of the mixing process, corroborate the assumption that $M^I_{\alpha\alpha}$ is in general of order unity (and actually is very close to unity for most of the time).

Finally, before closing the discussion of the mixing parameters, it is interesting to examine their form in a case of very simple mixing conditions, i.e. that corresponding to a tubular chemical reactor in which the reactants are injected through alternate jets clustered over the entire cross-sectional area of one end of the tube. For reactors of this type Toor (1969) predicted, and later confirmed by measurements, that reactants that are fed into the reactor in stoichiometric ratio and that subsequently undergo extremely fast reactions satisfy

$$\left\langle c'_A c'_B \right\rangle = \left\langle c^{I'}_A c^{I'}_B \right\rangle$$

(where ensemble averages are approximated by spatial averages over a cross-section of the reactor). This result provides a means of estimating $\mu = \mu_A = \mu_B$ for this reactor: If one makes the pseudo-steady state assumption $\partial \left\langle c_A \right\rangle / \partial t \simeq 0$, which is valid for very fast reactions, one finds that

$$\left\langle c_A \right\rangle = (1-\mu)\left\langle c^I_A \right\rangle$$

$$\langle c_B \rangle = (1-\mu) \left\langle c_B^I \right\rangle$$

(where the analysis of Chapter 4 has been applied). Utilizing the fact that for very fast reactions $\langle \alpha\beta \rangle \simeq 0$, one finally obtains

$$\mu_A = \mu_B = 1 - \sqrt{1 - M_{AB}^I}$$

The Reaction Parameter

The reaction parameter φ (equation (A4.1-2)) was assumed approximately equal to 1.0 in the point-source plume case. Although this again is essentially a closure approximation it seems sufficiently supported by the analysis of simplified cases.

The complete governing equation for φ can be formulated directly from the transport-rection balances for the various random fields, for a given reaction system such as $A + B \rightarrow P$, but it is too complicated to allow direct deduction of (even qualitative) conclusions for the behavior of φ. However, some insight can be gained if one considers some idealized situations. Thus, if one assumes a situation where the mean concentration fields are spatially uniform (although this contradicts the point source concept), as it was done by Lamb and Shu (1978), and that (a) $D_A = D_B = D$, (b) the reaction between A and B is irreversible (with rate constant k), then the φ-equation reduces to

$$\frac{1}{\varphi}\frac{\partial \varphi}{\partial t} = -2D\left(A_* - A_*^I\right) - k\frac{\langle \alpha\beta\,(a+\beta)\rangle}{\langle \alpha\beta \rangle} + k\varphi\frac{\left\langle \alpha^I \beta^I \right\rangle}{\left\langle \alpha^I \right\rangle \left\langle \beta^I \right\rangle} +$$

$$+\left(\frac{1}{\left\langle \alpha^I \right\rangle} - \frac{1}{\langle \alpha \rangle}\right)\frac{\partial \left\langle \alpha^I \right\rangle}{\partial t} + \left(\frac{1}{\left\langle \beta^I \right\rangle} - \frac{1}{\langle \beta \rangle}\right)\frac{\partial \left\langle \beta^I \right\rangle}{\partial t}$$

with

$$A_* = \frac{\left\langle \dfrac{\partial \alpha}{\partial x_i}\dfrac{\partial \beta}{\partial x_i} \right\rangle}{\langle \alpha\beta \rangle}$$

$$A_*^I = \frac{\left\langle \dfrac{\partial \alpha^I}{\partial x_i}\dfrac{\partial \beta^I}{\partial x_i} \right\rangle}{\left\langle \alpha^I \beta^I \right\rangle}$$

If one further assumes that $\langle \alpha\beta \rangle$ and $\langle \beta \rangle$ are in a pseudo-steady state, which is a reasonable approximation when a high-source/low-ambient concentrations (of A and B respectively) situation exists, one obtains

$$\frac{1}{\varphi}\frac{\partial \varphi}{\partial t} = 2DA_*^I + \left(\frac{1}{\left\langle \alpha^I \right\rangle} - \frac{1}{\langle \alpha \rangle}\right)\frac{\partial \left\langle \alpha^I \right\rangle}{\partial t} + \left(\frac{1}{\alpha} + \frac{1}{\left\langle \beta^I \right\rangle}\right)\frac{\partial \left\langle \beta^I \right\rangle}{\partial t}$$

Initially the reactants A and B are totally segregated with A uniformly distributed in the source emissions and B uniformly distributed in the ambient. However, suppose that B were present in the source stream of A in the same concentration as in the ambient fluid. In this case we have $\langle c_A^I \rangle = \langle \alpha^I \rangle$ and $\langle \alpha^I \beta^I \rangle = \langle \alpha^I \rangle \langle \beta^I \rangle$ and (during the time when $\langle \alpha^I \rangle \gg \langle \beta^I \rangle$) the above equation simplifies to

$$\frac{\partial \ln \varphi}{\partial t} = \frac{\partial}{\partial t} \ln \left(\frac{\langle \beta^I \rangle}{\langle \alpha^I \beta^I \rangle} \right) = 0$$

with initial consition

$$\varphi(0) = 1.0$$

Hence

$$\varphi(t) = 1.0$$

Considering a typical industrial stack and taking into account the great disparity in the initial levels of (source) NO and (ambient) O_3, whether ozone is actually present in the source stream has virtually no affect on the evolution of NO concentrations in the plume. One concludes, therefore, that $\varphi = 1$ is in general a reasonable approximation as long as $\langle \alpha^I \rangle \gg \langle \beta^I \rangle$ initially, and the reaction is fast, i.e.

$$k \langle \alpha^I \rangle \langle \beta^I \rangle \gg \frac{\partial \langle \beta^I \rangle}{\partial t}$$

Since the same result applies when the reaction is very slow (this can be seen easily by taking the limit $k \to 0$), Lamb and Shu (1978) assumed that in point source problems in general, $\varphi = 1$.

We will now finish this discussion of the estimation of φ by summarizing the conclusions from a simple one-dimensional microstructural model of the mixing-reaction process, studied by Shu (1976), that is similar to the laminar layers model for the estimation of the mixing parameters that was discussed earlier. This model is directly relevant to the multijet plug flow reactor case, that was also mentioned earlier, where, due to the reactor design, the regions of mixed and unmixed reactants compose a mosaic of small, intermingling patches of fluid which, statistically speaking, have identical concentration probability distributions (at any fixed axial distance from the reactor head), and give rise to time mean reactant concentrations that are uniform over any plane normal to the reactor axis.

Shu (1976) assumed that $D_A = D_B = D$, that the turbulent fluid has kinematic viscosity ν, and that turbulent energy is being dissipated at a rate ϵ . Since at scales large compared to ℓ_B, concentration gradients are too weak to cause significant mixing Shu futher assumed that the generation of the (laminar) mixed zone is confined primarily to those portions of the fluid where the reactant sheet thickness is comparable to ℓ_B . Thus he developed expressions for φ based on a one-dimensional model of slugs of reactant fluids of initial widths and separations of the order of ℓ_B immersed in an inert convecting fluid.

Since the expansion of reactant fluid sheets of widths smaller than or comparable to ℓ_B is dominated by molecular diffusion, the governing equations are assumed to be

$$\frac{\partial c_A}{\partial t} = D_A \frac{\partial^2 c_A}{\partial x^2} - k c_A c_B$$

$$\frac{\partial c_B}{\partial t} = D_B \frac{\partial^2 c_B}{\partial x^2} - k c_A c_B$$

$$\frac{\partial c_A^I}{\partial t} = D_A \frac{\partial^2 c_A^I}{\partial x^2}$$

$$\frac{\partial c_B^I}{\partial t} = D_B \frac{\partial^2 c_B^I}{\partial x^2}$$

with initial and boundary conditions

$$c_A\left(x,0\right) = c_A^I\left(x,0\right) \begin{cases} A_0, & -\frac{3}{2}\ell_B \le x \le -\frac{1}{2}\ell_B; \\ 0, & \text{otherwise}; \end{cases}$$

$$c_B\left(x,0\right) = c_B^I\left(x,0\right) \begin{cases} B_0, & -\frac{3}{2}\ell_B \le x \le -\frac{1}{2}\ell_B; \\ 0, & \text{otherwise}; \end{cases}$$

$$c_A\left(x,t\right) = c_B\left(x,t\right) = 0 \quad x \to \pm\infty$$

Shu (1976) solved these equations numerically for a variety of values of feed ratio $\varrho = B_0/A_0$, diffusivity ratio D_B/D_A, and local (molecular) Damköhler number

$$\kappa = \frac{k \ell_B^2 A_0}{D_A}$$

and from the results estimated φ using spatial (cross-section) averages. Although these estimates were based on reactant and surrogate concentrations averaged over only the two patches of material considered, rather than an entire reactor cross-section as is implicit in the mean values used in the definition of φ, the uniformity mentioned earlier of the concentration probability distributions within the multijet reactor renders the patch and the actual cross-sectional averages equal.

The calculations showed that for the case of stoichiometric feed ($\varrho = 1$) and given κ, φ drops quickly from unity to some minimum value (the higher the κ the lower this value) until $t^* = tD_A/\ell_B^2 \simeq 10^4$. However, when $\varrho \neq 1$ the value of φ returns to unity more quickly, but not, as it turns out, until the reactant in the smaller quantity has been almost completely consumed. Thus, during the period within which most of the chemical reaction occurs, φ has its minimum value $\varphi_{\min}$. Lamb and Shu (1978) found from the analysis of the above numerical results that the dependence of $\varphi_{\min}$ on the variables A_0, B_0, D_A, D_B is described by the simple expression

$$\varphi_{\min} = \frac{1}{1 + 0.16\kappa}$$

where

$$\kappa = \frac{k\ell_B^2 \min[A_0, B_0]}{\max[D_a, D_B]}$$

Shu (1976) also performed numerical calculations for the case of premixed reactants, in a completely analogous manner, considering the case of a single fluid pulse containing uniform concentrations of both A and B. The temporal behavior of φ in this case was found to show two distinct patterns: For the case of $\varrho = 1$, φ stays at unity for all times; but for the cases where $\varrho \neq 1$, φ decays to the same minimum value as its nonpremixed counterpart.

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for Appendix A4.1

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CHAPTER 5

Chapter 5 contains

- *an introduction to the problem of modeling concentration fluctuations in point source plumes, including a brief literature survey,*
- *an exposition of the fundamental concepts and problems of a meandering frame Eulerian Approach for modeling the instantaneous "internal" plume concentration variance, with extensive discussion of the self similarity concept,*
- *a detailed discussion of the new "Localized Production of Fluctuations Method," that is the first choice for use with the TRPM.*

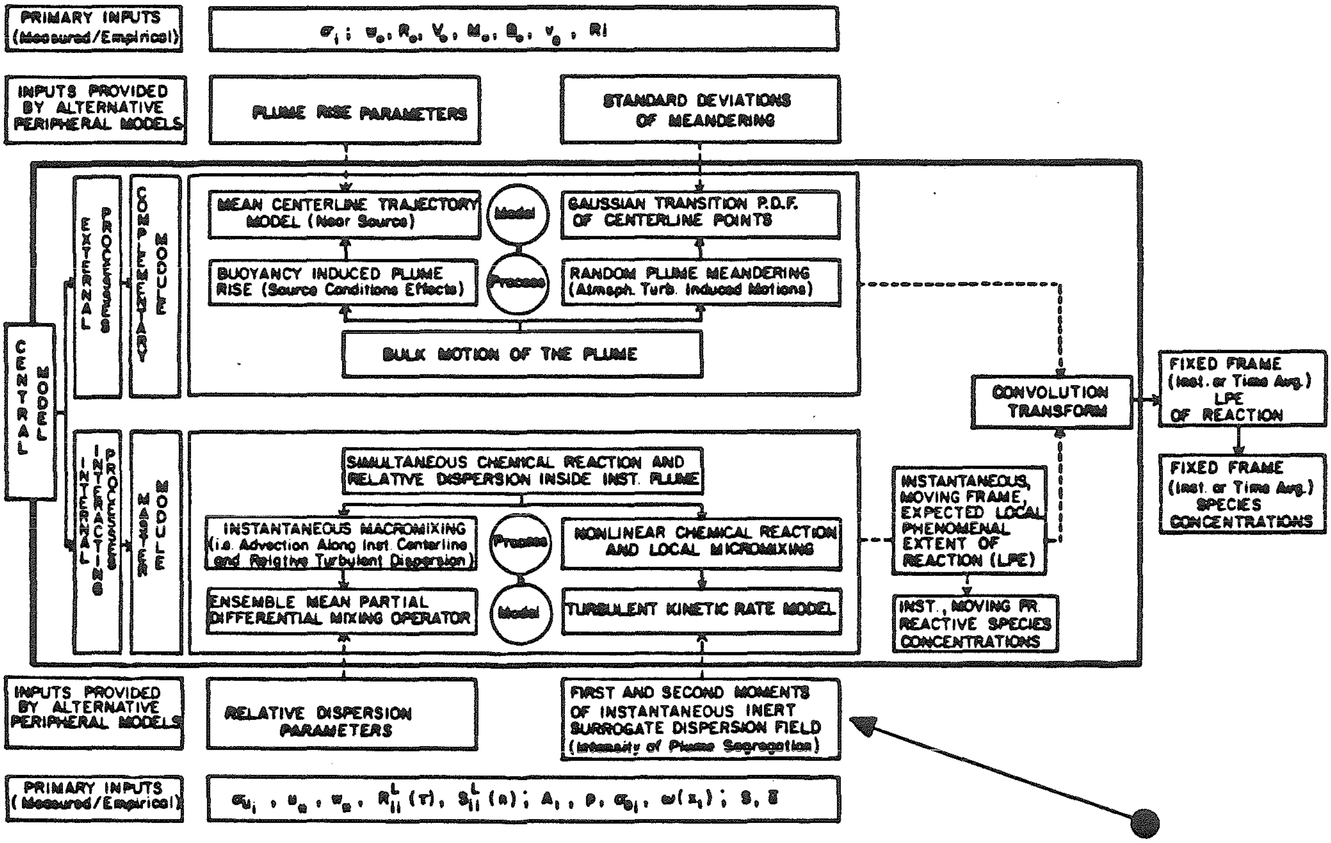

Figure 2-1b

TRPM Components Discussed in Chapter 5

CHAPTER 5

INSTANTANEOUS CONCENTRATION FLUCTUATIONS IN POINT SOURCE PLUMES

5.1 INTRODUCTION

Prediction of expected concentration fluctuation levels in point-source plumes is a key need that arises in many problems related to turbulent dispersion. Typical examples are:

(i) *Estimation of quantitative measures for the inherent uncertainty in models of contaminant dispersion in the environment.*

This uncertainty is associated with the stochastic nature of the dispersion phenomenon per se, as opposed to the potentially reducible uncertainty associated with errors and approximations in the model structure and the input data (Fox, 1984; Weil, 1985). Inherent uncertainty has to be taken into account for the proper interpretation of model calculations for the mean field, e.g., in their comparison with available measured values and in connection with the definition and evaluation of air quality standards.

Indeed, consider for example Figure 3-2a, where short-term averages of plume concentrations measured at source height at various distances downwind in a wind tunnel and reported by Builtjes (1981), are plotted versus the non-dimensionalized cross-wind distance y/σ_y. These are compared to calculations from a Gaussian plume model that utilizes parameters directly measured from the plume. At first sight, it would seem that the model predictions are not very relevant to the actual physical phenomenon. However, this is not true: the model calculations correspond to ensemble averages and not individual realizations of the random concentration field. When averages of the measurements corresponding roughly at the same y/σ_y (actually lying between $0.9ys_y$ and $1.1y/\sigma_y$) are taken as approximations of the respective ensemble values and compared against the model calculations (Figure 3-2b) the performance of the model should be considered satisfactory. Another, even more illustrating, example of the same nature is given in Figure 5-1 which is based on measurements reported in Csanady (1973).

(ii) *Modeling situations concerned with the exceedance of some critical value by a rapidly changing concentration, even for very short times.*

Examples of such situations are the accidental release of toxic or flammable gases (Chatwin, 1982), and the creation of smoke screens for defense purposes (Ohmstede et al., 1982). In these cases probabilistic properties of the concentration field are essential in assessing the environmental impact.

(iii) *Modeling nonlinear processes (usually chemical) within plumes.*

For processes such as reactions with nonlinear kinetics, the effective conversion rates may depend critically on the level and spatial distribution of turbulent concentration fluctuations (i.e., on the quality or completeness of the fine scale mixing locally inside the instantaneous plume boundaries). The local intensity of segregation I_s, involving the variance of fine scale "in plume" fluctuations, can be used to quantify the interaction of mixing and chemistry for second order chemical reactions.

In dealing with such problems it is essential to discern the spatial scales associated with a given portion of the fluctuations spectrum as they may affect the phenomenon under study and its consequenses in qualitatively very different ways. Thus turbulent eddies that at a given location are of size comparable to and larger than the local plume dimensions result in its irregular meandering, i.e., a bulk motion (Figure 5-2). Only eddies smaller than these are responsible for the mixing process inside the instantaneous plume boundaries, the state of which is described by the level of instantaneous "internal" concentration fluctuations and thus associated with the processes of relative or two–particle dispersion. Thus, for example, rates of nonlinear chemical reactions between plume constituents and the ambient are affected solely by the internal fine scale fluctuations. On the other hand, assessing physiological effects from the varying concentration of a pollutant requires taking into account the total variability of the concentration field at the fixed receptor location.

A complete description of the fluctuations problem would require knowledge of the entire probability density of random concentrations, and in the case of interacting concentration fields (e.g. of chemically reacting species) of their joint probability densities. Probability densities at every point in a fixed frame of reference, and the associated statistics, reflect the total randomness of the concentration field which results from absolute diffusion; the respective densities and statistics for every point in a frame of reference whose origin follows the random meandering motion of the center of mass of an instantaneous release, or the instantaneous centerline of a continuous plume, reflect internal randomness due to relative dispersion. To deduce fixed frame probability densities and non-central moments of concentrations from the corresponding moving frame quantities one has to calculate the convolution of the latter with the spatial position probability density of the meandering origin of the moving frame (see Appendix A5.1 and Csanady, 1973, Chapters IV and VII).

Although the problem of calculating probability densities of concentration fields (of both conserved and reactive scalars) has been pursued through a variety of approaches (see, e.g., Hill, 1976; O'Brien, 1980; Pope, 1982, 1985) its complexity does not presently allow for simple, practical models. (see also Chapter 4). A more feasible goal is the prediction of the second moment $\langle c^2 \rangle$, or of the variance σ_c^2, of the random instantaneous concentration field, which, combined with the knowledge of the mean $\langle c \rangle$, would provide a description adequate for most applications. Theoretical study of the σ_c^2 dynamics originated in the works of Corrsin (1952, 1964) and Batchelor (1959). Major results concerning σ_c^2 behavior in different turbulent flows are summarized in various sources (e.g. Brodkey, 1967; Monin and Yaglom, 1971, 1975; Hinze,

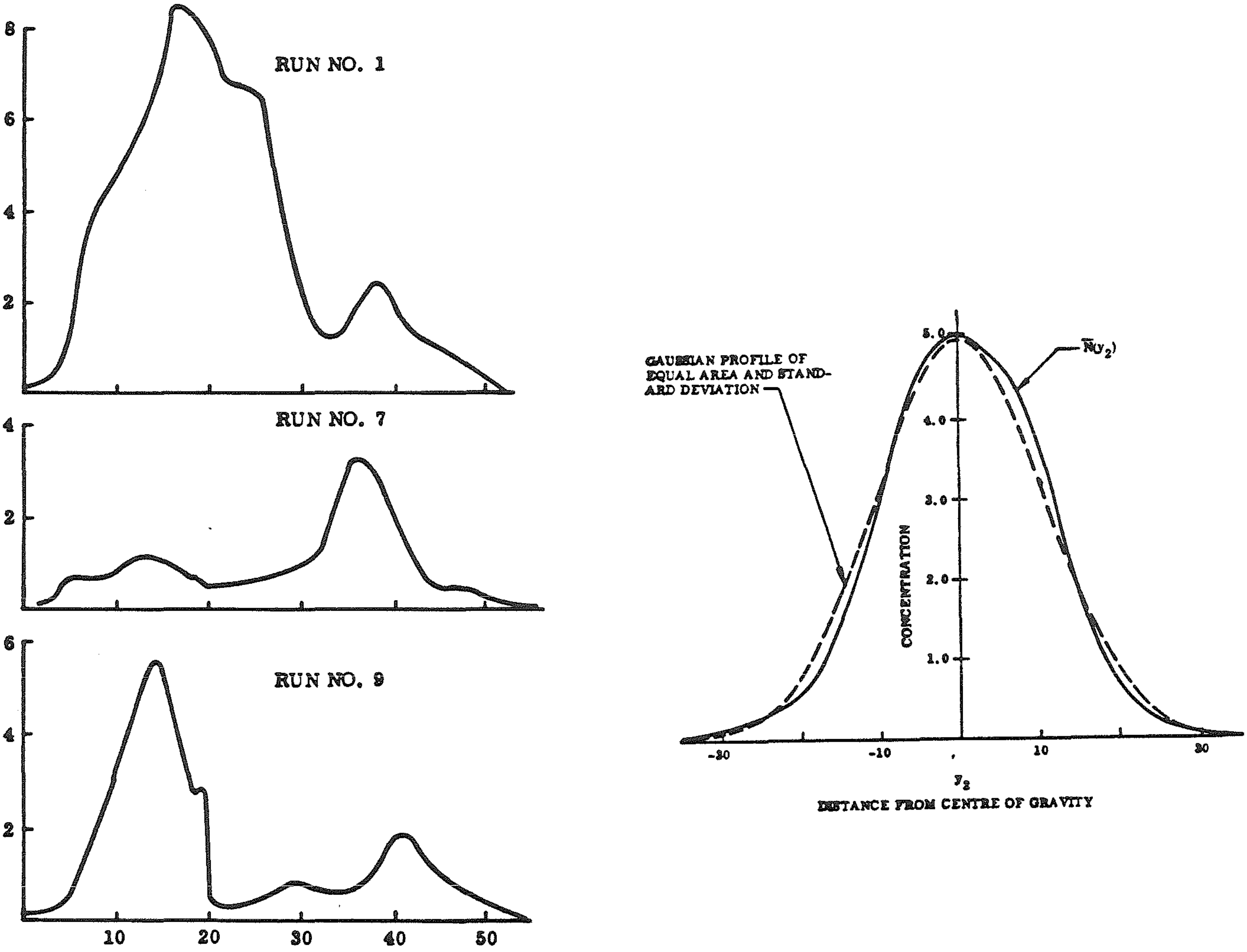

Figure 5-1

Instantaneous and average plume concentration profiles

measured relative to the plume centerline

(Source: Csanady, 1966, 1973)

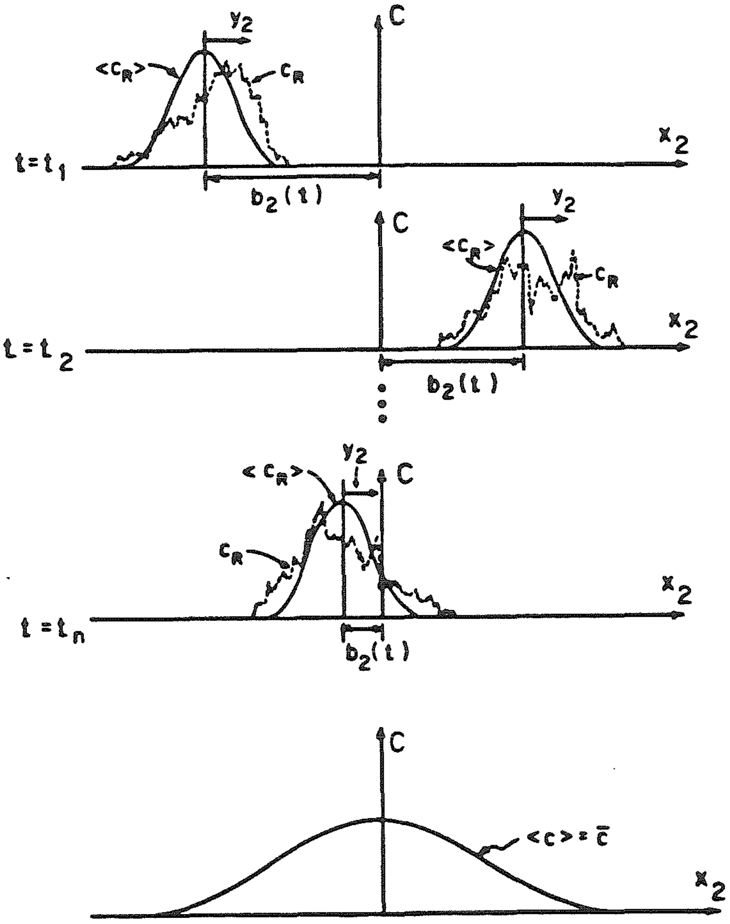

Figure 5-2

Cross-flow profiles of expected instantaneous concentrations in a fixed and in a meandering frame of reference ($\langle c \rangle$ and $\langle c_R \rangle$ respectively) at the same downwind distance x_1 and at various times $t_1, t_2, \ldots, t_n$, for a plume that is assumed to be transferred essentially intact by meandering. "Actual" instantaneous realizations of the concentration field $c \equiv c_R$ are also presented. (Note that $\langle c \rangle$ is the long term time average of the ensemble average $\langle c_R \rangle$ at a fixed position.)

1975; Townsend, 1976; Bradshaw, 1978; Fischer et al., 1979). As far as dispersion in ambient turbulence is concerned, the three major approaches commonly employed in modeling the mean field, i.e. Eulerian and Lagrangian statistical methods (including Langevin models) and dimensional (similarity) analysis have also been used, often combined, to study the variance of concentration fields resulting from *passive releases (*) from strongly localized sources* (Csanady, 1967, 1973; Thomas, 1979; Chatwin and Sullivan, 1979a, 1980; Robins and Fackrell, 1979; Durbin, 1980, 1982; Sawford, 1982, 1983, 1985; Sykes et al., 1984; Hanna, 1984 – see also Weil, 1985). A separate class of models originated with Gifford's (1959) fluctuating plume concept which considers fluctuations produced exclusively by the bulk meandering of the plume ("external" fluctuations), neglecting all randomness inside the instantaneous plume boundaries, and therefore calculates what we will call here the "external" variance. Various applications and extensions of this concept (Scriven, 1965; Diamante et al., 1976; Fackrell and Robins, 1982b) as well as related formulations (Venkatram, 1979; Hanna, 1984) have appeared in the literature. (A new generalization of the traditional fluctuating plume model so that it accounts *explicitly* for both the external and internal fluctuations is presented in Appendix A5.3 of the present chapter). Finally, the empirical models of Wilson et al. (1982ab) provide expressions for σ_c^2 constructed so as to fit wind tunnel data where meandering was recognized as the dominant source of observed fluctuations (Fackrell and Robins, 1982ab).

Available data of short term fluctuation statistics for pure plumes from point sources, that is for dispersion governed *exclusively by the ambient turbulence*, are basically relevant to the total variance observed at a fixed point, and include mainly wind tunnel (Fackrell, 1978, 1980; Fackrell and Robins, 1981, 1982ab; Robins, 1978, 1979; Gad El Hak and Morton, 1979) and atmospheric field (Gosline, 1952; Barry, 1971; Ramsdell and Hinds, 1971; Kimura et al., 1981; Jones, 1983; Sawford et al.,

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(*) The term "passive" is used in the sense that this release does not affect the properties of the ambient flow.

1985) measurements. Data on in-plume fluctuations, definitely more scarce, are also available, both from laboratory flows with insignificant meandering (Becker et al., 1966), and field measurements performed relevant to the meandering center of mass of continuous oceanic (Murthy and Csanady, 1971; Sullivan, 1971; Chatwin and Sullivan, 1979b) and atmospheric (Eidsvik, 1980) plumes. Finally, some related information can be found in the substantial fluid–mechanical literature on momentum jets and buoyant plumes (List, 1982; Gebhard et al., 1984).

The brief preceding analysis is complemented by Appendix A5.2 where one can find some further comments and explanations relevant to trhe works surveyed here.

Some rather general results on plume fluctuations, based mainly on data from pipe flows and from wind tunnels simulating either homogeneous and isotropic turbulence or the neutral atmospheric boundary layer are:

(i) Production of both internal and external fluctuations is in general significant only close to the source.

(ii) Meandering is typically the most significant source of fluctuations in the near field whereas internal fluctuations prevail far downwind. Further analysis suggests that the external intensity of fluctuations at the centerline (i.e. the ratio of external variance to the square of the mean concentration) reaches a maximum at some distance downwind and decays towards zero thereafter; the corresponding internal intensity does not decay but seems to to tend towards some constant nonzero value.

(iii) Intermittency effects are very significant in the near field and are typically associated with meandering; relative concentration measurements are very often free of intermittency effects in the "core" of the instantaneous plume.

(iv) The variance of atmospheric concentrations from ground level sources exhibits profiles that are approximately self-similar in both the horizontal and vertical directions; further, it does not show significant dependence on source size.

(v) The same variance for elevated sources initially shows dependence on source size that is eventually "forgotten." Horizontal profiles of σ_c^2 are again approximately self-similar, but vertical profiles show a more complicated behavior: In the immediate vicinity of the source they are self-similar until the effect of the ground is felt. In the far field, however, these profiles become again self-similar, resembling those of a ground level source.

(vi) A power law concentration probability density resulting from Gifford's fluctuating plume model seems to provide the best fit to experimentally measured densities of fixed frame data in most cases. Log-normal densities offer the best fit to sets of non-intermittent data.

However, in spite of the recent advances in analyzing and understanding the problem of turbulent concentration fluctuations, a simple, rational scheme for routine calculation of the instantaneous *internal* plume concentration variance, for use in conjunction with the Gaussian relative dispersion formulas for the instantaneous mean field does not exist. Such a model can, in fact, be viewed as a counterpart of Gifford's (1959) model for the *external* variance. The development of such a practical scheme is the object of this work. We start from the Eulerian transport equation for σ_c^2, modeling the processes described by its components in terms of known or measurable quantities, and continuing with an analysis of potential simplifications of the mathematical description through self–similarity assumptions for σ_c^2. The information that is systematized in this way is subsequently utilized in the formulation of a new model that provides simple, closed form, analytical expressions for σ_c^2 for the case of a continuous passive "point" release of material in a turbulent field of uniform mean velocity.

Before proceeding to the development of models for the concentration variance it is useful to recall the effects of averaging time on this property (compare also with the discussion of Appendix A6.1). When the ensemble under study contains time averages and not instantaneous values, the variance for this ensemble $\sigma_{c,T}^2$ is directly related to the variance of instantaneous concentrations σ_c^2 through (see, e.g., Tennekes and Lumley, 1972, p. 212)

$$\sigma^2_{c,T} = \frac{2\sigma_c^2}{T}\int_0^T \left(1 - \frac{\tau}{T}\right)\rho(\tau)\,d\tau \qquad (5.1-1a)$$

where T is the averaging time and $\rho(\tau)$ is the temporal auto-correlation coefficient of concentration fluctuations, commonly assumed of exponential form. For large times, i.e. for $T \gg T^*$, where T^* is the integral time scale of the correlation, (5.1-1a) reduces to the approximate relation

$$\sigma^2_{c,T} = 2\sigma_c^2\frac{T^*}{T} \qquad (5.1-1b)$$

(Note that in the special case of exponential correlation of concentration fluctuations (5.1-1b) is valid under the milder restriction $(T/T^*)^2 \gg 1$.)

5.2 THE TRANSPORT EQUATION FOR THE CONCENTRATION VARIANCE

5.2.1 General Considerations

Eulerian models for the estimation of σ_c^2 are based on the fundamental transport equation for c for a fixed frame of reference

$$\frac{\partial c}{\partial t} + u_i \frac{\partial c}{\partial x_i} = D \frac{\partial^2 c}{\partial x_i \partial x_i} \tag{5.2 - 1}$$

(summation convention implied) where u_i, c are stochastic variables that can be viewed as consisting of a mean and a fluctuating part (Reynolds decomposition), i.e. $u_i = \langle u_i \rangle + u_i'$, $c = \langle c \rangle + c'$. In the following the operation $\langle \cdot \rangle$ denotes always ensemble averaging; for (locally) homogeneous and stationary turbulence this can be replaced by spatial or temporal averaging,under an ergodic hypothesis (see, e.g., Hinze 1975) as far as the velocities are concerned. For strongly localized sources the concentration field cannot be homogeneous and thus only time averages can approximate ensemble means (when,of course,the specific phenomenon under study is in steady state).

The equation for the variance of c as obtained from (5.2-1) is

$$\frac{\partial \left\langle c'^2 \right\rangle}{\partial t} + \overbrace{\langle u_i \rangle \frac{\partial \left\langle c'^2 \right\rangle}{\partial x_i}}^{\text{(i)}} =$$

$$= \overbrace{-2 \langle u_i c' \rangle \frac{\partial \langle c \rangle}{\partial x_i}}^{\text{(ii)}} + \overbrace{\frac{\partial}{\partial x_i} \left(D \frac{\partial \left\langle c'^2 \right\rangle}{\partial x_i} - \left\langle u_i' c'^2 \right\rangle \right)}^{\text{(iii)}} \overbrace{- 2D \frac{\langle \partial c' \partial c' \rangle}{\partial x_i \partial x_i}}^{\text{(iv)}} \tag{5.2 - 2}$$

This equation expresses the fact that the level of $\sigma_c^2 = \left\langle c'^2 \right\rangle$ changes through an imbalance of

(i) advection,

(ii) the generation rate of scalar fluctuations by gradients in the mean concentration,

(iii) the diffusive transfer produced by molecular dispersion and turbulent velocity fluctuations (the former being usually negligible), and

(iv) the dissipation of fluctuations due to molecular diffusion in the fine scale structure.

The relative importance of the different proceses in the σ_c^2 budget depends on the particular type of flow (see e.g. Launder, 1978); bulk meandering and internal fine scale motions will contribute in a qualitatively different manner not only to the observed overall level of fluctuations at a given point but to the relative balance of terms in the governing equation for σ_c^2 as well. Here we confine attention to relative dispersion in turbulence with a uniform mean velocity $\overline{u}$, and to internal fluctuations in plumes that generate an ensemble of instantaneous realizations which is in a steady state with respect to a frame of reference that follows the randomly meandering centerline translating parallel to itself. (The steady state concept here is, of course, relevant to the mean of the ensemble and not to the actual concentration field.) Equations (5.2-1) and (5.2-2) with $\partial(\cdot)/\partial t = 0$, $\langle u_1 \rangle = \overline{u}$, $\langle u_2 \rangle = \langle u_3 \rangle = 0$ are assumed to hold for this moving frame of reference. In other words, if the moving frame coordinates in the crosswind plane at x_1 are y_2, y_3 where $y_2 = x_2 - b_2$, $y_3 = x_3 - b_3$, b_2, b_3 being the random coordinates of the instantaneous plume centerline in this plane, then (5.2-1) and (5.2-2) are assumed to adequately describe mass transport in the meandering frame (see Chapter 6, for further discussion of this point). In the case where flow conditions are such that the mean plume centerline is not a straight line parallel to the horizontal plane (i.e. $\langle b_k \rangle$, $k = 2,3$, are not constant for all x_1), then the above equations are still sufficient approximations (for a translating frame meandering about this centerline) for very small values of the derivatives $(\partial \langle b_k \rangle / \partial x_l)$, $k = 2,3$, $l = 1,2,3$. The situation considered here is schematically represented in Figure 5-2: The mean concentration in (5.2-1) is $\langle c_R \rangle$ and the fluctuations in (5.2-2) represent deviations of actual realizations c_R from this value. In the present work we limit attention to c_R and $\langle c_R \rangle$; fixed frame properties (such as $\langle c \rangle$ of Figure 5-2) will not be examined. Thus in the following the subscript R for the concentration will be dropped without any loss of clarity. Another point to note is that in this approach intermittency effects are attributed to bulk motions, in compliance with available experimental evidence; the probability of exactly zero concentrations in the vicinity of the origin of the meandering frame is assumed negligible.

5.2.2 Modeling Individual Terms of The Variance Transport Equation

(a) The Production Term

In the perspective of this study we will consider as adequate a description of $\langle u_i'c' \rangle$ in terms of eddy diffusivities K_{R_i} that will be assumed to be in general functions of the distance from the source, and to correspond to the effects of small scale dispersion processes (the subscript R used to denote the relevance to relative dispersion – or absolute dispersion without significant meandering). In this way (5.2-2) continues to hold locally inside the instantaneous plume. In a sense this is a "Lagrangian" modeling step, since K_{R_i}'s thus defined are not properties of the flow field but functions of the dispersion time for specific emissions. Thus, locally

$$\langle u_i'c' \rangle = -K_{R_i}(x_1)\,\frac{\partial \langle c \rangle}{\partial y_i} \tag{5.2 – 3}$$

where the point species source is located at $x_1 = 0$. The variation of K_{R_i} with downwind distance from the source will be calculated from

$$K_{R_i}(x_1) = \frac{\langle u_1 \rangle}{2}\frac{d\sigma_{R_i}^2}{dx_1} = \frac{1}{2}\frac{d\sigma_{R_i}^2}{dt} \tag{5.2 – 4}$$

where σ_{R_i} is the standard deviation of relative dispersion in the i direction. Methods for estimating σ_R's can be found in Hinze (1975, p.406), Monin and Yaglom (1975), and Seinfeld (1983). Thus

$$\Pi_c = -2\,\langle u_i'c' \rangle\,\frac{\partial \langle c \rangle}{\partial y_i} = 2K_{R_i}(x_1)\left(\frac{\partial \langle c \rangle}{\partial y_i}\right)^2 \tag{5.2 – 5}$$

(b) The Diffusive Flux Term

Most approaches for modeling the diffusive flux of σ_c^2 have also adopted a gradient type representation of $\left\langle u_i' c'^2 \right\rangle$, usually neglecting all molecular diffusion effects (see Launder, 1978). Various forms of gradient type formulas have been used (Bradshaw and Ferris, 1968; Spalding, 1971; Wyngaard, 1975; Thomas, 1979; Sykes et al., 1984). A simple approach, especially when eddy diffusivities are used in representing $\langle u_i' c' \rangle$, is to assume a gradient transport relationship of the form

$$\left\langle u_i' c'^2 \right\rangle - D\frac{\partial \sigma_c^2}{\partial x_i} = -\tilde{K}_i \frac{\partial \sigma_c^2}{\partial x_i} \tag{5.2-6}$$

Assuming that the same dispersive mechanisms account for the spread of both $\langle c \rangle$ and σ_c^2 we set $\tilde{K}_i = K_{R_i}$. Data from geophysical flows provide supportive but certainly not conclusive indication for the validity and the limitations of such a gradient transport scheme (Csanady, 1973; Netterville and Wilson, 1980). In any case, since higher order closure schemes are beyond the scope of the present analysis, we will adopt the closure assumption of (5.2-6) with $\tilde{K}_i = K_{Ri}$ given by (5.2-4).

(c) The Dissipation Term

Many studies have attempted to model this term by analogy to the dissipation of velocity fluctuations (kinetic energy dissipation) for which there is more extensive experimental information available. The most common procedure is to adopt an expression of the general form

$$\Phi \equiv 2\epsilon_c = 2D\frac{\langle \partial c' \partial c' \rangle}{\partial y_i \partial y_i} = \frac{nD\sigma_c^2}{\ell_d^2} = \frac{\sigma_c^2}{t_d} \tag{5.2-7}$$

where ℓ_d is a "dissipative length scale" (a "hybrid" Corrsin scale) analogous to the Taylor scale for the dissipation of velocity fluctuations, and $nD/\ell_d^2 = 1/t_d$ is the reciprocal of a characteristic *decay time* scale t_d. The choice of the numerical factor n in this relation is a matter of convention (e.g. n =4, 6 and 12 are used in the literature). The time scale t_d is the single most important quantity in the characterization of the mixing process; actually in most approaches all the effects of molecular diffusion on mixing are lumped into this parameter.

For the case of homogeneous, quasi–isotropic, turbulent velocity and concentration fields both theoretical considerations and experimental evidence suggest that (Gibson and Schwarz, 1963; Hinze, 1975; Launder, 1978; Warhaft and Lumley, 1978; Sreenivasan et al., 1980; Durbin, 1982).

$$t_d = kt + k_0 \tag{5.2-8}$$

where k lies in the range 1/3 to 2/3, $t = x_1/\langle u_1 \rangle$, and k_0 is a constant that can be assumed equal to zero when the production of fluctuations is localized at $t = 0$.

In the case of a continuous plume generated by a concentrated point (or line) source in a field of homogeneous turbulence we may also expect the rate of dissipation of concentration fluctuations to be proportional to fluctuation intensity σ_c^2, because essentially the same physical factors must govern across-the-spectrum transfer of contributions to σ_c^2, regardless of the manner in which the fluctuation were generated (Csanady, 1973). However, now the "ages" of the concentrations fluctuations cover a broad range and the decay time-scale may vary in an unknown manner. Thus one should set locally $\Phi = \sigma_c^2/t_d$ with $t_d = t_d(x_1, y_2, y_3)$, i.e. assume that t_d is some function of position that has to be determined.

The approach described by (5.2-7) has appeared in some works relevant to air pollution. Thus Donaldson and Hilst (1972) estimated a typical (constant) value of $t_d \simeq 5$min for a (hypothetical) average turbulent mass of atmospheric air. This (constant) value of the decay time scale was used by Kewley (1978) in a reactive plume model. However, in plumes, the factors affecting the intensity of dissipation (and therefore t_d) will change significantly with travel time and the assumption of constant t_d is not an appropriate one. In a more justifiable approach Csanady(1967, 1973) and Thomas (1979) adopted (5.2-8) with the theoretical value $k = 2/3$ (Hinze, 1975, p.301) and $k_0 = 0$. Modified forms of (5.2-8) were also suggested by Fackrell and Robins (1979) and Netterville (1979) and utilized by Wilson et al. (1982ab) in an empirical model for the total level of atmospheric plume fluctuations. However in the latter case the dominant component in the overall observed variance values was bulk variance (Fackrell and Robins, 1982ab), the dissipation of which mainly reflects the expansion of the instantaneous plume to the size of the time average envelope; the approach of Sykes et al. (1984) is more appropriate for this situation.

For the dissipation of fine scale fluctuations by molecular diffusion in the moving frame of reference we adopt (5.2-8) in the form

$$t_d = \frac{x_1 + x_0}{A_1 \langle u_1 \rangle} = \frac{1}{A_1}(t + t_0) \tag{5.2-9}$$

where $A_1 = 1/k$ and x_0 is a "virtual origin correction" which accounts for the initial production dominated region near the source. This equation should be viewed as a reasonable first estimate for $t_d(x_1, y_2, y_3)$ for a relatively "slender" plume. The success of this approximation for a given range of downwind distances will rely heavily on the proper choice of A_1; unfortunately, the uncertainty involved in this choice is large, even for relatively ideal flow situations. Some further insight on this problem can be obtained by examining the transport equation for Φ (Launder, 1978). Indeed, for point sources the generation terms involving mean concentration field gradients will play a significant role in the overall Φ balance, especially in the vicinity of the source, thus resulting in higher dissipation rates and lower characteristic dissipation times in comparison with the quasi-isotropic cases to which most of the available information is relevant.

5.2.3 The Effects of Boundaries

The presence of a boundary parallel to the mean flow $\overline{u}$ (e.g. the ground in the case of atmospheric dispersion) affects the balance of σ_c^2 in two ways:

First, if this boundary does not interact chemically or otherwise with the plume species, it imposes a condition of zero transfer of plume material, which, in addition to increasing the mean concentration near the surface, affects the intensity of concentration fluctuations by controlling the production of σ_c^2. Since $\partial \langle c \rangle / \partial x_1$ is normally small compared to the lateral gradients, a decrease in $\partial \langle c \rangle / \partial y_3$ will reduce the production of fluctuations significantly, especially near the horizontal centerline of the plume where $\partial \langle c \rangle / \partial y_2$ will also be small.

Second, the boundary affects the flow field in such a way that advection and turbulent transfer terms are expected to be small near the surface. In this analysis it will be assumed that the mean velocity is uniform except for a very thin layer near the boundary. However the no-slip boundary condition near the surface results in high local mean shear and intensity of turbulence which rapidly distort and stretch plume filaments, thus increasing the surface area available for molecular diffusion which dissipates concentration fluctuations. Thus, in general the presence of production and dissipation processes accounts for different behavior of $\langle c \rangle$ and σ_c^2 near the surface. Wind tunnel studies suggest that very close to the ground there might be a well mixed layer, where dissipation practically reduces σ_c^2 to zero; however, available data do not extend close enough to the surface to show explicitly this effect (Wilson et al., 1982a).

Hence, $\partial \sigma_c^2 / \partial y_3$ is not expected to approach zero gradually at the surface. It is more appropriate to view the latter as an absorbing (possibly not perfectly) boundary with respect to σ_c^2 and thus

$$\sigma_c^2 \rightarrow 0 \quad \text{at } x_3 = y_3 + b_3 = 0 \tag{5.2-10}$$

5.2.4 The Effects of Source Size

The assumption of a point source is an extreme idealization that is actually incompatible with the process of relative diffusion, since the latter requires a nonzero initial separation of the diffusing fluid particles (see, e.g., Durbin, 1980). The degree to which concentration fluctuations are influenced by source conditions, such as source size (or initial separation) has been a subject of both theoretical analysis (Chatwin and Sullivan, 1979a; Durbin, 1980, 1982; Sawford, 1983), and experimental study (Fackrell and Robins, 1982a). The available experimental evidence for continuous plumes relates important source effects to meandering processes and shows that they persist for distances where bulk fluctuations are dominant; far downstream the variance tends to "forget" these effects. Theoretical considerations (Durbin, 1980; Sawford, 1983) show that the intensity of internal fine scale fluctuations tends to a constant value that in general must depend on the initial size of an instantaneous release. However, the available data on relative dispersion of continuous plumes are not adequate to provide reliable quantitative estimates of source size effects. In fact, far enough from the source, data on both the total and the fine scale variance, and for both elevated and ground level sources, show that under constant flow conditions the centerline intensity of fluctuations approaches a constant value that is (almost) independent of source size. In the present work, in order to retain simplicity, source effects will not be accounted for explicitly; the species source is assumed localized at a point and necessary corrections to this idealization are invoked a posteriori when the mathematical manipulations cannot accommodate the point source concept. The effects of the finite size of the actual source will have to be incorporated (either explicitly or implicitly) in a parameter of the model.

5.2.5 The Assumption of Self Similarity

Introducing the approximation of (5.2-9) and the transport closure schemes of (5.2-3), (5.2-6), equation (5.2-2) reduces to the following form for the steady state (in the (x_1, y_2, y_3) frame) point source plume in a mean flow field $\overline{u} = \langle u_1 \rangle$ along the $x_1 \equiv y_1$ direction:

$$\overbrace{\overline{u}\frac{\partial \sigma_c^2}{\partial x_1}}^{\text{(i)}} = \overbrace{2K_{R_2}(x_1)\left[\left(\frac{\partial \langle c \rangle}{\partial x_1}\right)^2 + \left(\frac{\partial \langle c \rangle}{\partial y_2}\right)^2\right] + 2K_{R_3}(x_1)\left(\frac{\partial \langle c \rangle}{\partial y_3}\right)^2} ^{\text{(ii)}} +$$

$$+ \overbrace{K_{R_2}(x_1)\frac{\partial^2 \sigma_c^2}{\partial y_2^2} + K_{R_3}(x_1)\frac{\partial^2 \sigma_c^2}{\partial y_3^2}}^{\text{(iii)}} - \overbrace{\frac{\sigma_c^2}{t_d(x_1)}}^{\text{(iv)}} \qquad (5.2-11)$$

where terms (i) to (iv) represent the respective terms of (5.2-2).

A rational approach towards the simplification of (5.2-11) is based on the hypothesis of self-similarity for both the instantaneous $\langle c \rangle$ and σ_c^2 fields. As already mentioned, this hypothesis has considerable experimental support (Csanady, 1973; Fackrell and Robins, 1982a); it was first introduced as an approximation in the Eulerian modeling of σ_c^2 by Csanady (1967) who studied the construction of self-similarity models for isotropic turbulence and for an unbounded flow.

If (5.2-11) is satisfied by $\langle c \rangle$ and σ_c^2 that obey the self similar relations

$$\langle c \rangle = \langle c_0(x_1) \rangle \, f(\hat{r}) \ , \ \sigma_c^2 = \langle c_0(x_1) \rangle^2 g(\hat{r}) \qquad (5.2-12)$$

where

$$\langle c_0(x_1) \rangle = \frac{S}{2\pi \overline{u} \sigma_{R_2} \sigma_{R_3}}, \quad f(\hat{r}) = \exp\left(-\frac{\hat{r}^2}{2}\right)$$

(S is the source strength) and

$$\hat{r} = \check{r}/\check{s}$$

with

$$\check{r} = \sqrt{y_2^2 \sigma_{R_3}^2 + y_3^2 \sigma_{R_2}^2}, \quad \check{s} = \sigma_{R_2} \sigma_{R_3}$$

(notice that $\check{r}$,$\check{s}$ have units of (length)^2), then it can be shown that two necessary conditions for (5.2-11) to have self-similar solutions are

$$\frac{d\sigma_{R_3}}{d\sigma_{R_2}} = \frac{\sigma_{R_3}}{\sigma_{R_2}} \text{ or } \sigma_{R_3} = \kappa \sigma_{R_2} \qquad (5.2-13)$$

and

$$\frac{\sigma_{R_2} \sigma_{R_3}}{\overline{u} t_d} = \hat{\alpha} \left(\frac{\sigma_{R_2}^3 y_3^2}{\check{r}^2} \frac{d\sigma_{R_3}}{dx_1} + \frac{\sigma_{R_3}^3 y_2^2}{\check{r}^2} \frac{d\sigma_{R_2}}{dx_1} \right) \qquad (5.2-14)$$

where κ and $\hat{\alpha}$ are constants.

Here we will in general assume that the increase of σ_{R_2} and σ_{R_3} with distance from the source obeys *locally* the same exponential law within a multiplicative factor. (This exponential law will be different in the various phases of relative dispersion.) Regarding atmospheric dispersion, experience shows the above assumption to be usually a reasonable approximation.

Now, for $\sigma_{R_2} = \kappa \sigma_{R_3}$ one has

$$\hat{\alpha} = \frac{\sigma_{R_2}}{\left(\dfrac{d\sigma_{R_2}}{dx_1} \right)} \frac{1}{\overline{u} t_d}$$

If σ_{R_2} obeys the power law

$$\sigma_{R_2} = \sigma_{0_2} x_1^p$$

σ_{0_2} being a constant of appropriate dimensions, then

$$\hat{\alpha} = \frac{x_1}{p} \frac{1}{\overline{u} t_d}$$

and, employing (5.2-9),

$$\hat{\alpha} = \frac{A_1}{p} \frac{x_1}{x_1 + x_0}$$

Thus, if A_1 and p are constants over a finite range of x_1, the necessary condition for self-similar solutions of (5.2-11) becomes $x_0 = 0$, in which case $\hat{\alpha} = A_1/p$. Hence, the theoretical and empirical information that is available for p and A_1 can be used to provide first estimates for $\hat{\alpha}$.

When equations (5.2-13) and (5.2-14) hold then (5.2-11) becomes

$$\frac{d^2 g}{d\hat{r}^2} + \left(\frac{1}{\hat{r}} + \hat{r}\right) \frac{dg}{d\hat{r}} + (4 - \hat{\alpha})\, g = -2\left(\frac{df}{d\hat{r}}\right)^2 \qquad (5.2-15)$$

The boundary conditions for (5.2-11) arise from requirements of axial symmetry and a decay of σ_c^2 to zero at large radial distances:

$$\frac{dg}{d\hat{r}} = 0 \text{ at } \hat{r} = 0 \quad , \quad g \longrightarrow 0 \text{ at } \hat{r} \longrightarrow \infty \qquad (5.2-16)$$

We must remark here that boundary effects, which would complicate not only the formulation of boundary conditions but also the appropriate choice for $\hat{r}$, are not considered in the above analysis. Therefore this approach is formally valid for unbounded domains. Furthermore, for an elevated source, the existence of ground effects imposes an "external" length scale on the dispersion process. This "destroys" the conditions necessary for self similar characteristics of the physical problem, at least until far downwind where the source height becomes negligible compared to the distance traveled and a second range of self similarity is expected. Hence, the present self-similar model formulation will be a reasonable approximation only as long as boundary effects are not very significant, i.e. relatively close to the source.

The general solution of (5.2-15) can be shown to be

$$g(\hat{r}) \equiv g_*(\eta) = g_1(\eta) \int \frac{f_*(\eta) g_2(\eta)}{W(\eta)} d\eta - g_2(\eta) \int \frac{f_*(\eta) g_1(\eta)}{W(\eta)} d\eta \qquad (5.2-17)$$

where $\eta = -(\hat{r}^2/2)$, $f_*(\eta) \equiv f(\hat{r})$, and

$$g_1(\eta) = {}_1F_1(\hat{a}, 1; \eta) \equiv \sum_{k=0}^{\infty} \frac{\Gamma(\hat{a}+k)}{\Gamma(\hat{a})\Gamma(1+k)} \frac{\eta^k}{k!} \qquad (5.2-18a)$$

$$g_2(\eta) = {}_1F_2(\hat{a}, 1; \eta) \equiv -\frac{1}{\Gamma(\hat{a})} \sum_{k=0}^{\infty} \frac{\Gamma(\hat{a}+k)}{\Gamma(\hat{a})\Gamma(1+k)} \frac{\eta^k}{k!} \left[\psi(\hat{a}+k) - 2\psi(1+k) + \ln \eta\right] \qquad (5.2-18b)$$

$$\psi(x) \equiv \frac{\Gamma'(x)}{\Gamma(x)}$$

$$W(\eta) = W\left[{}_1F_1(\hat{a}, 1; \eta), {}_1F_2(\hat{a}, 1; \eta)\right] = -\frac{\exp(\eta)}{\eta \Gamma(\hat{a})} \qquad (5.2-18c)$$

and

$$\hat{a} = \frac{(4-\hat{\alpha})}{2}$$

${}_1F_1(\hat{a}, 1; \eta)$, ${}_1F_2(\hat{a}, 1; \eta)$ are confluent hypergeometric functions of the first and second kind respectively (Abramowitz and Stegun, 1964; Lebedev, 1965) and are linearly independent. $W(\eta)$ is their Wronskian determinant and $\psi(x)$ is the logarithmic derivative of the Gamma function. The constants of the integrations in (5.2-17) have to be calculated so as to satisfy the conditions of (5.2-16).

Alternatively, the boundary value problem defined by (5.2-15,16) can be solved numerically for specific values of $\hat{\alpha}$. Csanady (1967, 1973) pursued this approach for the isotropic case assuming Gaussian $f(\hat{r})$, and presented typical $g(\hat{r})$ profiles together with the relative intensity of stream segregation $I_s \equiv \sigma_c^2/\langle c\rangle^2 = g\langle c_0\rangle^2/\langle c\rangle^2$. These calculations show that while the variance σ_c^2 (which is proportional to $g(\hat{r})$) decreases from the center of the plume to the fringes, by analogy to the mean concentration, the relative intensity of segregation – describing the degree of micromixing of the plume with the ambient – increases at the fringes. Near the plume centerline both quantities have very small gradients and thus can be considered approximately constant in a "core region". For different values of $\hat{\alpha}$ different profiles of $g(\hat{r})$ are obtained. The center value $g(0)$ is a rapidly varying function of $\hat{\alpha}$. For $\hat{\alpha} > 4$ the origin becomes a saddle point (because $d^2g/d\hat{r}^2$ turns positive) and a full section across the plume will show a double-peaked profile for σ_c^2, a situation which is experimentally observed in free jets (Fischer et al., 1979; List, 1982). The physical reason is that the maximum rate of production occurs in the region of steepest gradients (around $\hat{r} = 1$) from where σ_c^2 diffuses both inwards and outwards. High diffusion and low dissipation (i.e., a low value of $\hat{\alpha}$) quickly smoothes the two peaks out resulting in a single peak at $\hat{r} = 0$. The problem in the development of self-similar solutions relies to a very large extent on the proper estimation of $\hat{\alpha}$. Csanady (1973) compared his approach to the experimental observations of Becker et al. (1966) by fitting $g(0)$ to the data. With the value of $g(0)$ obtained in this way, calculated profiles simulated measurements to a satisfactory degree with corresponding values of $\hat{\alpha}$ in the range 2.5 to 3.0. These values clearly are in very good agreement with the estimate $\hat{\alpha} = A_1/p$; indeed, for the theoretical values $p = 0.5$ and $A_1 = 1.5$, one obtains $\hat{\alpha} = 3.0$.

In conclusion, direct application of the self-similarity concept to the σ_c^2 transport problem, although it offers an integral representation of the solution of (5.2-11), does not lead to results appropriate for routine calculations (e.g. in conjuction with the common Gaussian solutions for $\langle c \rangle$). Indeed, the uncertainty in the parameters involved in (5.2-17) and the restricted range of conditions to which it applies would not justify the computational burden involved in its use. However, the conditions associated with the existence of self-similarity that are derived here are useful for reducing the complexity of the mathematical description of the fluctuations problem. These conditions will be further used in the next section combined with a scheme that is more appropriate for routine use than equation (5.2-15).

5.3 THE LOCALIZED PRODUCTION OF FLUCTUATIONS MODEL

In the following we present a new model that fulfills the need for simplicity by providing closed form analytical expressions for $\sigma_c^2(x_1, y_2, y_3)$, using a limited number of parameters. This "Localized Production of Fluctuations (LPF) Model" is based on the knowledge on the nature of the terms of (5.2-11) and of its solutions, already discussed in the previous sections. Self-similarity of σ_c^2 profiles is not an a priori assumption in the development of this model; however, when assumed to hold, it simplifies further the structure of the final equations.

To avoid excessive notational complexity in this section we adopt a (x, y, z) coordinate system and drop the subscript R from the dispersion parameters; however it must be kept in mind that throughout the following discussion (x, y, z) are coordinates relative to the meandering plume centerline and K's, σ's, as well as $\langle c\rangle$ and σ_c^2, describe relative dispersion.

5.3.1 Model Formulation

The solutions of (5.2-11) can in general be expressed in terms of the Green's function G of the corresponding non-dissipative equation (containing only terms (i) and (iii)), through

$$\sigma_c^2(x,y,z) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^x G(x,y,z|x',y',z')\Pi_c(x',y',z')\times$$

$$\times \exp\left[-\frac{1}{\bar{u}}\int_{x'}^{x}\frac{dx''}{t_d(x'')}\right] dx'dy'dz' \qquad (5.3-1)$$

where $\Pi_c(x',y',z')$ is the spatial distribution of variance production, given by (5.2-5).

Since production of σ_c^2 is of important magnitude, relevant to the other processes contributing to the balance of σ_c^2, mainly in the immediate vicinity of the source (where boundary effects can be neglected), an estimate of Π_c formulated in terms of a mean concentration field $\langle c\rangle$ for an unbounded flow should be a satisfactory approximation. Considering for simplicity the isotropic case (*) with

$$K_{R_y}(x) = K_{R_z}(x) = K(x), \quad \sigma_{R_y}(x) = \sigma_{R_z}(x) = \sigma(x) = \sigma_0 x^p$$

one has

$$\Pi_c(x,r) = 2\,K(x)\left[\left(\frac{\partial\langle c\rangle}{\partial x}\right)^2 + \left(\frac{\partial\langle c\rangle}{\partial r}\right)^2\right] = \Pi_x + \Pi_r \qquad (5.3-2)$$

where

$$r = \sqrt{y^2+z^2}$$

$$\Pi_x = 2K(x)\left(\frac{\partial\langle c\rangle}{\partial x}\right)^2, \quad \Pi_r = 2K(x)\left(\frac{\partial\langle c\rangle}{\partial r}\right)^2$$

In general, studies of (5.2-11) have implicitly neglected production of σ_c^2 due to gradients of $\langle c\rangle$ in the x–direction. In fact, *locally* (at a given point (x,r)) this term can be important; however, the *total* generation of fluctuations due to these gradients is small compared to the generation of gradients of $\langle c\rangle$ in the r–direction. Indeed, for Gaussian mean instantaneous concentration distributions in the meandering frame of reference:

$$\langle c(x,r)\rangle = \langle c_0(x)\rangle \exp\left(-\frac{r^2}{2\sigma^2}\right) = \frac{S}{2\pi\overline{u}\sigma^2(x)}\exp\left(-\frac{r^2}{2\sigma^2}\right)$$

the ratio

$$\frac{\Pi_r}{\Pi_x} = \frac{2x^2r^2}{p^2(r^2-2\sigma^2)^2}$$

is not necessarily much larger than unity for arbitrary (x,r).

Consider, however, the overall cross-wind fluctuations production at a given x from gradients of $\langle c\rangle$ in the r and x directions:

$$\Xi_r(x) = \int_0^\infty\int_0^{2\pi} r\Pi_r(x,r)\,d\phi dr = \frac{p}{x}\frac{S^2}{2\pi\overline{u}\sigma^2(x)} \qquad (5.3-3)$$

(*) These results are directly extendable to the anisotropic case by an appropriate transformation of coordinates.

$$\Xi_x(x) = \int_0^\infty \int_0^{2\pi} r\Pi_x(x,r)\, d\phi dr = \frac{2}{\exp 2}\sigma_0^2 p^3 x^{2p-3} \frac{S^2}{\pi \overline{u} \sigma^2(x)} \qquad (5.3-4)$$

Statistical diffusion theory for small travel times demands that $p = O(1.0)$ for both the processes of absolute and relative diffusion. Thus, in the vicinity of the source $\Xi_r(x)/\Xi_x(x) = O(1/\sigma_0^2)$, which typically is much larger than unity and therefore the production of fluctuations due to gradients of $\langle c \rangle$ in the x direction can be neglected. Thus, finally, for the overall cross-flow production of fluctuations

$$\Xi(x) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Pi(x,y,z)\, dydz$$

one can write $\Xi(x) \simeq \Xi_r(x)$ with $\Xi_r(x)$ given by (5.3-3).

The formulation of the LPF model consists of two steps. The first step utilizes the fact that at every cross-flow plane the production of fluctuations is strongly localized around its maximum value which is attained at $r = \sigma$. Figure 5-3 shows the dimensionless distribution of radial production of fluctuations, $1/4\, x\Pi_r(x,r)(\overline{u})^{-1} p^{-1} \langle c_0(x) \rangle^{-2}$, with respect to r/σ, for arbitrary x. It is reasonable therefore to approximate the distribution of production along a given radius by a delta function with strength estimated from (5.3-3). The optimal location of this delta function on each radius will be slightly off the value $r = \sigma$ since the production extends asymptotically to infinity; thus, for given ϕ, we fix this location at

$$r^* = \frac{\int_0^\infty r\Pi_r(x,r)\, rdr}{\int_0^\infty \Pi_r(x,r)\, rdr} = \Gamma\left(\frac{5}{2}\right)\sigma = \frac{3}{4}\sqrt{\pi}\sigma \qquad (5.3-5)$$

i.e. at the "center of mass" of the actual production distribution. The complete locus of these delta functions at any x will be a ring of radius r^*.

Thus (for the isotropic case)

$$\Pi_c(x,r) = \Xi_r(x)\, \delta(r - r^*\, ,\, \phi - \phi_s) \;\; \text{with } r^* = \frac{3}{4}\sqrt{\pi}\sigma \qquad (5.3-6)$$

where ϕ_s arbitrary in the interval 0 to 2π.

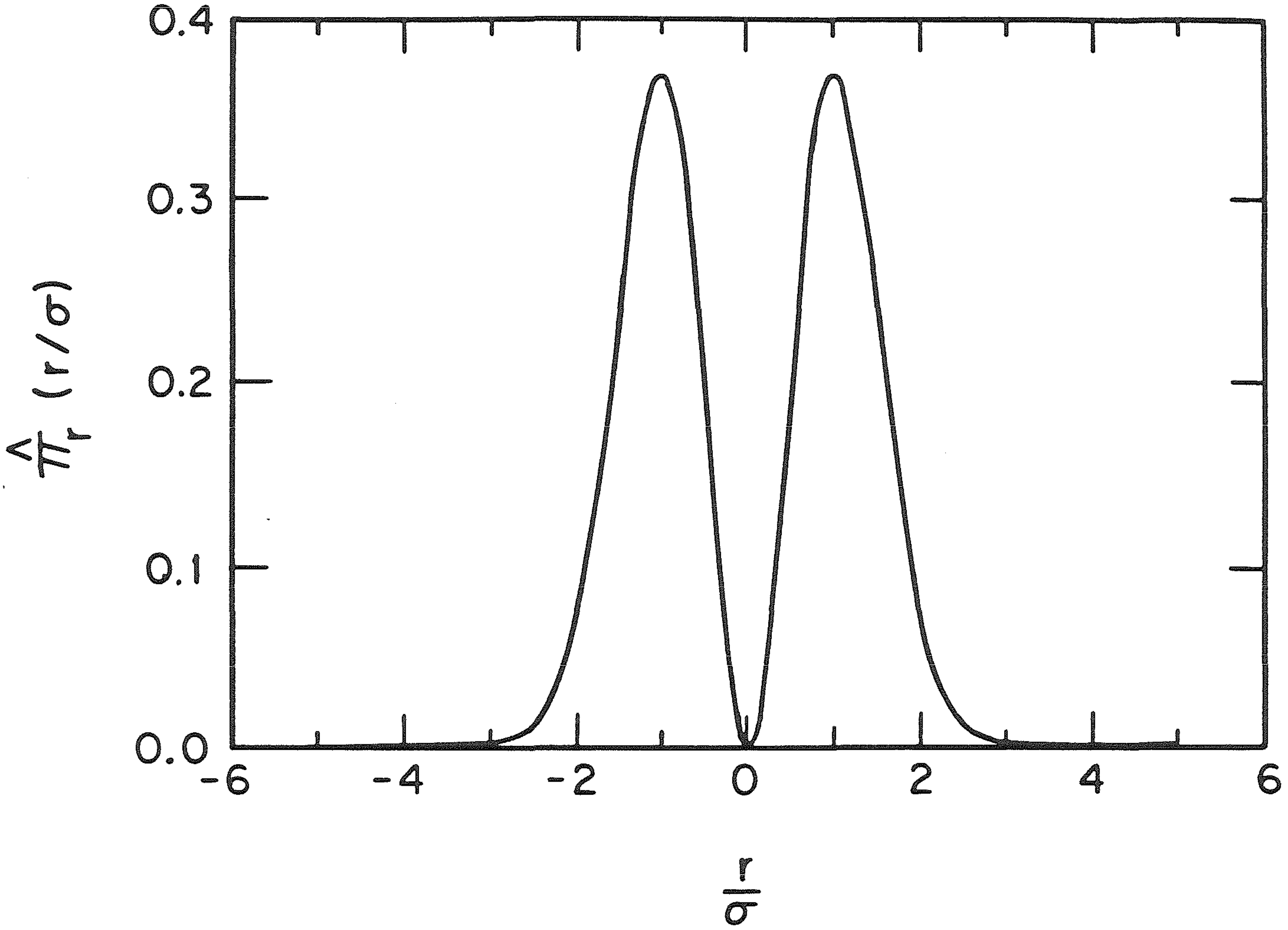

Figure 5-3

Dimensionless Radial Distribution of Fluctuation Production

at any Cross-Flow Plane

$(\hat{\Pi}_r(r/\sigma) = (1/4)x\Pi_r(x, r/\sigma)(\overline{u})^{-1})$

This Π_c can be introduced in (5.3-1). However, (because of the nature of the Gaussian solution of $\langle c \rangle$) production of fluctuations is infinite at $x = 0$ and the integral would diverge. Of course, this is just an artifact created from the assumed ideal "point" character of the source producing the theoretical Gaussian solution that creates a singularity at the origin. Since in reality the maximum field concentration is not infinite, it is justifiable to start the integration not at $x = 0$ but at some point $\hat{x}_0$. To apply (5.3-1), one should actually have to estimate $\hat{x}_0$ from available data so that it simulates measurements in a satisfactory manner. However, no general a priori estimate of it should be expected since it encompasses a variety of source and initial flow characteristics, specific to each particular application. Another major problem that inhibits direct integration of (5.3-1) is the changing character of the relative dispersion process with downwind distance. Thus, fundamental two-particle dispersion theory predicts three asymptotic values for the exponent p and even if one hypothesizes step changes and constant values in between there is significant uncertainty regarding the location of these changes; similar uncertainties are associated with the σ_0's. We circumvent these problems by introducing the second step in the formulation of the LPF model. Applying the mean value theorem of Lagrange to the isotropic form of (5.3-1) for the integration with respect to x, one has

$$\sigma_c^2(x,y,z) = \hat{\Xi}(\xi,x) \int_0^{\infty} \int_0^{2\pi} \frac{1}{r'} \delta(r' - r^*) \delta(\phi' - \phi_s) G(x,r,\phi|\xi,r',\phi')\, r' d\phi' dr'$$

$$\times \exp\left[-\frac{1}{\overline{u}} \int_{\xi}^{x} \frac{dx_1}{t_d(x_1)} \right] \qquad (5.3-7)$$

with

$$\hat{\Xi}(\xi,x) = \frac{S^2}{4\pi\overline{u}\sigma_0^2} 2p\xi^{-2p-1}(x - \hat{x}_0) \qquad (5.3-8a)$$

where ξ is some point between $\hat{x}_0$ and x (fixed for given $\hat{x}_0$,x). Setting $\xi = \omega x$, with $0 < \omega \leq 1$, and assuming that $x \gg \hat{x}_0$ one can further write

$$\hat{\Xi}(x) = \frac{pS^2}{2\pi\overline{u}\sigma_0^2 \xi^{2p}} \frac{x}{\xi} = \frac{\omega p S^2}{2\pi\overline{u}\,\sigma^2(\omega x)} \qquad (5.3-8b)$$

So, the problem of estimating $\hat{x}_0$, or, more generally, integrating (5.3-1), is essentially transferred to the problem of choosing the appropriate value (between 0 and 1) of the dimensionless *localization parameter* ω (that can possibly vary, within these limits, with distance x). Now, (5.3-7) associates σ_c^2 at x to the dispersion parameters corresponding only to x and to another single ωx. In this way all the different kinds of uncertainty implicit in (5.3-1) are now collectively lumped in one parameter, i.e. in the unknown value of ω.

5.3.2 Analytical Solutions

Equation (5.3-1) can now be used, through its reduced form (5.3-7), to obtain approximate closed solutions to the variance transport (5.2-11).

For an unbounded flow (and $\sigma_c^2 \to 0$ as $y, z \to \infty$) the corresponding Green's function of (5.2-11) (without terms (iv) and (ii)), is

$$G(x,y,z|x',y',z') = G(x-x', y-y', z-z') =$$

$$\frac{1}{2\pi\,\sigma_y(x-x')\,\sigma_z(x-x')\,\overline{u}} \exp\left[-\frac{(y-y')^2}{2\sigma_y^2(x-x')} - \frac{(z-z')^2}{2\sigma_z^2(x-x')}\right] \qquad (5.3-9)$$

when dispersion is assumed negligible compared to advection in the x direction and the σ's are related to the K's through (5.2-4).

Using (5.2-9) one obtains

$$\int_{x'}^{x} \frac{dx''}{t_d(x'')} = A_1\overline{u}\left[\ln(x+x_0) - \ln(x'+x_0)\right]$$

and

$$\exp\left[-\frac{1}{\overline{u}}\int_{x'}^{x}\frac{dx''}{t_d(x'')}\right] = \left(\frac{x'+x_0}{x+x_0}\right)^{A_1} \qquad (5.3-10)$$

Consider the general anisotropic (orthotropic) case, where the source of fluctuations takes the form of an elliptical ring (of infinitesimal thickness) located at $x = \xi$ with semiaxes a, b such that

$$a = 3/4\sqrt{\pi}\sigma_y(\xi), \quad b = \kappa a$$

where $\kappa = \sigma_z(\xi)/\sigma_y(\xi)$. We define

$$w^2 \equiv ab \ \text{and} \sigma^2(x) = \sigma_y(x)\,\sigma_z(x)$$

and introduce the new variables

$$y_1 = \kappa^{1/2} y \ \text{and} z_1 = \kappa^{-1/2} z$$

The transformation $(y, z) \mapsto (y_1, z_1)$ has a Jacobian equal to unity and therefore preserves areas. The phenomenal variance source coordinates will transform to

$$y_{1s} = w\cos\phi_s\ , \quad z_{1s} = w\sin\phi_s$$

where ϕ_s is now the polar angle of point (y_{1s}, z_{1s}) in the new coodinate system. The Cartesian form of (5.3-7) in this system will be

$$\sigma_c^2 = \frac{\hat{S}(\xi)}{2\pi\overline{u}\sigma^2(x-\xi)}\left(\frac{\xi + x_0}{x + x_0}\right)^{A_1}$$

$$\times \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp\left[-\frac{(y_1 - y_1')^2 + (z_1 - z_1')^2}{2\sigma^2(x-\xi)}\right]\delta(y_1' - y_{1s})\,\delta(z_1' - z_{1s})\,dy_1' dz_1'$$

where

$$\hat{S}(\xi) = \frac{pS^2}{2\omega\pi\overline{u}\sigma_y(\xi)\,\sigma_z(\xi)}$$

Introducing polar coordinates

$$r_1 = \sqrt{y_1^2 + z_1^2}, \quad y_1 = r_1\cos\phi, \quad z_1 = r_1\sin\phi$$

the integral in the above relation becomes

$$\int_0^{\infty}\int_0^{2\pi} \frac{1}{r_1'}\delta(r_1' - w)\,\delta(\phi' - \phi_s)\exp\left(-\frac{R^2}{2\sigma^2(x-\xi)}\right) r_1'\,d\phi' dr_1'$$

where

$$R^2 = (y_1 - y_1')^2 + (z_1 - z_1')^2 = r_1^2 + {r_1'}^2 - 2r_1 r_1'\cos(\phi - \phi')$$

Thus,

$$\sigma_c^2 = \frac{\hat{S}(\xi)}{2\pi\overline{u}\sigma^2(x-\xi)}\left(\frac{\xi + x_0}{x + x_0}\right)^{A_1} \exp\left(-\frac{r_1^2 + w^2}{2\sigma^2(x-\xi)}\right) \times$$

$$\int_0^{2\pi} \exp\left[\frac{r_1 w \cos(\phi' - \phi_s)}{2\sigma^2(x-\xi)}\right] d\phi'$$

which finally gives

$$\sigma_c^2 = \frac{\hat{S}(\xi)}{2\pi\overline{u}\sigma^2(x-\xi)}\left(\frac{\xi + x_0}{x + x_0}\right)^{A_1} \exp\left(-\frac{r_1^2 + w^2}{2\sigma^2(x-\xi)}\right) I_0\left(\frac{r_1 w}{\sigma^2(x-\xi)}\right) \qquad (5.3-11)$$

where $I_0(\cdot)$ is the modified Bessel function of order zero.

For $x, \xi \gg x_0$ (5.3-11) becomes

$$\sigma_c^2(x, r_1; \xi) = \left(\frac{S}{2\pi\overline{u}}\right)^2 \frac{p\,\omega(x)^{A_1-1}}{\sigma^2(\xi)\,\sigma^2(x-\xi)} \exp\left(-\frac{r_1^2 + w^2}{2\sigma^2(x-\xi)}\right) I_0\left(\frac{r_1 w}{\sigma^2(x-\xi)}\right) \qquad (5.3-12)$$

Now, a sufficient condition for self similarity of the σ_c^2 profiles for a given x–range (where p, A_1 are assumed constant) is that ω is a constant in this range. In this case

$$\sigma(\xi) = \omega^p \sigma(x), \quad \sigma(x-\xi) = (1-\omega)^p \sigma(x), \quad w = 3/4\sqrt{\pi}\omega^p \sigma(x)$$

and σ_c^2 becomes

$$\sigma_c^2 = \langle c_0(x)\rangle^2 g\left(\frac{r_1}{\sigma(x)}\right) = \langle c_0(x)\rangle^2 g(0) \exp\left(\frac{-1}{2\overline{\omega}^{2p}}\frac{r_1^2}{\sigma^2}\right) I_0\left(\frac{3\sqrt{\pi}\omega^p}{4\overline{\omega}^{2p}}\frac{r_1}{\sigma}\right) \qquad (5.3-13)$$

where $\overline{\omega} = 1 - \omega$ and $g(\cdot) = I_s\langle c\rangle^2/\langle c_0\rangle^2$ is the dimensionless absolute intensity of internal fluctuations. On the plume centerline $g(0)$ will be

$$g(0) = \frac{p\omega^{A_1-2p-1}}{(\overline{\omega})^{2p}} \exp\left(-\frac{9\pi\omega^{2p}}{32\overline{\omega}^{2p}}\right) \qquad (5.3-14)$$

When experimental information for this quantity is available it can be used in conjunction with information on parameters p and A_1 to estimate ω values (see next section).

Returning to the y,z coodinates, (5.3-12) takes the form

$$\sigma_c^2(x,y,z;\xi) = \left(\frac{S}{2\pi\overline{u}}\right)^2 \frac{p\,\omega(x)^{A_1-1}}{\sigma_y(\xi)\,\sigma_z(\xi)\,\sigma_y(x-\xi)\,\sigma_z(x-\xi)} \exp\left(-\frac{y^2}{2\sigma_y^2(x-\xi)}\right) \exp\left(-\frac{z^2}{2\sigma_z^2(x-\xi)}\right) \times$$

$$\times \exp\left(-\frac{ab}{2\sigma_y(x-\xi)\,\sigma_z(x-\xi)}\right) I_0\left(\frac{\sqrt{a^2z^2+b^2y^2}}{\sigma_y(x-\xi)\,\sigma_z(x-\xi)}\right) \qquad (5.3-15)$$

Equations (5.3-13) and (5.3-15) constitute basic, usable, forms of the LPF model when boundary effects can be assumed negligible, as in the immediate vicinity of the source.

When the dispersion field cannot be assumed unbounded, one must take into account the boundary condition of (5.2-10), i.e.

$$\sigma_c^2 \to 0 \quad \text{at} \quad z(=y_3) = -b_3$$

where, because of meandering effects b_3 is a random variable. Far downstream, where meandering is negligible and boundary effects most significant, one can obtain the following result, assuming that the plume centerline is at a constant height h from the boundary (notice that now the coordinates origin is fixed on the boundary):

$$\sigma_c^2(x,y,z;\xi) = \left(\frac{S}{2\pi\overline{u}}\right)^2 \frac{p\,\omega(x)^{A_1-1}}{\sigma_y(\xi)\,\sigma_z(\xi)\,\sigma_y(x-\xi)\,\sigma_z(x-\xi)} \exp\left(-\frac{y^2}{2\sigma_y^2(x-\xi)}\right) \times$$

$$\times \exp\left(-\frac{ab}{2\sigma_y(x-\xi)\,\sigma_z(x-\xi)}\right) \left[\exp\left(-\frac{(z-h)^2}{2\sigma_z^2(x-\xi)}\right) I_0\left(\frac{\sqrt{a^2(z-h)^2+b^2y^2}}{\sigma_y(x-\xi)\,\sigma_z(x-\xi)}\right)\right.$$

$$\left. -\alpha \exp\left(-\frac{(z+h)^2}{2\sigma_z^2(x-\xi)}\right) I_0\left(\frac{\sqrt{a^2(z+h)^2+b^2y^2}}{\sigma_y(x-\xi)\,\sigma_z(x-\xi)}\right)\right] \qquad (5.3-16)$$

The parameter α appearing in the above equation equals unity for a "perfectly absorbing" boundary i.e., σ_c^2 actually equal to 0 at the surface. However, the effects of dissipation might not be so strong, and a lower value for α may be more appropriate.

5.4 MODEL TESTING AND DISCUSSION

The LPF model is a simple formulation for the internal concentration variance that is directly derived from the physics of the point release problem, starting from "rigorous" equations and utilizing empirical information and approximations to simplify the analysis. The required inputs reduce to a set of "physical" parameters and a "model specific" one. The "physical" parameters are the relative dispersion σ's (which are assumed to obey simple power laws, at least locally) and a factor relating dispersion time to the local dissipation time scale t_d. The "model specific" or "localization" parameter ω actually defines the location of an effective source of fluctuations.. As already mentioned, uncertainties associated with a variety of factors such as source size, flow conditions, and the relative dispersion process itself, are "lumped" into ω. Introduction of ω reduces the uncertainty associated with the physical parameters since, instead of their complete – and unknown – variation with downstream distance, only estimates of their local values are needed.

The problem of estimating ω is facilitated by two facts: (1), the often observed validity of self similarity, which is expressed by (5.2-12); (2), the observation that $g(0)$ is "at most a weak function of the distance from the source" – even for the total fluctations variance (Sawford et al., 1985). This $g(0)$ for given flow conditions tends to a constant value after a certain distance (Becker et al., 1966; Fackrell and Robins, 1982ab; Wilson et al., 1982ab, etc). These facts, although deduced from observations that do not cover the entire range of possible conditions encountered in laboratory and environmental flows, suggest that adequately reliable estimates of ω are possible, at least for specified ranges of the dispersion, even without a complete understanding and analysis of all the mechanisms that affect the level of $g(0)$. It is therefore often justified to treat $g(0)$ as an empirical constant typical of given flow conditions. In this simplified approach ω is completely determined from the physical parameters (including $g(0)$) of the problem. Of course in order to be able to construct empirical estimates of, say, typical values of $g(0)$ (and therefore ω) for ambient turbulence of various Reynolds numbers, many more experimental data bases than they are currently available are needed. In a more fundamental approach $g(0)$ or closely related functions have been modeled theoretically, in terms of statistical correlations of the turbulent flow field, for source configurations that create mean concentration fields approximately equivalent to that of the continuous "point" source. Numerical simulations and analytical expressions that in general involve a measure of effective source size are available (Durbin, 1980, 1982; Sawford, 1983). However, because of the existing uncertainties and limitations in the formulation of the theoretical models, it presently seems reasonable to confine this discussion to the previously mentioned simplified approach.

As far as atmospheric dispersion is concerned, present knowledge suggests that for neutral stability the far field value of $g(0)$ is of order unity (for elevated sources), and use of the typical ("theoretical") values $p = 0.5$ (for the "far field"), $A_1 = 1.5$ to 2.5 seems to offer a qualitatively acceptable simulation of many available relevant field and wind tunnel data sets. (For example, see Figure 5-6). However the scatter, the resolution and the uncertainty of these data often make quantitative comparisons meaningless or impossible. The problems are even more severe in cases of more complicated atmospheric conditions.

The measurements most appropriate for comparing with and testing LPF model calculations are those of Becker et al. (1966) for point source dispersion in homogenous, quasi–isotropic, pipe flow turbulence. Indeed, in the conditions of these experiments meandering was insignificant and the structure of the turbulent flow, being relevant to the conditions for which (5.2-8) was suggested, reduces the uncertainty regarding the proper choice of A_1; further, $p = 0.5$ fits accurately the entire range of the data. Thus, the uncertainty regarding the physical parameters is minimum. Self similarity of σ_c^2 profiles and a constant value of $g(0)$ are observed in all these experiments. Comparisons of LPF calculations with reported absolute and relative intensities of internal fluctuations are shown in Figures 5-4a, 5-4b, 5-4c and 5-5. The parameter ω is estimated directly (for $A_1 = 1.5$) from the centerline value $g(0)$, whose square root value, for all the flows studied, lies in the range 1.0 ± 0.2. The agreement obtained by using solely the centerline value to "adjust" ω, while p and A_1 are pre-set equal to their theoretical values, must be considered very satisfactory (Somewhat different values of A_1, can improve slightly the success of the simulation, especially near $r/\sigma = 0.75$ where the difference between predictions and observations seems higher).

A comparison with atmospheric field data is also shown in Figure 5-6. The data are of Ramsdell and Hinds (1971) and the typical values $p = 0.5$, $A_1 = 1.5$ were used while ω is determined directly by the centerline intensity. Although the uncertainty of the data is very significant the agreement can be considered satisfactory in this case too.

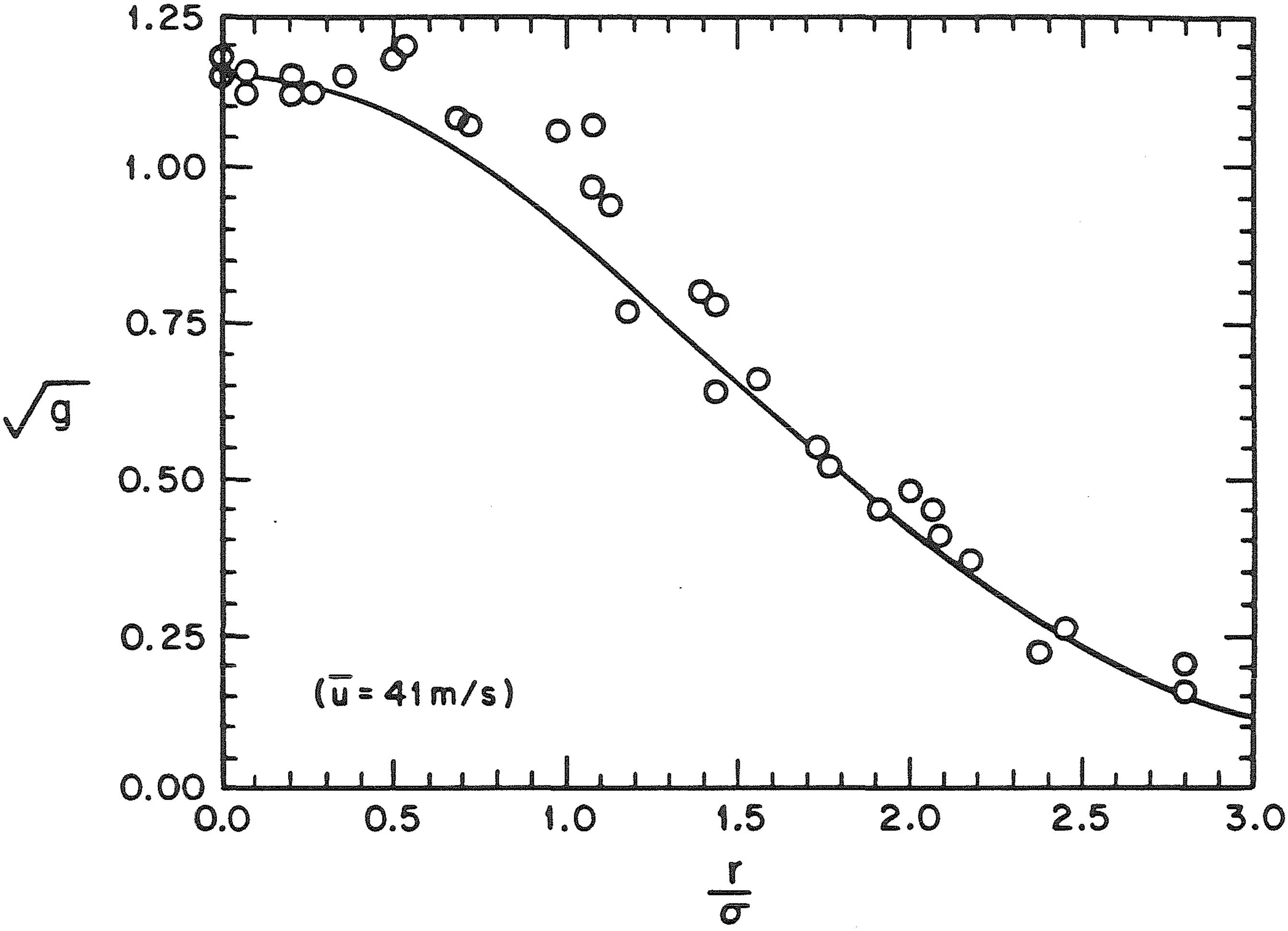

Figure 5-4a

Dimensionless Absolute Square Root Intensity of Segregation, $\sqrt{g(r/\sigma)}$ as Predicted by the LPF Model, Compared with Data from Becker et al., (1966) Data (at five downstream distances) for Centerline Velocity 41 m/s LPFM Calculations for $p = 0.5$, $A_1 = 1.50$ ($g(0) = 1.15$)

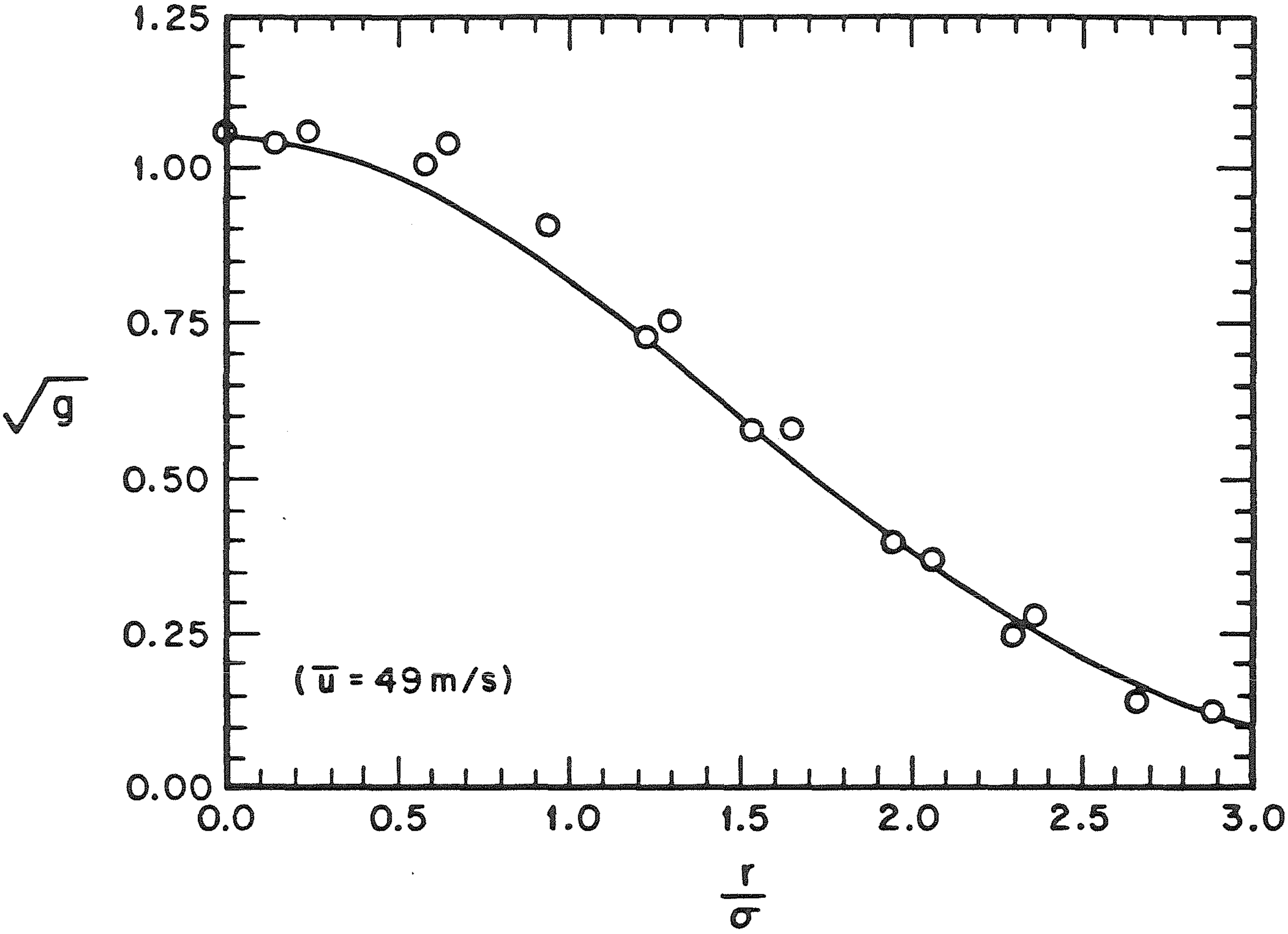

Figure 5-4b

Dimensionless Absolute Square Root Intensity of Segregation, $\sqrt{g(r/\sigma)}$
as Predicted by the LPF Model, Compared with Data from Becker et al., (1966)
Data (at two downstream distances) for Centerline Velocity 49 m/s
LPFM Calculations for $p = 0.5$, $A_1 = 1.50$ ($g(0) = 1.05$)

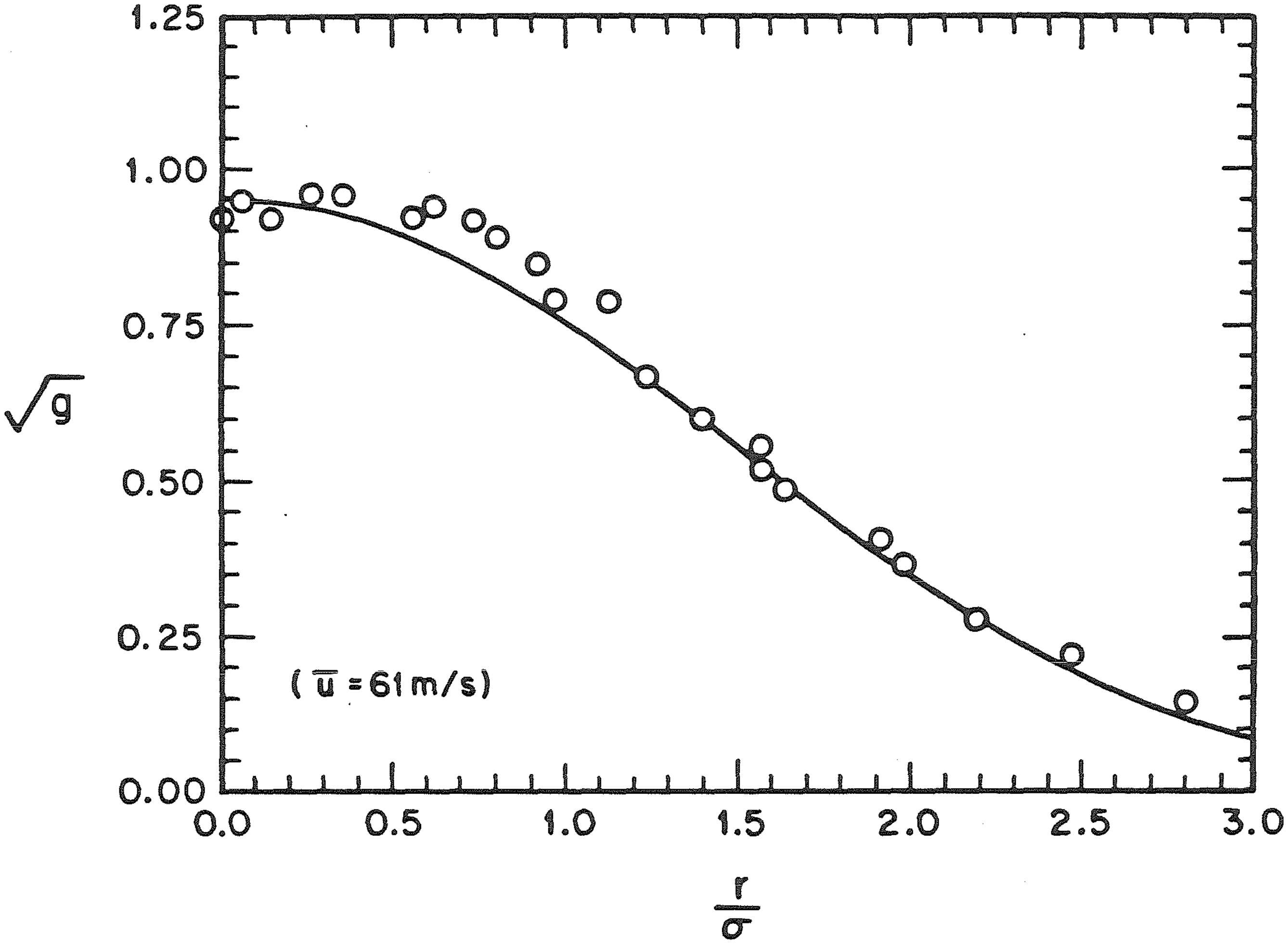

Figure 5-4c

Dimensionless Absolute Square Root Intensity of Segregation, $\sqrt{g(r/\sigma)}$
as Predicted by the LPF Model, Compared with Data from Becker et al., (1966)
Data (at four downstream distances) for Centerline Velocity 61 m/s
LPFM Calculations for $p = 0.5$, $A_1 = 1.50$ ($g(0) = 0.95$)

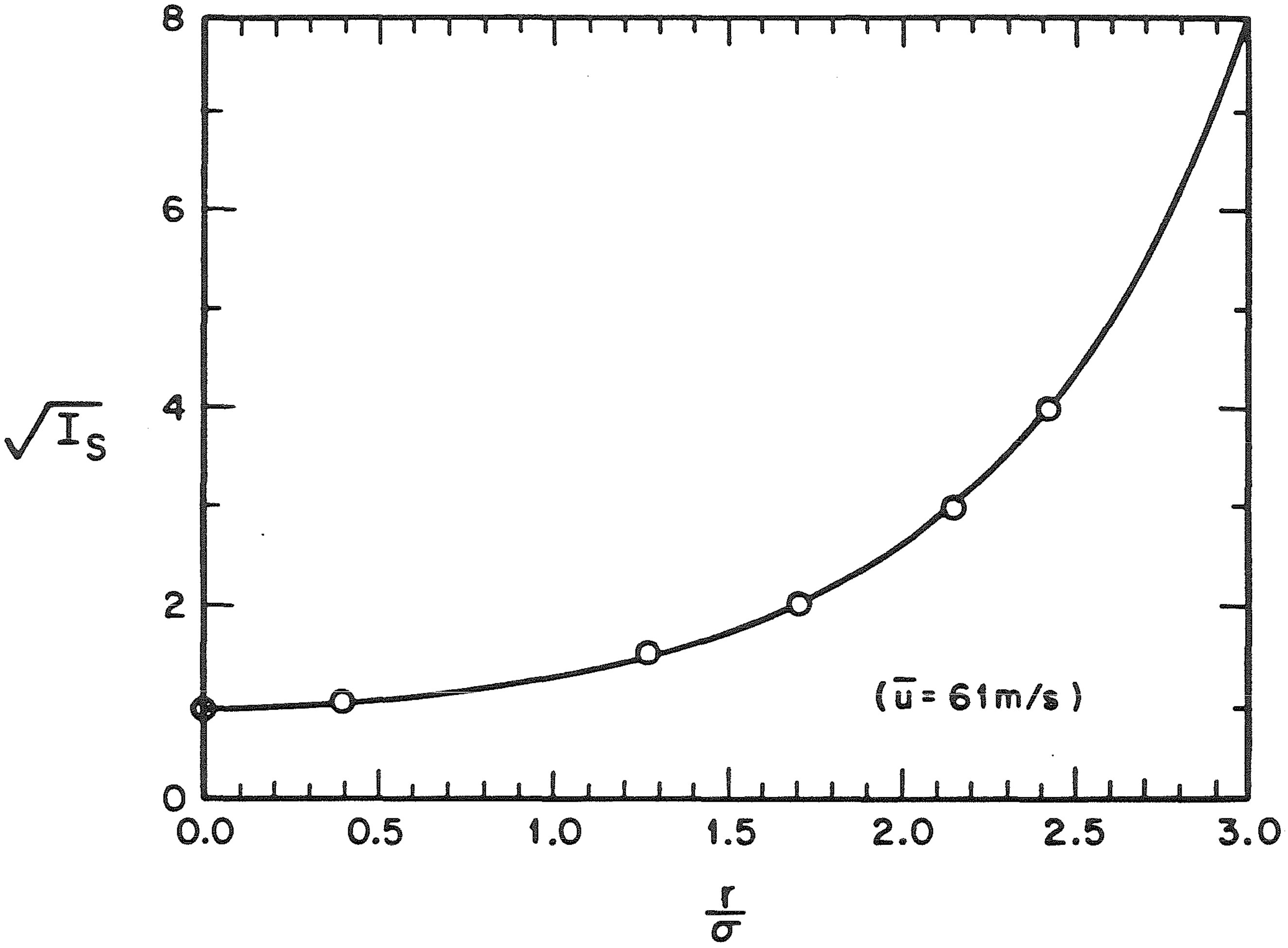

Figure 5-5

Dimensionless Square Root Relative Intensity of Segregation, $\sqrt{I_s}$ as Predicted by the LPF Model, Compared with Data from Becker et al., (1966) (The data were obtained at five downstream distances for centerline velocity 61 m/s and the points shown correspond to the experimental curve in Figure 7 of Becker et al. (1966) (note that in that figure $\sqrt{I_s}$ is plotted versus $r/r_{1/2}$); LPFM calculations for $p = 0.5$, $A_1 = 1.50$.)

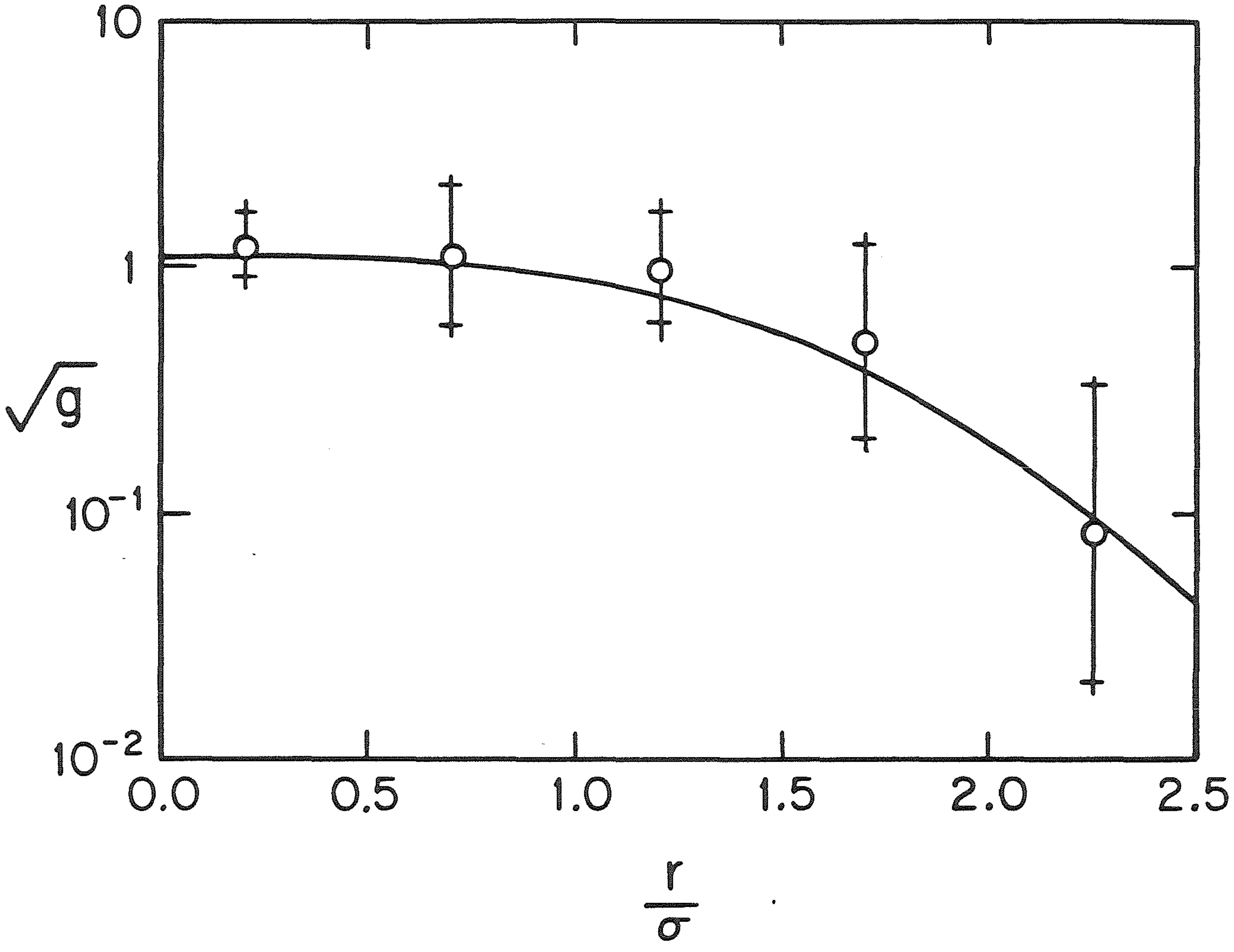

Figure 5-6

Dimensionless absolute intensity of segregation, $\sqrt{g(r/\sigma)}$

as Predicted by the LPF Model

Compared with Atmospheric Field data from Ramsdell and Hinds (1971)

(LPFM calculations for $p = 0.5$, $A_1 = 1.5$)

5.5 CONCLUSIONS

Knowledge of statistical properties of point-source plume concentrations, such as the variance σ_c^2 or the intensity of segregation, is essential in many situations calling for plume modeling (e.g. in assessing the impact of releases of pollutants in the environment), and in particular in estimating the effects of local turbulent mixing on relatively fast nonlinear chemistry. Although recent experimental and theoretical work has enhanced significantly the available information on the behavior of σ_c^2, this had not resulted in the development of practical predictive methods, especially with regard to fine scale in-plume fluctuations – as opposed to total observed fluctuations that encompass bulk motion effects (meandering) which do not interact with the chemical processes.

A new model for the "internal" σ_c^2, at a level of sophistication analogous to that of the Gaussian formulas for the mean concentration field, has been developed here, starting from the Eulerian transport equation for σ_c^2. A series of approximations utilizing existing experimental and theoretical information for the processes involved, combined with the Localized Production of Fluctuations (LPF) scheme allowed the construction of closed analytic expressions for σ_c^2, directly from its governing equation. The capability of this "LPF model" to simulate the variance profile was succesfully tested against available data on point source plume concentrations.

In conclusion, the model developed in this work provides a rational, yet computationally simple, means for describing concentration fluctuations and the corresponding intensity of segregation inside instantaneous plume boundaries. Although its applicability is restricted by assumptions such as the uniform mean flow (or "mild" mean plume motion), and slender plumes, this model can serve as a first approximation to a wide range of point source dispersion problems. Further experimental information will be useful to provide accurate estimates of its parameters for specific flows.

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APPENDIX A5.1

Concentration Probabilities: Summary of Basic Concepts and Definitions

The main volume of work relevant to air pollutant concentration statistical characteristics is concerned with defining concentration distributions and estimating extreme value statistics for use with air quality standards; in this perspective the air pollution system is typically viewed as a "black box" although in some approaches physical reasoning have been invoked to explain qualitatively the statistical results (see Chapter 8). The aforementioned work is directed primarily towards statistically describing long-time averages (usually 1 hr and upwards) of concentration. Thus it must be remembered that (empirical) results relevant to this work cannot be applied directly in the study of very short term ("instantaneous" up to a few minutes averages) fluctuations in a rapidly changing concentration field that results from an isolated source. In the following we summarize certain basic concepts related to the probabilistic properties of instantaneous concentration fields.

The (cumulative) probability distribution associated with the random concentration c at the fixed space–time point $(\mathbf{x}, t)$ of the flow field is defined as

$$F(C, \mathbf{x}, t) = Prob\,\{c(\mathbf{x}, t) \leq C\} \qquad (A5.1-1)$$

The moments of c are defined formally by the relations

$$E^n\{c\} \equiv \langle c^n\,(\mathbf{x}, t)\rangle = \int_{F=0}^{1} C^n\, dF(C, \mathbf{x}, t) \qquad (A5.1-2)$$

$$E^n\{c'\} \equiv \langle c'^n\,(\mathbf{x}, t)\rangle = \int_{F=0}^{1} (C - \langle c\rangle)^n\, dF(C, \mathbf{x}, t) \qquad (A5.1-3)$$

In particular we set $E^1\{c\} \equiv \langle c\rangle$, $E^2\{c'\} \equiv \sigma_c^2$.

In steady state cases, i.e. in continuous plumes (which are of interest in this work) the distribution (and of course moments of all orders) become independent of time.

The probability density function (pdf) $p(C, \mathbf{x}, t)$ of $c(\mathbf{x}, t)$ is defined as

$$p\,(C, \mathbf{x}, t) = \frac{dF\,(C, \mathbf{x}, t)}{dC} \qquad (A5.1-4)$$

for all C for which F is continuous. For certain C, F may not be continuous. In fact $c(\mathbf{x},t) = 0$ usually occurs with finite probability, at least for certain $(\mathbf{x},t)$, and thus arises a discontinuity of $F(C,\mathbf{x},t)$ at $C = 0$. (This is the only case of discontinuity of F that will concern us here.)

Various functional forms can be assigned to the distribution of the non-zero fraction of the ensemble of concentration values. In practice, such a distribution must be determined by appropriate statistical treatment of data at a fixed point. Experience has shown that skewed distributions such as the lognormal are usually a satisfactory choice for the non-zero fraction ("subensemble") of concentration values in atmospheric plumes. Semi-Gaussian or "clipped-Gaussian" (i.e. linear combinations of Gaussian functions, defined over bounded ranges of values, and Dirac deltas), exponential, and other types of distributions have been used to fit the entire range of concentration values, especially at points close to the average boundaries of the plume.

A variety of theoretical methods for determining p *a priori*, from physical principles, is available in the literature dor both conserved and reactive scalars (see, e.g., Hill, 1976; Pope, 1982, 1985). However most of these methods are either limited to highly idealized turbulent scalar fields and are formulated for very specific flows, or represent formulations so general that are of little practical use (see, e.g., O'Brien, 1980). Analogous formulations for the moments of c are in general much more tractable and these are pursued in Chapter 5.

An *intermittency factor* or *function* $\gamma_c(\mathbf{x},t)$ can be introduced, specifying the fraction of the ensemble in which the concentration is not zero (i.e the subensemble conditioned by $c \neq 0$):

$$1 - \gamma_c(\mathbf{x},t) = F(0,\mathbf{x},t) \qquad (A5.1-5)$$

The *complementary intermittency factor* ,defined through

$$\tilde{\gamma}_c = 1 - \gamma_c(\mathbf{x},t) = F(0,\mathbf{x},t) \qquad (A5.1-5a)$$

is also used by some authors.

We will not elaborate here on the subtle and important concept of intermitency in turbulent fields; for an illuminating discussion of both physical and mathematical aspects of this property one may consult the monograph of Mandelbrot (1983).

With the introduction of γ_c one can express the probability density function for all the members of the concentration ensemble as

$$p(C,\mathbf{x},t) = \gamma_c(\mathbf{x},t)\, p_*\,(C,\mathbf{x},t) + [1 - \gamma_c(\mathbf{x},t)]\,\delta(C) \qquad (A5.1-6)$$

where $p_*(C,\mathbf{x},t)$ is the "conditioned" pdf that describes the subensemble $\{c_*\}$ of nonzero concentrations and $\delta(C)$ is the Dirac delta.

$F(C,\mathbf{x},t)$ is a result of absolute diffusion; so is $\gamma_c(\mathbf{x},t)$. However, a "decomposition" of the results of relative diffusion and meandering is sometimes necessary in the study of the plume dispersion phenomenon, as it has already been discussed. To study relative diffusion effects one can consider a reference frame attached to the center of mass of a diffusing cloud (for an instantaneous release of material) or "following" through parallel translation the line defined by the infinite sequence of the centers of mass of "thin cross-wind slices" of a continuous plume (the centerline of the plume). An extensive discussion of the description of turbulent dispersion in this frame can be found in Chapter 6 of the present work.

Thus let $\mathbf{y}$ be the distance of a fluid particle from the origin of this meandering frame (for uniform wind $\mathbf{y} = (y_1, y_2, y_3)$ reduces to a two dimensional vector $\mathbf{y} = (x_1, y_2, y_3)$, with the origin taken at x_1, since it is always perpendicular to the wind vector). Let also $\mathbf{b}(t)$ be the position of the center of mass of the cross–section relative to which $\mathbf{y}$ is measured: $\mathbf{y} = \mathbf{x} - \mathbf{b}$. Then if

$$F_r(C,\mathbf{y},\mathbf{b},t) = Prob\,\{c(\mathbf{x},t) = c_r(\mathbf{y},\mathbf{b},t) \le C\} \qquad (A5.1-7)$$

moments of c_r, a pdf p_r, an intermittency function γ_{r_c} and a conditioned pdf p_{r_*} can be defined exactly as for the c–field.

The general functional form of p_{r_*} is expected to display the same typical characteristics as p_* (a skewed distribution) and experience shows that lognormal type distributions again offer successful fit (Csanady, 1973). However, γ_{r_c} is expected now to behave in a more predictable manner than γ_c because the effect of meandering has been removed and $F_r(C,\mathbf{y},\mathbf{b},t)$ characterizes the process of relative diffusion alone. Of course the spatial distribution of both γ_c and γ_{r_c} is in general unknown for most cases; however in a frame moving with the centerline of a continuous plume, $\gamma_{r_c}(\mathbf{y})$ is known to be near unity in the center portion of the plume and to be zero outside the plume, its distribution across the plume being probably like that of the intermittency of turbulent velocities across a jet (see Townsend, 1976; compare also with Eidsvik, 1980). In a fixed frame of reference $\gamma_c(\mathbf{x})$ can be as low as 0.65 even at the axis of the plume (Csanady, 1973) and much lower at the fringes, showing the pronounced effect of meandering (see also Fackrell and Robins, 1982; Jones, 1983). The fact that in a moving frame formulation the intermittency factor is likely to be near unity for much of the field is a certain advantage of this description. Indeed, when using a frame of reference attached to the centerline of the plume, $\gamma_{r_c} \simeq 1$ everywhere is an acceptable first approximation. In this way we assign all intermittency effects to meandering: they assumed "bulk intermittency" effects. Seeing this from an alternative viewpoint, we *define* the instantanous plume through the condition $\gamma_{r_c} = 1$.

Plume meandering is described by the spatial probability density function of the position of the center of mass:

$$P_k(\mathbf{x},t) = \text{Prob}\ \{\text{at time } t,\ \mathbf{b}(t) \text{ has its endpoint in the volume element } d\mathbf{x} \text{ surrounding } \mathbf{x}\}$$

$P_k(\mathbf{x},t)$ and $F_r(C,\mathbf{b},\mathbf{x}-\mathbf{b},t)$ are statistically independent in general and thus the following *convolution* relation connects F, F_r, and P_k:

$$F(C,\mathbf{x},t) = \int_{all\ \mathbf{b}} F_r(C,\mathbf{x},\mathbf{x}-\mathbf{b},t)P_k(\mathbf{b},t)\,d\mathbf{b} \qquad (A5.1-8)$$

As a consequence of this general relationship, we have a similar connection between pdf's (for continuous F_r's) and non–central moments of the ensembles $\{c\}$ and $\{c_r\}$:

$$\langle c^n(\mathbf{x},t)\rangle = \int_{all\ \mathbf{b}} \langle c_r^n(\mathbf{x},\mathbf{x}-\mathbf{b},t)\rangle\, P_k(\mathbf{b},t)\,d\mathbf{b} \qquad (A5.1-9)$$

As far as $P_k(\mathbf{x},t)$ is concerned, this pdf is typically approximated by the probability density function for a fluid particle's location at time t, in a turbulent field, $\overline{\psi}(\mathbf{x},t)$. (See Chapter 6). Thus $P_k(\mathbf{x},t)$ can be expressed as the product of:

- the pdf that the center of mass was at $\mathbf{x}'$ at t', $P_k(\mathbf{x}',t')$, integrated over all possible starting points $\mathbf{x}'$.
- the transition probability density for a fluid particle in the turbulent field under consideration $Q(\mathbf{x},t|\mathbf{x}',t')$ = Prob{if the particle is at $\mathbf{x}'$ at t' it will undergo a displacement to $\mathbf{x}$ at t}. (This probability will be introduced formally and discussed in more detail in Chapter 6 where it is denoted by G.)

$$P_k(\mathbf{x},t) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^t Q(\mathbf{x},t|\mathbf{x}',t')P_k(\mathbf{x}',t')\,d\mathbf{x}'\,dt'$$

Invoking initial conditions (at $t'=t_0=0$) for a *point source* located at $\mathbf{x}_0$ we have

$$P_k(\mathbf{x},t) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^t Q(\mathbf{x},t|\mathbf{x}',t')\delta(\mathbf{x}'-\mathbf{x}_0)\,d\mathbf{x}'\,dt'$$

and therefore

$$P_k(\mathbf{x},t) = \int_0^t Q(\mathbf{x},t|\mathbf{x}_0,t')\,dt'$$

The analytical form of the transition probability density $Q(\mathbf{x},t|\mathbf{x}',t')$ has been one of the main concerns of the Lagrangian methodology for describing turbulent diffusion and extensive discussions are presented elsewhere (see Chapter 6 and Monin and Yaglom, 1975). Gaussian type distributions are the typical choice for Q; such a choice is theoretically founded for stationary and homogeneous turbulence where, after a certain time has passed, can be deduced formally if the turbulent velocity fluctuations are assumed normally distributed (Seinfeld, 1983). In this case $P_k(\mathbf{x},t)=P_k(\mathbf{x})$ for a steady plume will also be a Gaussian distribution in $\mathbf{x}$. Then, relations (A5.1-8), (A5.1-9) define convolution transforms with Gaussian kernel; these are known as *Weierstrass transforms* (see, e.g., Zemanian, 1968).

Finally, we must note that equations (A5.1-8) and (A5.1-9) relating the statistics of the c and c_r fields should not be misinterpreted as providing relations connecting analogous statistical characteristics of the c and c_* fields. Although it is possible to identify the sets of c_r and c_* values by limiting appropriately the range of the spatial variable $\mathbf{y}$ for c_r, the information "carried" by each set is not equivalent. (See also Fackrell and Robins, 1982, their Section 5.2.) To obtain statistics of c from c_* (and vice versa), the spatial (and perhaps the temporal) dependence of γ_c is needed. Then it can be shown that from equation (A5.1-6) follows

$$\langle c \rangle = \gamma_c \langle c_* \rangle \qquad (A5.1-10)$$

and

$$\sigma_c^2 = \gamma_c \left\langle {c'_*}^2 \right\rangle + \gamma_c (1 - \gamma_c) \langle c_* \rangle^2 \qquad (A5.1-11)$$

References
for Appendix A5.1

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APPENDIX A5.2

Discussion of Earlier Work on Plume Concentation Fluctuations and the Empirical Model of Wilson et al. (1982ab)

Experimental measurements of short term fluctuation statistics in plumes under conditions met in cases of interest to air pollution (either in situ or in wind tunnels simulating the atmospheric boundary layer) are relatively limited. Most of these works have been reviewed by Csanady (1973) and Hanna (1984). Useful information of closely related nature can be found in the substantial fluid-mechanical literature about momentum jets and buoyant plumes (see e.g., the reviews of List, 1982, and Gebhard et al., 1984).

A brief chronological survey of results that are of direct interest to the present analysis follows:

An early investigation of concentration probability distributions was carried out by Gosline (1952) who measured "instantaneous" (10 s averages) ground level NO and NO_2 concentrations downwind of a 24 m tall chimney at distances of 5 to 10 chimney heights. His measurements showed the importance of intermittency effects (he noted that only 14 to 34% of the time there was a measurable concentration at the site chosen). Also the duration of each NO bearing eddy at a given site was between 30 and 90 s. The non-zero measurements were found to obey a log-normal distribution to a very good approximation.

Becker et al. (1966) studied plume dispersion and fluctuations in pipe flow. Their experiments show self-similarity of σ_c^2 profiles up to significant dispersion times. The specific characteristics of these profiles varied significantly with changing properties of the ambient turbulent flow. Self-similarity of fluctuation intensities was also clearly observed in experiments involving diffusing dye plumes in the Great Lakes, reported by Csanady (1966) and Murthy and Csanady (1971).

Lognormal curves were found to fit successfully the non-zero data from the Fort Wayne experiments reported in Csanady (1973). An instantaneous line source was considered in this case.

Barry (1971) reported on the continuous monitoring of argon–41 emitted from a reactor stack, his basic data being in the form of 6-minute averages. From his data Barry deduced a probability density for these concentration time averages that is of exponential form. The same density was suggested by Csanady for instantaneous fluctuations from the experiments of Becker et al. (1966).

Ramsdell and Hinds (1971) made limited measurements of short term (38.4 s averages) field concentration values in the wake of a continuous near ground level (at 1m) point source of krypton gas. Near zero readings occupied from 35 to 80% of the time at the locations investigated (200 and 800 m from the source). A replot of the non-zero readings again approximated a lognormal distribution.

Eidsvik (1980) presented data from transverse line sampling of continuous plumes 500 m from the source. He indicated that concentration distributions at fixed transverse location relative to the center of gravity of the plume are well described by a log-normal curve for the non-zero measurements. The parameters of the log-normal distribution are given as functions of the distance r from the centerline in a cross wind plane. Thus the concentration pdf is of the form

$$p(C) = \frac{1}{\sqrt{2\pi}\sigma_*(r)C(r)} \exp\left\{-\frac{1}{2\sigma_*^2(r)}[\ln C(r) - lnC_0(r)]^2\right\}$$

where $C_0(r)$ is the measured time averege concentration that was found to have a nearly Gaussian profile and $\sigma_*(r)$ is estimated to increase from approximately $\sigma_*(0) \simeq 1$ at the center to $\sigma_*(r) \simeq 1.5$ at the boundaries of the mean cloud). Eidsvik stressed the fact that the transverse concentration fluctuation profile was dominated by large scale variations. He also estimated the probability of zero concentrations $F(0,r)$; he found it to be of the order of only 1% in the interior of the mean cloud and increase rapidly near the edges.

The most extensive experimental work directly related to atmospheric plume situations – yet still confined mainly to studies of non-buoyant plumes in neutrally stable environments – is carried by the research team under Fackrell and Robins for CEGB, UK (see Fackrell, 1978, 1980; Fackrell and Robins, 1981, 1982ab; Robins, 1978, 1979; Robins and Fackrell, 1979). Their research reveals a large amount of useful information which we use extensively in the following sections, in our critical examination of the transport equation for σ_c^2 to suggest or justify approximation schemes and simplifications of the mathematical analysis. Some of this work has been incorporated in an emiempirical model developed by Wilson et al. (1982a,b, 1985) which is briefly discussed in the following.

To summarize briefly the experimental results of Fackrell and Robins ,their major conclusions were:

(i) Meandering is the most significant source of fluctuation in the near field.

(ii) Production of fluctuations is in general significant only very close to the source.

(iii) The variance of concentrations from ground level sources exhibits profiles that are approximately self-similar in both the horizontal and vertical directions; further, it does not show significant dependence on source size.

(iv) The same variance for elevated sources initially shows dependence on source size which is eventually "forgotten." Horizontal profiles of σ_c^2 are again approximately self-similar, but vertical profiles show a more complicated behavior: In the immediate vicinity of the source they are self-similar;

then, as the effect of the ground is felt by the dispersing material, they differentiate. In the far field, however, these profiles become again self-similar, resembling those of a ground level source.

(v) The power law distribution resulting from Gifford's fluctuating plume model (see Section 5.7) seemed to provide the best fit to experimentally measured pdf's in most cases. Log-normal pdf's offered the best fit to sets of non-intermittent data.

Other sets of instantaneous plume concentrations measurements are presented by Kimura et al. (1981) and Jones (1983); in general, the nature of these data is consistent with the observations mentioned above. In particular, Jones' (1983) data reveal an exceptionally strong effect of the meandering processes, even for downwind, as the total intensities of fluctuations reported are consistently almost an order of magnitude larger than the respective in-plume intensities.

The theoretical study of the σ_c^2 dynamics was originated in the works of Corrsin (1952, 1964) and Batchelor (1959). Since then, various approaches have been followed in dealing with the statistics, especially $\langle c \rangle$ and σ_c^2, of scalar fields in turbulent flows (see, e.g. Monin and Yaglom, 1971, 1975; Hinze, 1975; Bradshaw, 1978; Libby and Williams, 1980).

As far as the specific atmospheric plume situation is concerned, the three major approches commonly employed in modeling the mean field, i.e. *Eulerian and Lagrangian statistical methods* and *dimensional (similarity) analysis* (see, e.g., Pasquill, 1974; Seinfeld, 1975) can also be used to model second moments. In addition, *heuristic* models focusing on particular characteristics of the fluctuation problem and *empirical* schemes, utilizing the information embodied in experimental data, have been developed and applied in various cases.

Eulerian modeling for the atmospheric plume fluctuations has been pursued mainly by Csanady (1967, 1973); some relevant work can also be found in Harris (1979) (see, e.g., Thomas, 1979). Csanady (1967) formulated a model for the mean-square fluctuation of concentration (variance of the concentration field) as a solution of the transport equation for this quantity, in the case of a continuous point source in a uniform wind, for axisymmetric conditions of spreading. He avoided the problem of accounting for meandering effects (large scale turbulence effects) by formulating his description in a reference frame attached to the centerline of the plume, assuming intermittency effects to be negligible in this reference frame. The crucial assumptions in Csanady's model are the validity of a (modified) gradient transfer-type theory for the transport of both the mean and the mean-square concentration field and self-similarity for both these fields. As already mentioned the latter assumption has been evaluated to some extent against experiments; for the first see also the works of Netterville and Wilson (1980) and Wilson et al. (1982a,b). Csanady's approach has been extended to less restrictive conditions in Chapter 5.

Lagrangian modeling has been given more attention in recent years (Chatwin and Sullivan, 1979;

Durbin, 1980; Lamb, 1981; Sawford, 1982, 1983, 1984,1985; see also Weil, 1985). A particularly clear exposition of the concepts and methods related to this approach, together with a critical review of the work on the subject, can be found in Sawford (1983). To summarize briefly, in the works mentioned σ_c^2 is typically related to the joint probability density for particle-pair displacements. Lamb (1980) and Durbin (1980) used systems of coupled Langevin equations to model the particle pair velocities. Sawford (1983) showed that the predicted behavior of σ_c^2 in dispersing puffs depended critically on the form of the probability density for particle separations; he further showed that Gaussian densities for these separations are not realistic because they smooth out the internal structure of the cloud and the relative fluctuations, thus leaving meandering as the only source for randomness. For further information, the interested reader should consult Sawford (1983, 1984).

Variances of scalars in the surface atmospheric layer can also be studied through dimensional analysis following the Monin-Obukhov theory (see, e.g., Panofsky and Dutton, 1984). In a study more closely related to the point source case Chatwin and Sullivan (1979) used dimensional analysis and simplifying assumptions to deduce, from the fundamental transport equations, results concerning the relative dispersion of a puff from instantaneous emissions that had an initial linear dimension. Their analysis concludes that, in the bulk of the cloud $\sigma_c^2 \sim Q^2/\sigma^3\sigma_0^3$, where σ and σ_0 respectively are the current and the initial linear dimensions of the puff and Q is the source strength, whereas in a central core region, which decreases with time, fluctuations are of greater magnitude, that is, of order Q^2/σ_o^6 i.e., conditioned by the initial puff size. Extensions of this model were proposed and applied by Hanna (1984).

Among the heuristic formulations, Gifford's (1959) fluctuating plume model still remains the single most influential work in the field. Gifford (1959) formulated a model of a meandering Gaussian plume such that fluctuations in concentration are produced *only* by the random displacements (meandering) of sections of the plume, ignoring fluctuations within each section. One cannot deduce predictions for the detailed structure of the fluctuating concentration field from a model such as Gifford's, however, some of its more general conclusions may be sufficient approximations under certain conditions and have been tested against experiments (see, e.g. Fackrell, 1978). Thus in the immediate vicinity of the source, where meandering is the more dominant source of fluctuations, it is a valid approximation and can offer reasonable estimates of the total σ_c^2. Two major conclusions of the model are that on the plume axis the pdf of the concentration should obey a simple power law (see also Appendix A5.3), and that the "peak to mean" ratio, which is often used to represent observational studies of atmospheric diffusion along with the mean concentration (the "peak" value of a random variable can be specified precisely as a high quantile of the probability distribution of concentration), tends to unity for large distances (see Gifford 1960, Csanady 1973).

Extensions of the original model have also been presented in the literature (see, e.g., Scriven, 1965; Diamante et al., 1976). Other formulations that are related to the spirit of Gifford's model have been developed by Vencatram (1979, 1983) and Hanna (1984); however, in general the latter schemes deal with averaged and not instantaneous–pointwise concentrations.

Finally, empirical models utilizing the experimental results of Fackrell and Robins (1979, 1982ab) have been developed by Wilson et al. (1982ab, 1985) in the form of closed algebraic expressions for ground level and elevated sources. The general model equations are

$$\left\langle c'^2 \right\rangle = \left(\frac{\tilde{q}(x)}{B\bar{u}\sigma_y(x)\sigma_z(x)} \right)^2 G\left(\frac{y}{\sigma_y}\right) F\left(\frac{z}{\sigma_z}\right)$$

where

$$B = 2\pi$$

for an elevated source, and

$$B = \frac{4 \ln \sqrt{2}\pi \Gamma(1/m)}{m(\ln 2)^{1/m+1/2}}$$

for a ground level source. The dimensionless functions F, G are

$$G\left(\frac{y}{\sigma_y}\right) = \frac{1}{2}\left\{ \exp\left[-\left(\frac{y}{\sqrt{2}\sigma_y} - \beta\sqrt{\ln 2} \right)^2 \right] + \exp\left[-\left(\frac{y}{\sqrt{2}\sigma_y} + \beta\sqrt{\ln 2} \right)^2 \right] \right\}$$

and

$$F\left(\frac{z}{\sigma_z}\right) = \exp\left[-\ln 2 \left(\frac{z - h_v}{\sqrt{2 \ln 2}\sigma_z} \right)^m \right] - \alpha \exp\left[-\ln 2 \left(\frac{z - h_v}{\sqrt{2 \ln 2}\sigma_z} \right)^m \right]$$

where $m = 2.0$ for an elevated source and $m = 1.7$ for a ground level source. h_v is defined through

$$h_v = \sigma_z \left[\left(\frac{h}{\sigma_z} \right)^2 + 2 \ln 2\beta^2 \right]^{1/2}$$

h being the source height. The "source" function $\tilde{q}(x)$ and the constants α, β are estimated so as to fit the observations. This model, although its structure is partially defended by physical reasoning, is definitely an empirical formulation constructed so as to describe specific sets of available data. This reliance on the aforementioned sets of data can be seen as a relative advantage (an "a priori validation") of the model; nevertheless, it limits significantly arguments for its applicability in situations not closely resembling the conditions corresponding to these measurements. Further, even for these conditions (i.e., neutral atmospheric stability), its parameters are estimated under the condition $\sigma_y \sim \sigma_z \sim x^{0.5}$ which limits the validity of the model to dispersion times (i.e., downwind distances from the source) large enough for this assumption to hold to a sufficient approximation. However, the major disadvantage of this model is that from the nature of its source data it estimates values of σ_c^2 that contain contributions from both internal fluctuations and partially "filtered" random meandering (a portion of meandering processes related to very large time scales is "cut off" as the measurements are typically 1hr averages). Actually, Fackrell and Robins (1982ab), commenting on the data on which the model is based, say that their analysis "shows meandering to be the main source of fluctuations." This fact about the model does not allow its application to situations where only internal fluctuations effects must be considered, as, for example, in modeling nonlinear chemical processes in plumes. Far downwind however, where internal fluctuations dominate the value of σ_c^2 the model could be an acceptable scheme for such applications.

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for Appendix A5.2

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APPENDIX A5.3

A New, Simple, Model
for the Probability Density
of Instantaneous Plume Concentrations

The (experimentally supported) lognormality of instantaneous plume concentrations in the meandering frame of reference can be directly combined with the closed form solutions that we now have available for both $\langle c_r \rangle$ (the Gaussian type formulas) and σ^2_{cr} (from the LPF model), to produce pdf curves for the concentration, at each point inside the instantaneous plume. Indeed, the parameters of the log normal pdf

$$p_r^L(C) = \frac{1}{C\sigma_L(2\pi)^{1/2}} \exp\left[-\frac{(C-\mu_L)^2}{\sigma_L^2}\right] \qquad (A5.3-1)$$

are directly related to $\langle c_r \rangle$, σ^2_{cr}, at each point, through

$$\mu_L = 2\ln\langle c_r\rangle - \frac{1}{2}\ln\left(\langle c_r\rangle^2 + \sigma^2_{cr}\right) \qquad (A5.3-2)$$

$$\sigma_L^2 = \ln\left(\langle c_r\rangle^2 + \sigma^2_{cr}\right) - 2\ln\langle c_r\rangle \qquad (A5.3-3)$$

Thus, substituting (A5.3-2), (A5.3-3) in (A5.3-1), one has $p_r^L(C)$ as a function of position (relative to the moving frame) inside the instantaneous plume:

$$p_r^L(C) = p_r^L(C; x, y_r, z_r)$$

For ranges of the downwind distance x where the profiles of $\langle c_r \rangle$ and σ^2_{cr} are self-similar p_r^L becomes independent of x with the introduction of the transformation

$$\chi_r = \frac{C}{\langle c_0\rangle_r} \qquad (A5.3-4)$$

where $\langle c_0\rangle_r$ is the expected concentration at the instantaneous centerline. Then

$$p_r^L(\chi_r; y_r, z_r) = \langle c_0\rangle_r p_r^L\left(\frac{\chi_r}{\langle c_0\rangle_r}; x, y_r, z_r\right) \qquad (A5.3-5)$$

Introducing the relations (5.2-12) (Chapter 5) one obtains

$$p_r^L(\chi_r; \hat{r}) = \frac{1}{\sqrt{2\pi}\chi_r \ln\left(\frac{f^2+g}{f^2}\right)} \exp\left\{-\frac{\left[\ln\left(\frac{\chi_r\sqrt{f^2+g}}{f^2}\right)\right]^2}{2\left[\ln\left(\frac{f^2+g}{f^2}\right)\right]^2}\right\} \qquad (A5.3-6)$$

where $f(\hat{r})$, $g(\hat{r})$ are estimated through the Gaussian and the LPF Models respectively (Chapter 5, Section 5.3). For this choice of f and g the form of the resulting pdf is shown in Figure A5.3-1 at dimensionless distances $\hat{r} = 0, 0.5, 1.0$ and 2.5 from the instantaneous plume centerline. The parameters used to calculate g are the "most typical ones" (i.e., $p = 0.5$, $A_1 = 1.5$) and a centerline value of g of order unity is assumed. The figure shows the increasing probability of near-zero χ_r, and the corresponding movement of the mode of the distribution, equal to $\exp(\mu_L - \sigma_L^2)$, towards zero, as one moves from the centerline to the edges of the instantaneous plume.

The rate of the relative dispersion process (i.e., the value of the exponent p) is the most important factor in determining the shape of the pdf at a given dimensionless distance from the centerline. This results from the fact that the overall production of fluctuations up to a given downwind distance is an increasing function of p. So, intuitively, one expects the resulting pdf to show "increasing randomness" for the values χ_r for increasing p. This indeed appears in Figure A5.3-2 where the pdf at $\hat{r} = 0.0$ is shown for the three different values that, according to the theory of two-particle dispersion, are assumed by the exponent p at the different stages of dispersion, i.e., $p = 1.0$, 1.5, and 0.5. For increasing p the tails of the pdf cover more extensive area in the $p_r^L - \chi_r$ graph and values of χ_r very close to zero (as well as values $\chi_r \gg 1$) become more probable than for lower p. If p could approach zero the most probable values of χ_r would occur in the vicinity of its deterministic expected value.

The LPF model parameters ω has an effect that is roughly the opposite of p. Figure A5.3-3 shows the effect of changing the value of ω on the pdf at the centerline. Low values of ω result in increased randomness and the probability of near zero values of χ_r rises. For larger values of ω the pdf mode moves towards the expected centerline value ($\chi_r = 1$) and for $\omega \to 1$ the pdf reduces to a delta function at $\chi_r = 1$ (since for this value of ω the LPF model "places" the production of fluctuations exactly at the point where the calculation is performed, thus no fluctuations have diffused to the centerline). These results are easily extended to the behavior of the pdf at points not on the centerline. It must be made clear at this point that, whereas the dependence of the pdf on the value of p reflects the physical mechanism by which fluctuations are produced and transported, the respective dependence on the values of ω results simply from the structure of the LPF model and the artificial description of the physical processes embodied in it. Knowledge of this dependence, however, allows the proper choice and adjustment of this parameter for a given physical situation when some experimental information regarding the pdf is available.

The general convolution relation (A5.1-8) can now be used for the estimation of probability densities for the instantaneous concentration C observed with respect to a fixed frame of reference. For convenience we define the dimensionless fixed frame concentration at (x, y, z) by

$$\chi = \frac{C}{\langle c_0 \rangle_r} \qquad (A5.3-7)$$

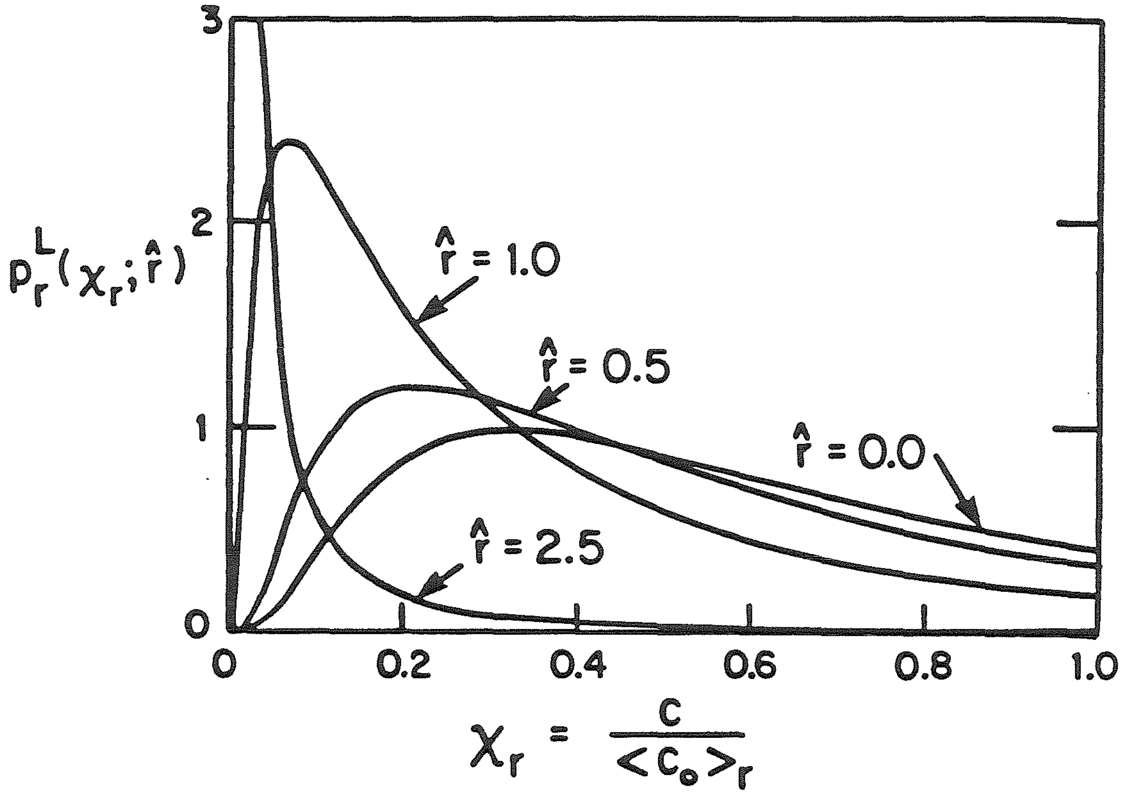

Figure A5.3-1

Probability p_r of the instantaneous dimensionless concentration χ_r
in the meandering frame of reference
at dimensionless crosswind distances r/σ = 0.0, 0.5, 1.0, 2.5 from the instant. centerline

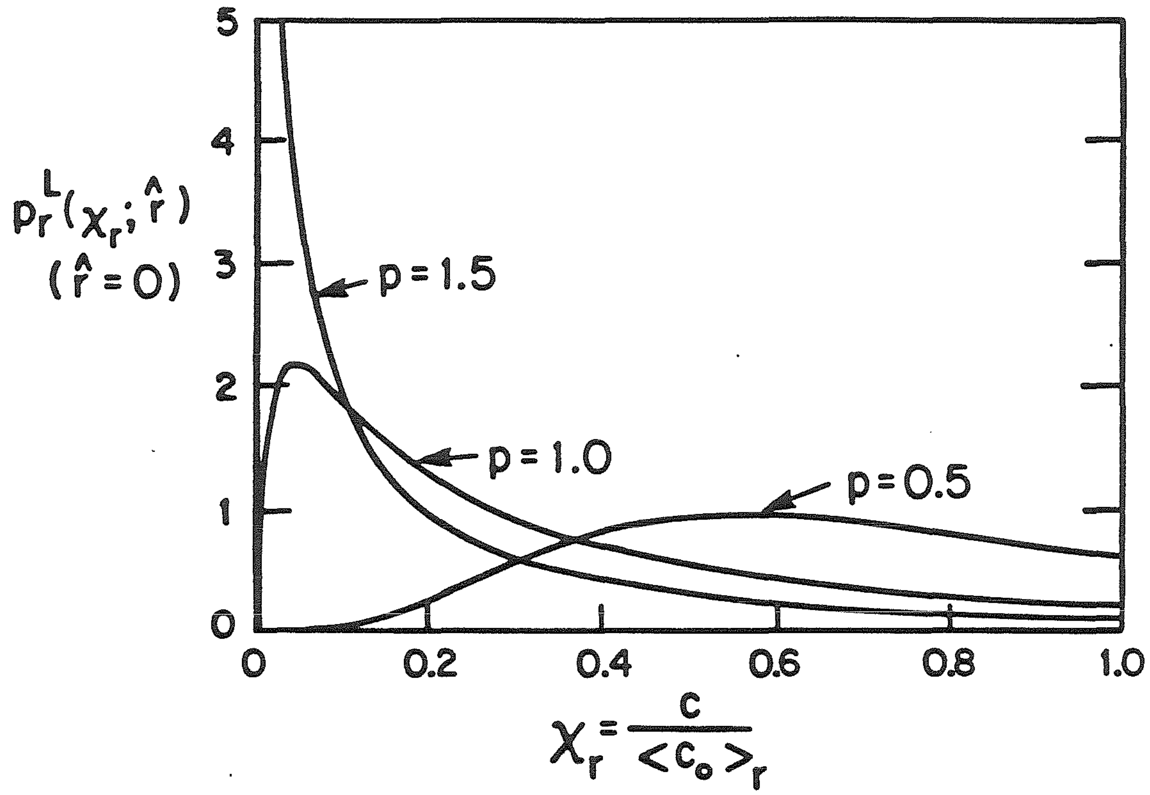

Figure A5.3-2

Effect of dispersion intensity (expressed via the parameter p)
on the probability p_r
(calculations for $r = 0$)

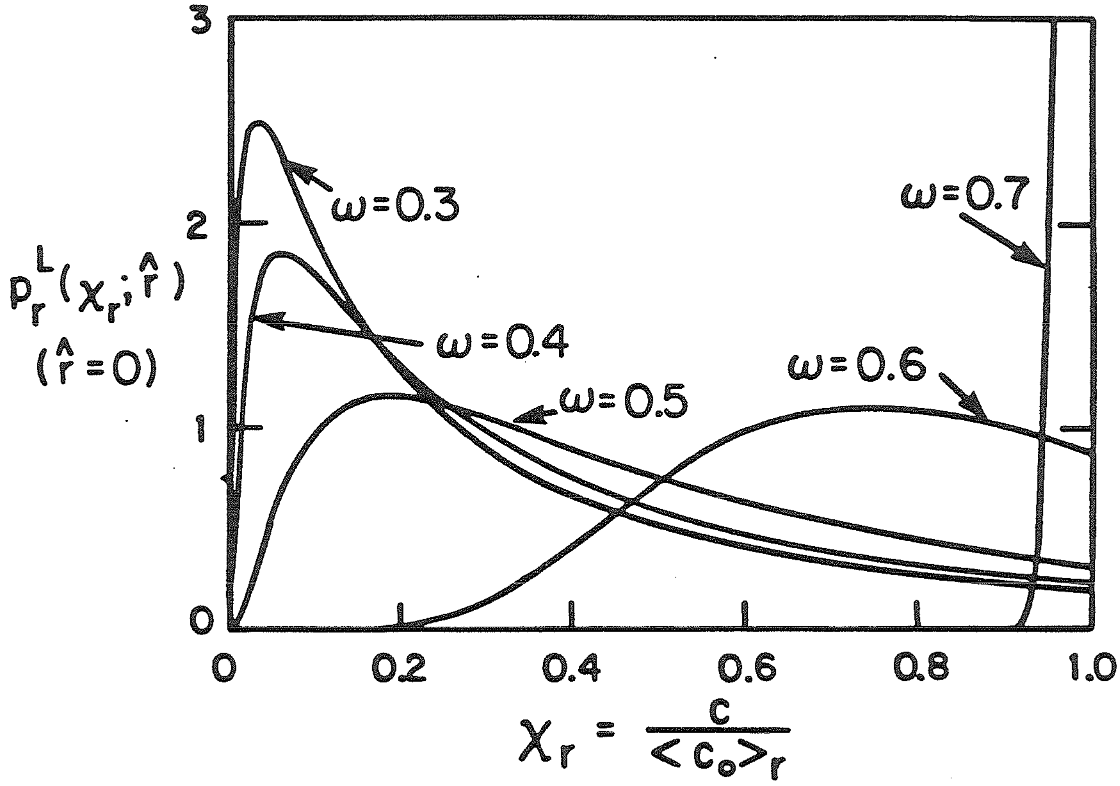

Figure A5.3-3

Effect of the parameter ω on the probability p_r

(calculations for $r = 0$)

(Notice that the concentration scale addopted above is again the expected concentration at the instantaneous centerline and not at the mean centerline.)

To apply (A5.1-8) we consider for simplicity the isotropic case with relative dispersion parameters $s_y = s_z = s$ and meandering parameters $m_y = m_z = m$. Then, for Gaussian $P_k(b_y, b_z)$ it can be shown that (A5.1-8) becomes

$$p^L\left(\chi;\hat{R}\right) = \frac{1}{2\pi}\int_0^{\infty}\int_0^{2\pi} \hat{B}\exp\left(-\frac{\hat{B}^2}{2}\right) p_r^L\left(\chi;\hat{R},\hat{B},\phi\right) d\phi d\hat{B} \qquad (A5.3-8)$$

where

$$\hat{B} = \frac{\sqrt{b_y^2 + b_z^2}}{m}\ ,\ \hat{R} = \frac{\sqrt{y^2 + z^2}}{m}$$

and the argument $\hat{r}$ of f, g is

$$\hat{r} = \left(\frac{m}{s}\right)\sqrt{\hat{R}^2 + \hat{B}^2 - 2\hat{B}\hat{R}\cos\phi}\ , 0 \le \phi < 2\pi$$

Thus, (A5.3-8) gives the pdf of instantaneous concentrations in plumes relative to a fixed frame, at the dimensionless distance $\hat{R}$, accounting for both the effects of meandering and internal plume fluctuations.

The estimates provided by (A5.3-8) can be compared directly to the results of Gifford's (1959) fluctuating plume model where all the randomness in the concentration field is attributed exclusively to the process of meandering. In the case of Gifford's model the pdf of instantaneous concentrations in the moving frame corresponds to a delta function located at the expected value of C (since in this frame the concentration is assumed equal to its expected value in all realizations):

$$p_r(C; x, y_r, z_r) = p_r^{\delta}(C; x, y_r, z_r) = \delta\left(C(x, y_r, z_r) - \langle c_r(x, y_r, z_r)\rangle\right) \qquad (A5.3-9)$$

For this (most ideal) choice of p_r equation (A5.3-8) can be integrated analytically to give, for isotropic dispersion and unbounded atmosphere,

$$p^{\delta}(\chi;\hat{R}) = \left(\frac{s}{m}\right)^2 \chi^{(s/m)^2-1}\exp\left(-\frac{\hat{R}^2}{2}\right) I_0\left(\frac{s}{m}\sqrt{2\ln\left(\frac{1}{\chi}\right)}\right) \qquad (A5.3-10)$$

This relation on the mean centerline reduces to

$$p^{\delta}(\chi;\hat{R}=0) = \left(\frac{s}{m}\right)^2 \chi^{(s/m)^2-1} \qquad (A5.3-11)$$

The above equations, directly derived through the present formalism, are exactly the classical results of Gifford (1959).

Figures A5.3-4 and A5.3-5 show the estimates of the classic fluctuating plume model and of the combined lognormal internal pdf–fluctuating plume model, with parameters provided by the LPF formulation, for $m/s = 2.0$ and $m/s = 1$, respectively, on the mean plume centerline. As expected, the integrated model "adds randomness" to the concentration characteristics predicted by the simple fluctuating plume model for $m/s = 2.0$, thus giving higher probabilities for near-zero values of χ and reducing the probabilities for near-expected ($\chi = 1$) values. The effect is more pronounced as $m/s \to 1.0$; for $m = s$ Gifford's model gives equal probability to all values of χ. Clearly in this limit the internal fluctuations are dominant in determining the probabilistic characteristics of the plume concentration field, and Gifford's model is insufficient. For $s \gg m$ the LPF model can be used to predict total randomness on a "stand alone" basis.

References
for Appendix A5.3

Gifford, F.A. (1959) "Statistical Properties of a Fluctuating Plume Dispersion Model," in *Adv. in Geophys.*, *6*, 117-137

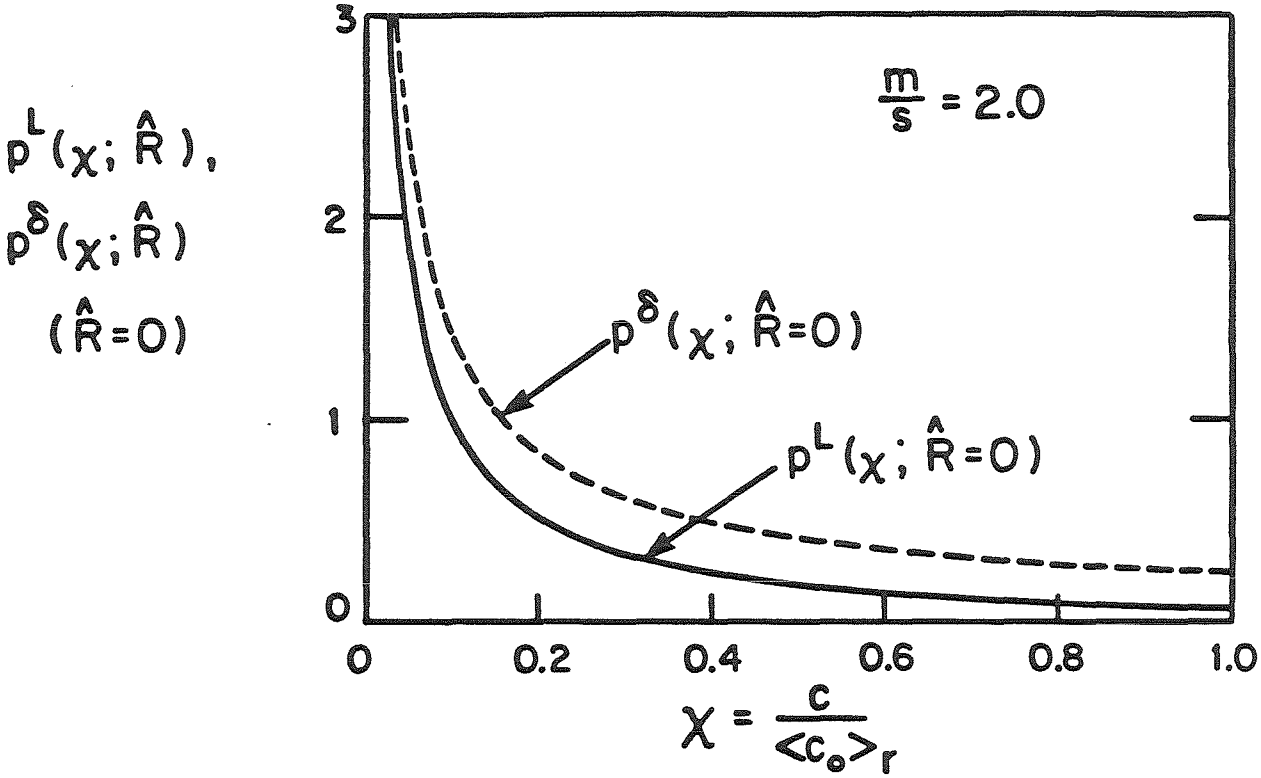

Figure A5.3-4

Probability density p of the instantaneous dimensiomless concentration χ in the fixed frame of reference on the mean centerline for $m/s = 2$ (solid line: calculations using the LPF-lognormal model) (dashed line: calculations using Gifford's fluctuating plume model)

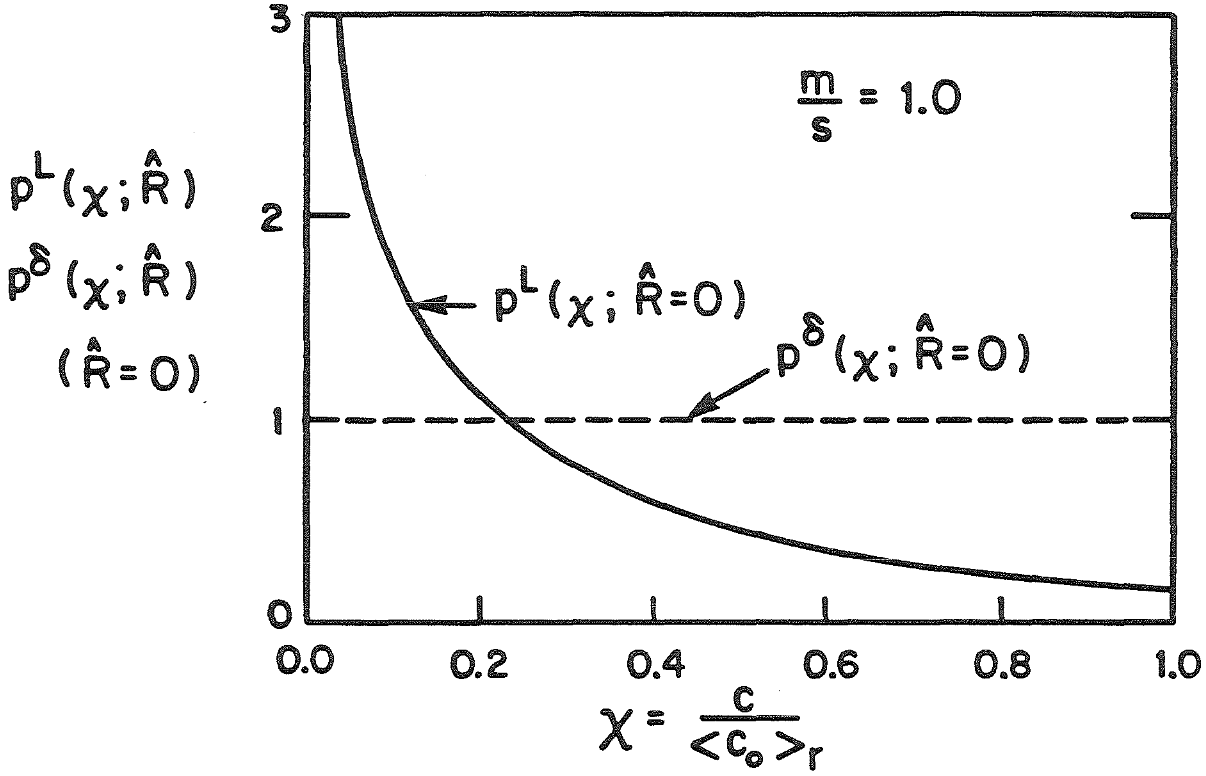

Figure A5.3-5

As in Figure A5.3-4 for $m/s = 1$

CHAPTER 6

Chapter 6 contains

- *an introduction to the formal description of fluid particle dispersion (in both inertial and non-inertial frames) via stochastic and deterministic Green's functions,*
- *a discussion of the modified A.D.E. in relation to other dispersion models,*
- *a review of time-domain methods for determining relative dispersion parameters (including similarity analysis, Langevin equation methods and conditioned motion methods),*
- *a discussion of spectral methods for determining relative dispersion parameters and presentation of an iterative filtering algorithm that utilizes observed atmospheric spectra for this objective.*

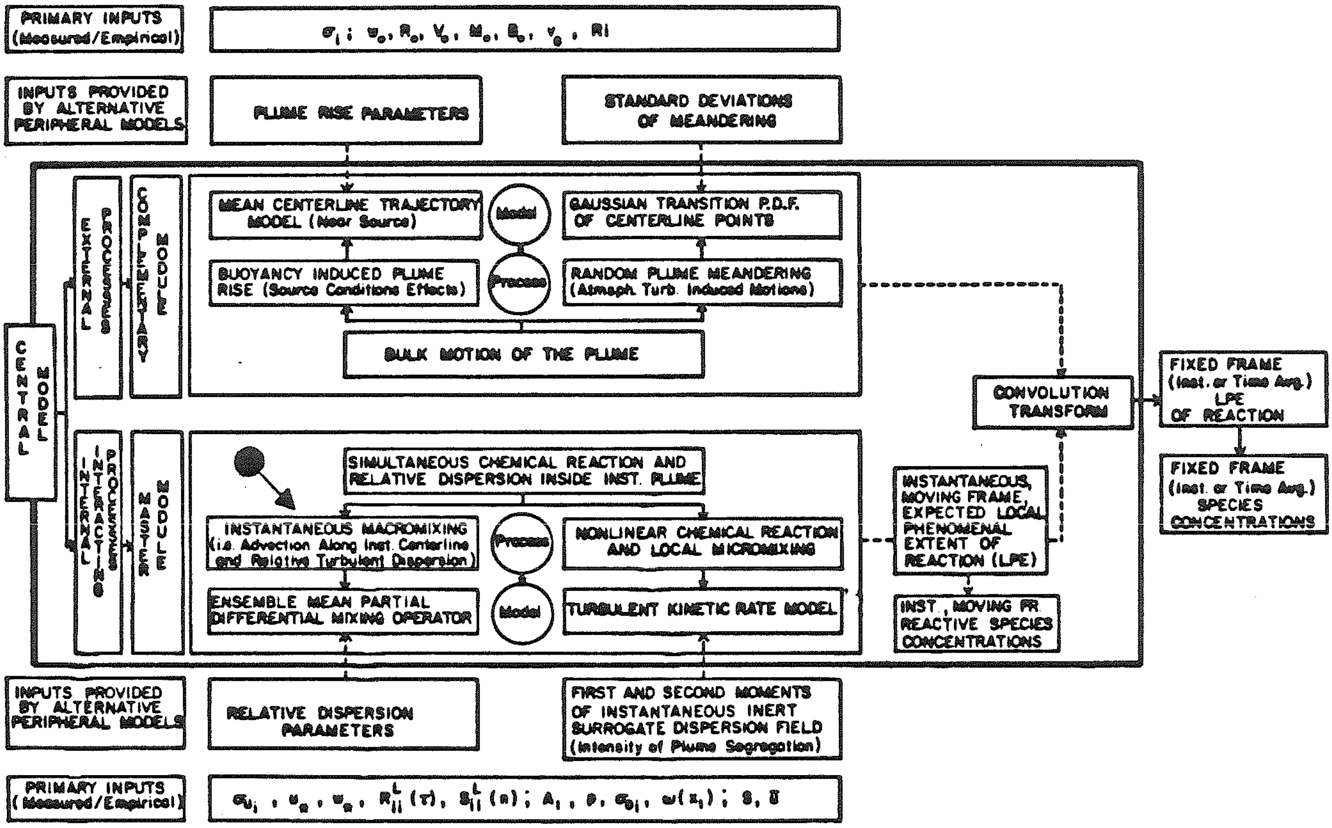

Figure 2-1c

TRPM Components Discussed in Chapter 6

CHAPTER 6

PARAMETERIZATION OF RELATIVE DISPERSION

6.1 INTRODUCTION

This chapter discusses some aspects, both formal and practical, of the multi-scale turbulent dispersion problem, as it appears in the overall reactive plume phenomenon. The treatment of dispersion adopted in the TRPM formulation is explained here in more detail than this was done in Chapter 2.

The present chapter is intended as a tutorial introduction to the subjects of absolute and relative diffusion (in particular atmospheric), and a brief review of the various modeling approaches in the area, which cover an enormous range, from simple dimensional and similarity analyses, to sophisticated formulations involving complex numerical schemes and methods of functional analysis.(*) What we intend to do here is, in parallel to presenting and discussing the formulations of the particular schemes proposed for use with the TRPM, to bring together and summarize various concepts

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* Among many excellent general introductions to the subject of turbulent transport we mention Tennekes and Lumley (1972, Chapters 7 and 8), Csanady (1973), Monin and Yaglom (1971, Section 10) and Hinze (1975, Chapter 5). Some of the more advanced methods of analysis are discussed in Leslie (1973, Chapters 8 and 12) and Monin and Yaglom (1975, Section 24). The work of Monin and Yaglom focuses in particular on atmospheric dispersion; for other specialized analyses of this topic see Seinfeld (1975, Chapter 6; 1983), Hanna et al. (1982), Pasquill and Smith (1983) and Tchen (1984ab). Further information directly related to the atmospheric dispersion problem can be found in Panchev (1971), Haugen (1973, 1975), Berlyand (1975), Vinnichenko et al. (1980), Nieuwstadt and von Dop (1982), Plate (1982), Randerson (1984) and Panofsky and Dutton (1984).

that are useful for a better understanding of these formulations, the conditions for their validity, and their relation to other approaches. Thus this chapter should be seen not only as an elaboration on a particular component of the TRPM but also as a guide to the relative dispersion literature, linking ideas and methods that can be found scattered in a variety of sources.

Formally, description of dispersion in the TRPM was based on the linear stochastic Eulerian Mixing Operator $\mathcal{L}^M$, as given by equation (1.3-4), whose "ensemble mean action" (equation (1.3-7)) was approximated by the action of the "modified K-theory operator" $\mathcal{L}_K^M(\cdot)$ (also linear), given by equation (2.3-2), on the mean concentration field $\langle c \rangle$.

These operators were assumed capable of describing dispersion in a frame of reference following the meandering motion of the plume centerline. Some further discussion is needed on this point, which may be a source of confusion. *Our approach is Lagrangian*, in the sense this term has been used to describe a certain class of air pollution models (trajectory models) but *at a scale smaller* than relevant to those models. To make this more clear we must emphasize the fact that the term "Lagrangian description" is in general used in a very loose manner in air pollution modeling. In fact, in the trajectory models mentioned above the "Lagrangian description" concept applies only to the process of advection by the mean wind and *not* to random movements caused by the smaller scales of atmospheric motion. Turbulent transport processes inside the large scale (macroscopic) control volume (between the different computational cells) that follows the trajectory are most often described in Eulerian terms in these models, typically through conventional K theory (see, e.g., Appendix A1.2) with all the subsequent limitations (see, e.g., Corrsin, 1974). Thus these models are essentially hybrid formulations. (The governing equations in the moving frame are Eulerian equations with transformed coordinates.) A "fully" Lagrangian description of an advection-dispersion field would be formulated in terms of fluid particles (see also Chapter 4) and would necessarily be statistical in nature. (This kind of approach would perhaps conform better to the essense of Lagrangian methodology of continuum mechanics, which focuses on the kinematics and dynamics of material points rather than on finite control volumes and their infinitesimal limiting approximations to describe processes in continua). However, the whole problem is essentially one of terminology and semantics and as long as the concepts and assumptions involved are clearly identified there should not be confusion in using the term "Lagrangian methodology" either to refer to the description in terms of fluid particles, which are subject to the entire spectrum of motions existing in the field under observation, or to the formulation of transport-balance equations in a frame of reference that moves along some, appropriately defined "mean flow." We could call these two descriptions "micro-Lagrangian" and "macro-Lagrangian" respectively, understanding that the latter might be a hybrid approach; then the dispersion scheme of the TRPM could be called a "meso-Lagrangian" hybrid description (not to be confused, of course, with meso-scale air pollution models) in the following sense: the moving frame of reference follows not only the "mean" flow but is also affected by an additional portion of the velocity spectrum (of higher frequency than what is included in the estimation of mean velocities), i.e., the portion that "causes plume meandering." The effects of this portion of the spectrum can only be estimated in a probabilistic fashion. In this frame one can form Eulerian type equations accounting for transport due to the rest ("unused") portion of the motion spectrum. Nevertheless, we will not adopt any further use of the macro-, meso- and micro- prefixes neologism to discriminate between different Lagrangian methodologies, hoping that the concept of the advected-meandering frame (with the axes always parallel to fixed directions) has been sufficiently clarified.

A final question (that has already been addressed in earlier chapters) in under what conditions does the fixed frame form of the mixing operator (in either its stochastic original version or in any approximate form that results from closure) remain a valid representation in the advected-meandering frame. A similar question appears in Lagrangian Trajectory model formulation (see Liu and Seinfeld, 1975) where the ADE is assumed valid, in its fixed frame form, in the transformed coordinates. There the answer is obtained by examining the equations resulting from a straightforward Galilean transformation of coordinates. The requirement is that the local curvature of the plume centerline is locally small. This limitation exists also in our approach as far as the *mean* centerline trajectory, determined mainly by buoyancy effects, is concerned; however one should expect the above requirement not to be violated except in extreme cases.

Hence the main question here is: what is the effect of the random meandering motions of the moving reference frame? This question is discussed in Section 6.3 where we justify the assumption that, at least for homogeneous and stationary turbulene, these motions should not affect the form of the mixing operator (although of course they alter its parameters).

In the following we proceed in a more detailed analysis of the relative dispersion and meandering concepts and of the modified ADE model.

6.2 BASIC LAGRANGIAN CONCEPTS AND FLUID PARTICLE DISPERSION

6.2.1 Lagrangian Methods

Proceeding from the stochastic representation of the mixing operator (1.3-5) to the 1st order (non-local) closure scheme given by equation (2.3-2), involving coefficients that depend on dispersion time, cannot be justified on a strictly Eulerian basis (via, e.g., a conventional mixing length–gradient transport hypothesis). This would result to a local, dispersion-time independent, scheme, i.e. a differential equation model with eddy diffusivities that are properties of the flow field and not of the particular dispersion process. Furthermore, the associated practical problem of estimating the appropriate values of the plume dispersion parameters and the related diffusivities in terms of statistical characteristics of the velocity field represents another essential aspect of the modeling scheme for dispersion.

Having set the a priori requirement that the operational form of the dispersion model adopted by the TRPM should be at the level of the complexity of the ADE, in combination with the necessity to account for the non-local character of dispersion, leads us to consideration of Lagrangian schemes. Indeed, the Lagrangian description of dispersion (the term to be exclusively associated in the following with the representation of flow in terms of fluid particles) inherently offers a more general perspective in a first order description of the phenomenon than a straightforward Eulerian formulation.

The statistical fluid particle description of turbulent dispersion, originated by Taylor (1921), has been pursued via three major approaches.

(a) In the direct kinematic approach, that follows the original analysis by Taylor, the moments of the displacement of a fluid particle are related kinematically to the Lagrangian velocity correlation functions. Since typically Eulerian and not Lagrangian correlations are more conveniently measured and are available, the basic fundamental problem encountered in this approach is the derivation of the Lagrangian velocity correlation from the respective Eulerian function. Although the original exact analysis was limited to the case of homogeneous stationary turbulence, the kinematic approach has been extended over the years to approximate various more realistic situations (see, e.g., Pasquill and Smith, 1983; Hunt, 1985). A point that needs to be mentioned here (and on which we will further elaborate in Section 6.5) is that applying the direct approach in the frequency (or wavenumber) rather than in the time domain, and the consequent use of spectra instead of correlations, offers some advantages, both conceptual and computational, that can facilitate relative dispersion parameters estimation.

(b) In the second approach, originated by Batchelor (1949, 1952), one tries to determine the transition probability densities of the fluid particles positions, to be briefly referred to as *transition functions* in the following. Originally this was done on the basis of dimensional and similarity analysis, and it was thus limited to idealized flow fields. From the perspective of current research the essence of this approach is to construct a "master" equation that gives the evolution of the transition function in space and time. From a practical standpoint what is necessary is to reduce the master equation into a tractable form on the basis of reasonable assumptions and, finally, express it in terms of Eulerian velocity correlation functions. A derivation of the form of the master equation that most closely resembles the A.D.E., namely the Fokker-Planck equation, can be found in Seinfeld (1975, Section 6.2.4), the analysis there being in terms of an appropriate ensemble mean concentration (instead of the equivalent transition function). One should mention here that according to the *independence approximation* (Corrsin, 1959), to be discussed in the following, the Lagrangian-Eulerian transformation requires the determination of a weighting function, which is equivalent to the transition function.

(c) The third approach conceptually lies between the two others mentioned above. It is based on the use of Langevin equations for the fluid particles velocities and although it is more narrow in perspective than the general transition function methods (*) it seems able to provide more directly simple results relevant to both absolute and relative dispersion providing at the same time conceptually simple models for these processes. This approach was originated by Obukhov (1949) and currently receives revived interest, in particular in connection with relative dispersion models (see Sections 6.42, 6.4.3).

In the presentation that follows we will first briefly review some fundamental concepts related to the approaches outlined in the preceding paragraphs and also introduce the problem of relative dispersion. In the following sections we will use this information, first to examine the transition function approach in order to explain where the modified ADE adopted in the TRPM formulation (essentially of course a Fokker-Planck equation) stands conceptually in this general Lagrangian framework, and what assumptions are involved in its construction, and then to treat the practical aspect of relative dispersion parameters estimation.

6.2.2 Fundamental Concepts and Definitions

Let $\mathbf{x} = (x_1, x_2, x_3)$, $\mathbf{u} = (u_1, u_2, u_3)$ be the Eulerian coordinates and velocities in the flow field under consideration and $\mathbf{y} = (y_1, y_2, y_3)$, $\mathbf{v} = (v_1, v_2, v_3)$ the corresponding Lagrangian (fluid particle) quantities. An elegant method of defining $\mathbf{u}$ and $\mathbf{v}$ fields is to consider them as special cases of a generalized or Kraichnanian velocity field $\mathbf{w}$ (see Leslie, 1973). The Kraichnanian velocity $\mathbf{w}(t|\mathbf{x}, t^*)$ is defined as the velocity at time t of fluid particle that was at $\mathbf{x}$ at time t^* (t is called the *measuring time* and t^* the *labelling time*). Then the Eulerian velocity is identified with $\mathbf{w}$ for $t = t^*$:

$$\mathbf{u}(\mathbf{x}, t) = \mathbf{w}(t|\mathbf{x}, t) \qquad (6.2-1)$$

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* In fact this approach, in its most common form, is equivalent to a Fokker-Planck equation governing the transition function of the derivatives of the fluid particles positions (i.e. the Lagrangian velocities). For a brief but very informative discussion of the relationship between the Fokker-Planck and Langevin equations methods of description of random processes see van Kampen (1981, Chapter VIII)

and the Lagrangian velocity is identified with $\mathbf{w}$ for $t > t^*$ with $t^* = t_0$ (and $\mathbf{x} = \mathbf{x}_0$):

$$\mathbf{v}\left(\mathbf{x}_0, t\right) = \mathbf{w}\left(t | \mathbf{x}_0, t_0\right) \qquad (6.2-2)$$

The assumptions regarding the nature and properties of the fluid particles in a general Lagrangian analysis may vary widely. In the present study we consider for simplicity "ideal volume fluid particles" (see also Chapter 4) and ignore any transformations on the identity of these particles that may be due to molecular level processes. If we assume that the differential volume element $d\mathbf{x}^3$ "surrounding" the position coordinates $\mathbf{x}$ can be "occupied" by one particle only at a time, we can view these particles "marked" (or uniquely identified) by their position in Eulerian coordinates at some fixed labelling time instant t_0. However this would be inconsistent with the concept of the ideal instantaneous point source. To avoid further elaboration of this point here (and of the associated need to properly define continuity requirements) we proceed as follows:

Suppose that during the total period of observation (say from time 0 to t) a total number of N marked particles each carrying mass m of some given species, has been introduced (and remains) into the continuum field under consideration and each one is assigned an abstract "identity number" $k = 1, 2, \ldots, N$ (which remains unchanged through the entire "life" of the fluid particle). If the particle with "identity number k" was at $\mathbf{x}_0$ at time t_0 (*), then its Lagrangian position vector will be denoted by the equivalent notation

$$\mathbf{y}\left(\mathbf{x}_0, t\right) \equiv \mathbf{y}\left(t | \mathbf{x}_0, t_0\right) \equiv \mathbf{y}^{(k)}\left(t\right)$$

Two points are worthy of mentioning here:

(a) Different initial sets of assumptions regarding the fluid particle concept may be more useful in specific situations. Thus for example one may want to apply the

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[*] A more precise expression of this statement would be: "in the differential volume element surrounding the coordinate vector," but in the following we will avoid these rather tedious clarifications assuming that the meaning of statements like this are obvious.

Lagrangian analysis to the case where an arbitrary number of fluid particles can simultaneously occupy the same position coordinates, a condition that may be convenient when one wants to model interactions between the fluid particles, or one may consider volume particles (see Chapter 4) that after any finite time interval since their introduction in the flow field they obey conventional volume and mass continuity constraints.

(b) The principles of the analysis to be presented here are valid if other properties of the fluid particle - such as e.g. chemical composition, temperature etc. - besides its spatial-temporal coordinates are taken into account. These properties can be viewed as additional coordinates in which case the Lagrangian position vector **y** will follow the evolution path of the particle in an *extended configuration space* that incorporates these properties as extra dimensions. The only such property that we are going to use in the present analysis is the *age* of the fluid particle, i.e. the time elapsed since its introduction in the flow field. Identifying the subset of all particles with the same age is useful not only in dealing with instantaneous releases but also with respect to continuous releases where advection dominates turbulent diffusion in the downstream direction.

Now, having the possibility of the aforementioned generalization of the present analysis in mind, we return to the more standard version of the problem.

The stepping stone for

(i) a formal development of the transition function approach and,

(ii) establishing and understanding the relationship between Eulerian and Lagrangian methodologies,

is the introduction of the quantity

$$\psi\left(\mathbf{x},t|\mathbf{x}_0,t_0\right) \equiv \psi^{(k)}\left(\mathbf{x},t\right) \equiv \delta\left[\mathbf{x}-\mathbf{y}\left(\mathbf{x}_0,t\right)\right] \qquad (6.2-3)$$

subject to the initial condition

$$\psi\left(\mathbf{x},t|\mathbf{x}_0,t_0\right) = \delta\left(\mathbf{x}-\mathbf{x}_0\right) \qquad (6.2-3a)$$

which can be identified with

- the fundamental *"conservative characteristic"* of Monin and Yaglom (1971, p. 534),
- the *"Lagrangian position function"* of Leslie (1973) (see also Batchelor, 1952),
- the *"microdistribution"* or *"instantaneous transition function"* of Jiang (1985),
- the *"stochastic Green's function"* of Adomian (1963, 1983) employed by Seinfeld (1983) in the description of turbulent dispersion,

and is also conceptually identical to

- the *"fine grained density function"* of quantum statistical mechanics that has also been employed in studies of turbulent fluid mechanical phenomena (Lundgren, 1967; O'Brien, 1980)

(There are other terms that are also appropriate for ψ – e.g., stochastic Euclidean propagator, stochastic resolvent kernel, etc.).

Some comments are necessary at this point regarding the nature of $\psi(\mathbf{x}, t|\mathbf{x}_0, t_0)$. This quantity is a *function* of the position variable $\mathbf{x}$ and a *functional* of the random field $\mathbf{y}(\mathbf{x}_0, t)$, depending on the structure of the *entire ensemble* of values $\mathbf{y}$ can assume. Consider a fixed value of $\mathbf{x}$, say $\mathbf{x}_F$ and fix $(\mathbf{x}_0, t)$. Then $\psi(\mathbf{x}_F, t|\mathbf{x}_0, t_0)$ is zero if $\mathbf{y}(\mathbf{x}_0, t) \neq \mathbf{x}_F$ in any one realization of the random field $\mathbf{y}$ and infinite if $\mathbf{y}(\mathbf{x}_0, t) = \mathbf{x}_F$. For a given realization ψ has all the properties of a pdf, including normalization since

$$\int \psi(\mathbf{x}, t|\mathbf{x}_0, t_0)\, d\mathbf{x} = 1$$

by the definition of the delta function.

Also the n-th moment of $\mathbf{x}$ is by direct calculation equal to $\psi^n(\mathbf{x}_0, t)$ for all n. In other words, the fine grained density or microdistribution is a device through which each and every realization of the random field can be expressed in a pdf-like manner. However it must be realized that it is a *generalized* and not an ordinary function.

Now, appropriate averaging of $\psi(\mathbf{x}, t|\mathbf{x}_0, t_0)$ leads to the rational construction of various quantities employed in the analysis of turbulent dispersion:

(I) Averaging $\psi\left(\mathbf{x},t|\mathbf{x}_0,t_0\right)$ over all possible starting positions $(\mathbf{x}_0,t_0)$ (i.e. averaging over all particles k) for arbitrary but fixed $(\mathbf{x},t)$ produces a *random function* of $(\mathbf{x},t)$, $\overline{\psi}\left(\mathbf{x},t\right)$

$$\overline{\psi}\left(\mathbf{x},t\right)=\frac{\int\int\psi\left(\mathbf{x},t|\mathbf{x}_0,t_0\right)d\mathbf{x}_0dt_0}{\int\int d\mathbf{x}_0dt_0} \qquad (6.2-4a)$$

or

$$\overline{\psi}\left(\mathbf{x},t\right)=\frac{1}{N}\sum_{k=1}^{N}\psi^{(k)}\left(\mathbf{x},t\right) \qquad (6.2-4b)$$

that can be identified with the random fluid particle concentration (and within an appropriate factor that accounts for the dimensions involved in the definition of concentration used) with mass or molar concentration. Thus, in the idealized case under consideration, the random instantaneous mass concentration at $(\mathbf{x},t)$ will be

$$c\left(\mathbf{x},t\right)=Nm\overline{\psi}\left(\mathbf{x},t\right)$$

When the particular random realization corresponding to a random value of $(\mathbf{x},t)$ (i.e. for a given random choice of $(\mathbf{x},t)$) is to be specified, say through an index α, we will use the left subscript notation

$$\overline{\psi}\left(\mathbf{x},t\right)={}_{\alpha}\overline{\psi}\left(\mathbf{x},t\right)$$

Nevertheless, it must be clear that (even when this notation is not employed) $\overline{\psi}\left(\mathbf{x},t\right)$ is different for every realization of the turbulent field.

(II) Ensemble averaging $\overline{\psi}\left(\mathbf{x},t\right)$ over all possible realizations of the dispersion field (essentially over the ensembles of $\mathbf{y}$-trajectories corresponding to all initial $(\mathbf{x}_0,t_0)$) produces the probability density function that a fluid particle (i.e. *any* fluid particle) will be at $\mathbf{x}$ at time t, which is equivalent to the ensemble mean (number) concentration of fluid particles at $(\mathbf{x},t)$. The corresponding mean mass concentration will be

$$\left\langle c\left(\mathbf{x},t\right)\right\rangle=Nm\left\langle\overline{\psi}\left(\mathbf{x},t\right)\right\rangle$$

(III) Ensemble averaging $\psi(\mathbf{x},t|\mathbf{x}_0,t_0)$ for fixed $(\mathbf{x}_0,t_0)$ produces the *deterministic transition probability function* G, giving the probability that a fluid particle, starting from $\mathbf{x}_0$ at time t_0 will be at $\mathbf{x}$ at time t:

$$G(\mathbf{x},t|\mathbf{x}_0,t_0) = \langle \psi(\mathbf{x},t|\mathbf{x}_0,t_0)\rangle \tag{6.2 – 5}$$

G is of course the (conventional) Green's function for the *forward* diffusion of the *mean* concentration field. Similarly, ensemble averaging $\psi(\mathbf{x},t|\mathbf{x}_0,t_0)$ for fixed $(\mathbf{x},t)$ (i.e. over all trajectories passing from $\mathbf{x}$ at time t) produces the Green's function for *backward* or *reversed* diffusion, $G(\mathbf{x}_0,t_0|\mathbf{x},t)$.

Thus, when we have adequate information about ψ we can (in principle) solve the one particle dispersion problem completely. The dynamics of of $\psi(\mathbf{x},t|\mathbf{x}_0,t_0)$ are governed by the generalized conservation (Liouville) equation (*)

$$\left\{\frac{\partial}{\partial t^*} + w_j(t|\mathbf{x},t^*)\frac{\partial}{\partial x_j}\right\}\psi(\mathbf{x},t|\mathbf{x}_0,t^*) = 0 \tag{6.2 – 6}$$

which has the following Eulerian $(t = t^*)$ form

$$\left\{\frac{\partial}{\partial t} + u_j(\mathbf{x},t)\frac{\partial}{\partial x_j}\right\}\psi(\mathbf{x},t|\mathbf{x},t) = 0 \tag{6.2 – 6a}$$

and the following Lagrangian form $(t^* = t_0 = \text{const})$

$$v_j(\mathbf{x}_0,t)\frac{\partial}{\partial x_j}\psi(\mathbf{x},t|\mathbf{x}_0,t_0) = 0 \tag{6.2 – 6b}$$

Thus the essence of "approach (b)" of Section 6.2.1 is to introduce appropriate closure approximations in (6.2-6a) in order to finally derive a solvable master equation for G (see Section 6.3.2).

Knowledge of G allows direct calculation of the mean concentration field $\langle c\rangle$ at $(\mathbf{x},t)$, given its spatial distribution at t', as long as this is affected solely by linear processes, through the "fundamental Lagrangian theorem"

$$\langle c(\mathbf{x},t)\rangle = \int G(\mathbf{x},t|\mathbf{x}',t')\langle c(\mathbf{x}',t')\rangle \exp\left[-\int_{t'}^{t} k(t'')\,dt''\right] d\mathbf{x}' +$$

---

* We note here that in more complicated Lagrangian models, that incorporate interactions between the fluid particles, the dynamics of the instantaneous transition function will be governed by appropriate extensions of the Liouville equation, analogous to the Janossy equations described in Srinivasan (1969).

$$+\int\int_{t'}^{t} G\left(\mathbf{x},t|\mathbf{x}',t''\right)\, S\left(\mathbf{x}',t''\right)\exp\left[-\int_{t''}^{t} k\left(t'''\right)dt'''\right]dt''d\mathbf{x}' \qquad (6.2-7)$$

where S represents the spatial-temporal distribution of sources and k the rate of linear removal of the species with mean concentration $\langle c\rangle$.

At this point a digression is needed in order to clarify that, formally, the above equation must be written in terms of the Green's function for backward diffusion, i.e. with the point $(\mathbf{x},t)$ determing the constraint of the conditional density, as realized by Corrsin (1952) – see also Tennekes and Lumley, (1972, p.236). Nevertheless, for homogeneous-stationary turbulence, i.e. for the case to which most of the theoretical knowledge on turbulent dispersion is typically confined (and the starting approximation for more realistic descriptions),

$$G\left(\mathbf{x},t|\mathbf{x}_0,t_0\right) = G\left(\mathbf{x}_0,t_0|\mathbf{x},t\right)$$

as it was formally proved by Corrsin (1972) twenty years later. Thus the above requirement becomes a matter of notation rather than of substance; the same however is not true with regard to many-particle transition functions and the estimation of higher concentration moments (see relevant discussion later in the present subsection).

Another important point is that G also provides the connection between the Lagrangian methodology and the approaches (typically Eulerian) that result directly in some governing equation for $\langle c\rangle$. Indeed if G and $\langle c\rangle$ are related through (6.2-7), and G is governed by

$$\frac{\partial G}{\partial t} + \mathcal{L}G = 0 \qquad (6.2-7a)$$

where $\mathcal{L}$ is an *arbitrary* linear operator, then $\langle c\rangle$ must obey the equation

$$\frac{\partial\langle c\rangle}{\partial t} + \mathcal{L}\langle c\rangle + k(t)\langle c\rangle = S(\mathbf{x},t) \qquad (6.2-7b)$$

At this point it is useful to introduce the Eulerian space-time and the Lagrangian temporal velocity correlation functions (tensors), whose elements for stationary and homogeneous turbulence are

$$R_{ij}^{E}\left(\mathbf{x}-\mathbf{x}_0,t-t_0\right) = \left\langle u_i\left(\mathbf{x},t\right)u_j\left(\mathbf{x}_0,t\right)\right\rangle$$

$$R_{ij}^{L}(t-t_0|\mathbf{x}_0) = R_{ij}^{L}(t-t_0) = R_{ij}^{L}(\tau) = \langle v_i(\mathbf{x}_0,t)\, v_j(\mathbf{x}_0,t_0)\rangle$$

(Typically the turbulent velocity fluctuations about the corresponding ensemble mean values are used in these definitions.) Now, the formal relation between R_{ij}^{E} and R_{ij}^{L} can be obtained by writing R_{ij}^{L} as

$$\begin{aligned} R_{ij}^{L}(t-t_0) &= \langle u_i(\mathbf{x}=\mathbf{y}(\mathbf{x}_0,t),t)\ u_j(\mathbf{x}_0,t_0)\rangle = \\ &= \int \langle u_i(\mathbf{x},t)\, u_j(\mathbf{x}_0,t)\ \delta[\mathbf{x}-\mathbf{y}(\mathbf{x}_0,t)]\rangle = d\mathbf{x} \\ &= \int \langle u_i(\mathbf{x},t)\, u_j(\mathbf{x}_0,t)\ \psi(\mathbf{x},t|\mathbf{x}_0,t_0)\rangle\, d\mathbf{x} \qquad (6.2-8) \end{aligned}$$

The above equation reduces to an "applicable" form through a hypothesis introduced by Corrsin (1959, p.162), and known as *"Corrsin's conjecture"* or *"independence hypothesis,"* which, in the present framework of analysis, can essentially be stated as

$$\langle u_i(\mathbf{x},t)\, u_j(\mathbf{x}_0,t)\ \psi(\mathbf{x},t|\mathbf{x}_0,t_0)\rangle = \langle u_i(\mathbf{x},t)\, u_j(\mathbf{x}_0,t)\rangle \langle \psi(\mathbf{x},t|\mathbf{x}_0,t_0)\rangle \qquad (6.2-9)$$

The conditions under which this hypothesis should be valid, as well as corrections for other conditions, have been studied and discussed by Weinstock (1976).

Introducing (6.2-9) in (6.2-8) one has

$$R_{ij}^{L}(t-t_0) = \int R_{ij}^{E}(\mathbf{x}-\mathbf{x}_0,t-t_0)\, G(\mathbf{x}-\mathbf{x}_0,t-t_0)\, d\mathbf{x} \qquad (6.2-10)$$

From a practical viewpoint the applicability of (6.2-10) is limited by our lack of knowledge about G; in fact the most straightforward methods available for theoretically predicting G are based on an a priori knowledge of R_{ij}^{L}.

Finally, to complete this summary of basic concepts, we mention that two-particle (and many-particle) stochastic (and deterministic) Green's functions are similarly defined:

$$\begin{aligned} &\psi\left(\mathbf{x}^{(1)},t_1;\mathbf{x}^{(2)},t_2|\mathbf{x}_0^{(1)},t_{01};\mathbf{x}_0^{(2)},t_{02}\right) = \\ &= \delta\left[\mathbf{x}^{(1)}-\mathbf{y}\left(t|\mathbf{x}_0^{(1)},t_{01}\right);\mathbf{x}^{(2)}-\mathbf{y}\left(t|\mathbf{x}_0^{(2)},t_{02}\right)\right] \end{aligned}$$

$$G\left(\mathbf{x}^{(1)},t_1;\mathbf{x}^{(2)},t_2|\mathbf{x}_0^{(1)},t_{01};\mathbf{x}_0^{(2)},t_{02}\right)=\left\langle\psi\left(\mathbf{x}^{(1)},t_1;\mathbf{x}^{(2)},t_2|\mathbf{x}_0^{(1)},t_{01};\mathbf{x}_0^{(2)},t_{02}\right)\right\rangle$$

However the use of many-particle Green's functions (e.g., for the calculation of two-point covariances of concentration through equations similar to (6.2-7)) is associated with some subtle problems, relevant to the concept of backward diffusion, that have often been neglected in atmospheric dispersion modeling (see Sawford, 1983b, for a relevant discussion). Indeed, contrary to what holds for single-particle transition functions, for the corresponding two-particle functions one has

$$G\left(\mathbf{x}^{(1)},t_1;\mathbf{x}^{(2)},t_2|\mathbf{x}_0^{(1)},t_{01};\mathbf{x}_0^{(2)},t_{02}\right)\neq G\left(\mathbf{x}_0^{(1)},t_{01};\mathbf{x}_0^{(2)},t_{02}|\mathbf{x}^{(1)},t_1;\mathbf{x}^{(2)},t_2\right)$$

even for homogeneous–stationary turbulence. However, in connection to relative dispersion, that can be directly seen as a two-particle problem, these subtleties are more relevant to modeling higher order moments, whereas mean concentrations require only appropriate "distance-neighbour" functions – to be discussed later – that are obtained through integration of the two-particle transition functions. Thus, by examining dispersion relative to the meandering center of mass, we essentially use always single-particle Green's functions.

6.2.3 Fixed and Meandering Frame Representations: Position Moments and Relative Dispersion

We now proceed to define and discuss some quantities that are essential in the description of relative or two-particle turbulent dispersion (equivalently dispersion with respect to the center of mass of dispersion or with respect to a meandering frame). Use of the stochastic and deterministic functions defined in the previous section allows a formal construction of these definitions. For simplicity we confine attention to instantaneous releases(*), or, equivalently, to subsets of particles that

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(*) A continuous release will be viewed as a sequence of instantaneous releases. For a (slender) atmospheric plume in particular, where dispersion is negligible compared to advection in the direction of the mean wind, every cross-section of the plume perpendicular to its centerline (of differential thickness) can be seen as the result of such an instantaneous release.

have the same age. Without any loss of generality we set $\mathbf{x}_0 = 0$, $t_0 = 0$ (and assume this implicitly included in the definitions that follow).

(I) The position of the center of mass of the marked fluid particles in any instantaneous (say the α-th) realization of the dispersion field will be

$$_\alpha\overline{\mathbf{y}}\,(t) = \int {}_\alpha\overline{\psi}\,(\mathbf{x},t)\,\mathbf{x}d\mathbf{x} \qquad (6.2-11)$$

Clearly this quantity is a random function of time. An alternative interpretation of $_\alpha\overline{\mathbf{y}}\,(t)$ is that of the random spatial average position of any single fluid particle in the α-th realization.

(II) The ensemble average position of the center of mass of all fluid particles at time t (i.e. averaged over all possible positions of all fluid particles) will be

$$\langle\overline{\mathbf{y}}\,(t)\rangle = \int \mathbf{x}\left\langle\overline{\psi}\,(\mathbf{x},t)\right\rangle d\mathbf{x} \qquad (6.2-12a)$$

i.e.

$$\langle\overline{\mathbf{y}}\,(t)\rangle = \int \mathbf{x}G\,(\mathbf{x},t)\,d\mathbf{x} \qquad (6.2-12b)$$

When there is no mean flow (or if we consider an *inertial* coordinate system that follows the mean flow) $\langle\overline{\mathbf{y}}\,(t)\rangle \equiv 0$.

At this point we introduce the following definitions:

- ***Absolute Diffusion*** is diffusion with respect to $\langle\overline{\mathbf{y}}\,(t)\rangle$, i.e. with respect to a frame of reference with axes that remain parallel to fixed directions and origin that follows $\langle\overline{\mathbf{y}}\,(t)\rangle$. Since, for steady mean flow, motion in this frame is given by a straightforward Galilean transformation of the corresponding motion with respect to a frame fixed to the ground, we may use the term *"fixed frame representation"* for the description of turbulent dispersion in this frame. A more exact term is *"deterministic inertial frame representation."* Here the term "deterministic" has been used to discriminate from the representation with respect to ensembles of inertial frames, each frame moving with constant velocity randomly selected from an appropriate set. This description constitutes a conceptually subtle but very important approach that will be discussed later, in Section 6.4.2.

- *Relative Diffusion* is diffusion with respect to the (random) ${}_\alpha\overline{\mathbf{y}}(t)$, i.e. with respect to a frame of reference with axes that remain parallel to fixed directions and origin that follows the random motion of ${}_\alpha\overline{\mathbf{y}}(t)$. This is a *"meandering"* or *"non-inertial"* frame (undergoing random accelerations). (In the following we will further discuss the terms "two-particle dispersion", "puff" or "cluster" dispersion and "conditioned dispersion".)

(III) The "extent of dispersion" of the systems of fluid particles, in the non-inertial and inertial frames of reference, will be described by:

(IIIa) a *dyadic* (2nd order tensor) of instantaneous weighted deviations from the (instantaneous) center of mass (of course these deviations will be stochastic variables)

$$ {}_\alpha\left[\tilde{\Sigma}_{ij}^{(R)}\right] = \int \left(\mathbf{x} - {}_\alpha\overline{\mathbf{y}}(t)\right)\left(\mathbf{x} - {}_\alpha\overline{\mathbf{y}}(t)\right) {}_\alpha\overline{\psi}(\mathbf{x},t)\, d\mathbf{x} \qquad (6.2-13a) $$

(Note the use of the indefinite or dyadic product of the deviation vectors in the above definition).

Now, let

$$ \mathbf{r} = \mathbf{x} - {}_\alpha\overline{\mathbf{y}}(t) $$

and let $\mathbf{y}^{(R)}$ be defined exactly as $\mathbf{y}$ but in the system of $\mathbf{r}$-coordinates (i.e. $\mathbf{y}^{(R)}$ is the position vector of the fluid particle in the meandering frame of reference). Then

$$ \left\langle \left[\tilde{\Sigma}_{ij}^{(R)}\right] \right\rangle = \int \mathbf{r}\mathbf{r} \left\langle \overline{\psi}(\mathbf{x},t) \right\rangle d\mathbf{x} = $$

$$ = \int \mathbf{r}\mathbf{r} \left\langle \overline{\psi}\left(\mathbf{r} + \int \overline{\psi}(\mathbf{x},t)\, \mathbf{x} d\mathbf{x}, t\right) \right\rangle d\mathbf{r} $$

We define

$$ G^{(R)}(\mathbf{r},t) = \left\langle \overline{\psi}\left(\mathbf{r} + \int \overline{\psi}(\mathbf{x},t)\, \mathbf{x} d\mathbf{x}, t\right) \right\rangle \qquad (6.2-13b) $$

(compare Monin and Yaglom, 1975, eq.24.56), to be discussed in the following sections, and

$$ \left[\Sigma_{ij}^{(R)}\right] \equiv \left\langle \left[\tilde{\Sigma}_{ij}^{(R)}\right] \right\rangle = \left\langle \mathbf{y}^{(R)}\mathbf{y}^{(R)} \right\rangle \qquad (6.2-13c) $$

(IIIb) a dyadic of standard deviations from the ensemble average center of mass (a deterministic tensor)

$$[\Sigma_{ij}] = \int (\mathbf{x} - \langle \overline{\mathbf{y}}\,(t)\rangle)\,(\mathbf{x} - \langle \overline{\mathbf{y}}\,(t)\rangle)\,\langle \overline{\psi}\,(\mathbf{x},t)\rangle\,d\mathbf{x} =$$

$$[\Sigma_{ij}] = \int (\mathbf{x} - \langle \overline{\mathbf{y}}\,(t)\rangle)\,(\mathbf{x} - \langle \overline{\mathbf{y}}\,(t)\rangle)\,G\,(\mathbf{x},t)\,d\mathbf{x} \qquad (6.2-14a)$$

Thus, when the reference frame is chosen so that $\langle \overline{\mathbf{y}}\,(t)\rangle = 0$, as is typically done for the definition of Σ_{ij},

$$[\Sigma_{ij}] = \langle \mathbf{y}\mathbf{y}\rangle \qquad (6.2-14b)$$

From definition (6.2-13a) now follows that

$${}_{\alpha}\left[\tilde{\Sigma}_{ij}^{(R)}\right] = \int {}_{\alpha}\overline{\psi}\,(\mathbf{x},t)\,\times$$

$$\times\left[(\mathbf{x} - \langle \overline{\mathbf{y}}\,(t)\rangle)\,(\mathbf{x} - \langle \overline{\mathbf{y}}\,(t)\rangle) - ({}_{\alpha}\overline{\mathbf{y}}\,(t) - \langle \overline{\mathbf{y}}\,(t)\rangle)\,({}_{\alpha}\overline{\mathbf{y}}\,(t) - \langle \overline{\mathbf{y}}\,(t)\rangle)\right] d\mathbf{x}$$

and, after ensemble averaging,

$$\left[\Sigma_{ij}^{(R)}\right] = [\Sigma_{ij}] - \langle({}_{\alpha}\overline{\mathbf{y}}\,(t) - \langle \overline{\mathbf{y}}\,(t)\rangle)\,({}_{\alpha}\overline{\mathbf{y}}\,(t) - \langle \overline{\mathbf{y}}\,(t)\rangle)\rangle$$

or

$$[\Sigma_{ij}] = \left[\Sigma_{ij}^{(R)}\right] + \left[\Sigma_{ij}^{(M)}\right] \qquad (6.2-15)$$

where

$$\left[\Sigma_{ij}^{(M)}\right] = \langle({}_{\alpha}\overline{\mathbf{y}}\,(t) - \langle \overline{\mathbf{y}}\,(t)\rangle)\,({}_{\alpha}\overline{\mathbf{y}}\,(t) - \langle \overline{\mathbf{y}}\,(t)\rangle)\rangle \qquad (6.2-16a)$$

or, for $\langle \overline{\mathbf{y}}\,(t)\rangle = 0$

$$\left[\Sigma_{ij}^{(M)}\right] = \langle {}_{\alpha}\overline{\mathbf{y}}\,(t)\,{}_{\alpha}\overline{\mathbf{y}}\,(t)\rangle \qquad (6.2-16b)$$

In other words expression (6.2-15) states that each element of the variance tensor of the ensemble of positions of all the fluid particles is equal to the ensemble average of the corresponding element of the tensor of instantaneous spatial variances from the instantaneous center of mass plus an ensemble mean square deviation of the individual centers of mass of possible realizations from the ensemble average center of mass. More simply, the above states that total (i.e. absolute) dispersion is the "sum" of relative dispersion and meandering.(*) The situation discussed in the preceding paragraphs is also depicted schematically in Figure 6-1.

Typically, in atmospheric modeling, the off-diagonal elements of the above tensors, Σ_{ij} etc., are assumed negligible (see also Seinfeld, 1975, for the relevant discussion concerning K-theory applications). In the present work we have also adopted this assumption (nevertheless, it should be noted that the analysis of the following sections is not in general restricted by this approximation). Discussion of its validity is beyond the scope of this presentation; however, the interested reader is referred to Tavoularis and Corrsin (1985) for a relevant study.

The diagonal elements of Σ_{ij} etc. will be denoted as

$$\Sigma_{ii} = \sigma_i^2 \qquad (6.2-17a)$$

$$\Sigma_{ii}^{(R)} = \sigma_{R_i}^2 \qquad (6.2-17b)$$

$$\Sigma_{ii}^{(M)} = \sigma_{M_i}^2 \qquad (6.2-17c)$$

and are recognized as the absolute dispersion relative dispersion, and meandering parameters respectively.

Two-Particle Dispersion Concepts and Distance-Neighbour Functions (or Special Transition Functions)

In the preceding paragraphs relative dispersion was identified as dispersion with respect to the instantaneous center of mass of the system of fluid particles. Another description of the same process is formulated in terms of the separation of two arbitrary fluid particles in the instantaneous release (or two particles of the same age

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[*] This is true for homogeneous-stationary turbulence. In general one can also identify components of the total observed dispersion due to other effects, such as buoyancy and shear (see, e.g., Pasquill, 1975; McRae et al., 1982). For an introduction to the dispersive action of these effects one may consult Csanady (1973) or Fischer et al. (1979) – see also the discussion of the kinematic analysis of dispersion in Section 6.3 for further relevant references.

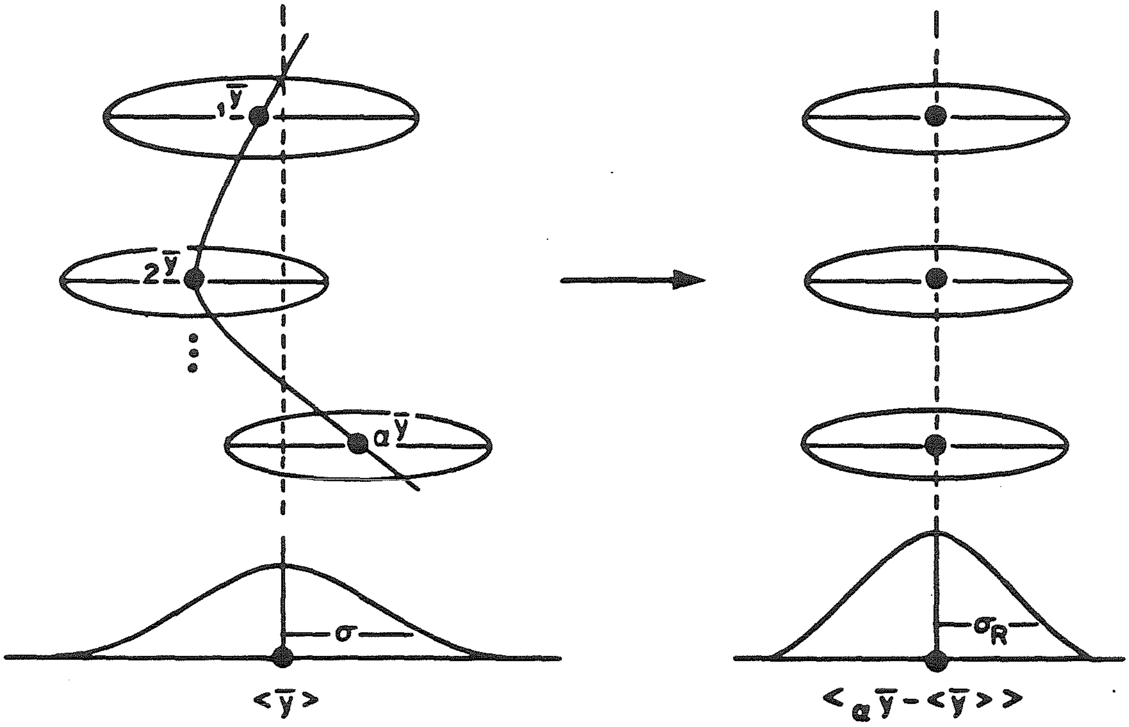

Figure 6-1

Schematic Representation of

Relative and Absolute (Relative plus Meandering) Dispersion in a continuous release). Indeed, it was first perceived by Richardson (1926), and exploited theoretically by Batchelor (1952), that relative diffusion is closely linked to the rate at which two individual fluid particles separate. The first analyses of instantaneous dispersion were actually in terms of the probability densities of two-particle separations.

The equivalence between two-particle dispersion and dispersion with respect to the center of mass in an instantaneous release is implicitly or explicitly assumed in almost all standard references of the subject of turbulence and turbulent dispersion. However, there are various subtle points in formally relating the statistics of the motion of a single pair of particles to the "observable" statistics of puffs and plumes that are typically attributed to relative dispersion. Many authors simply do not address this problem; however one can find an informative discussion of relevant concepts in Monin and Yaglom (1975, pp.536-584 – see in particular pp.551-555, 577). What needs to be stressed here is that the equivalence between single pair motion and relative dispersion is strictly valid only for homogeneous turbulence and after the fluid particles have "forgotten" their initial separation (see also Fischer et al. 1979, p.75).

Studying the separation of a pair of fluid particles is of course, always equivalent to studying the random motion of a single particle (labelled, say, #1), with "fixed" frame position vector $\mathbf{y}^{(1)}$, in a (noninertial) reference frame 0s that follows the random motion of another arbitrary particle (#2) with "fixed" frame position vector $\mathbf{y}^{(2)}$, (in the same way the meandering frame that was introduced earlier follows the motion of the instantaneous center of mass). The first step towards defining the equivalent of the inertial frame transition function G in the 0s frame (which of course gives the expected concentration in the random non-inertial frame 0s), to be called $G^{(S)}$, is to integrate the joint (two-particle) deterministic Green's function $G\left(\mathbf{x}^{(1)}, t_1; \mathbf{x}^{(2)}, t_2 | \mathbf{x}_0^{(1)}, t_{01}; \mathbf{x}_0^{(2)}, t_{02}\right)$ with respect to $\mathbf{x}^{(2)}$ (see also Leslie, 1973, p.179). In fact, setting $\mathbf{x}_0^{(2)} = \mathbf{x}_0$, $\mathbf{x}_0^{(1)} = \mathbf{x}_0 + \mathbf{s}_0$, $\mathbf{x}^{(2)} = \mathbf{x}$, $\mathbf{x}^{(1)} = \mathbf{x} + \mathbf{s}$, we define

$$G^{(2P)}(\mathbf{s}, t_1, t_2 | \mathbf{x}_0, \mathbf{s}_0, t_{01}, t_{02}) =$$

$$= \int G(\mathbf{x} + \mathbf{s}, t_1; \mathbf{x}, t_2 | \mathbf{x}_0 + \mathbf{s}_0, t_{01}; \mathbf{x}_0, t_{02})\, d\mathbf{x}_0 \qquad (6.2-18)$$

Thus $G^{(2P)}$ is the transition probability density of the two-particle separation vector, conditioned on the initial separation. In the special case of homogeneous-stationary turbulence and fluid particles of the same age $(t_{01} = t_{02} = 0, t_1 = t_2 = t)$ we have

$$G^{(2P)} = G^{(2P)}(\mathbf{s}, t | \mathbf{s}_0)$$

If $q(\mathbf{s}_0)$ is the probability density of the initial separation vector, then $G^{(S)}$ is defined as

$$G^{(S)}(\mathbf{s}, t) = \int G^{(2P)}(\mathbf{s}, t | \mathbf{s}_0)\, q(\mathbf{s}_0)\, d\mathbf{s}_0 \qquad (6.2-19)$$

After sufficient time from the release (when initial separations are forgotten)

$$G^{(2P)}(\mathbf{s}, t) = G^{(S)}(\mathbf{s}, t)$$

The dispersion process described by $G^{(S)}$ is typically what is called "puff" or "cluster" diffusion in the literature; for Monin and Yaglom (1975) this is is defined to be the "relative dispersion process".

Another common approximation is that the information carried by $G^{(S)}(\mathbf{s}, t)$ is equivalent to the information carried by $G^{(R)}(\mathbf{r}, t)$, as this was defined through (6.2-13b). Of course $G^{(S)}$ is the transition probability of the position of any fluid particle as seen in the frame of another (arbitrary but fixed) fluid particle; this transition function is essentially equivalent to the *distance-neighbour function* introduced (in a less formal manner) by Richardson (1926), although this term is often attributed to $G^{(2P)}$ rather than to $G^{(S)}$ (e.g. Leslie, 1973). $G^{(R)}$ is the transition probability of fluid particle positions in the meandering center of mass frame. We will refer to $G^{(2P)}$, $G^{(S)}$ and $G^{(R)}$ as "special" (non-inertial frame) transition functions and focus on $G^{(R)}$ which has been the basis for the description of instantaneous dispersion in the TRPM model.

The single most important direct relationship between the 0r and 0s descriptions concerns the second order dispersion tensors in these frames. Letting $\mathbf{y}^{(S)}$ be the position vector of *any* fluid particle in the 0s frame one can define the second moments of $G^{(S)}$ with respect to the separation vector. The corresponding dyadic is

$$\left[\Sigma_{ij}^{(S)}\right] = \int \left(\mathbf{s} - \mathbf{y}^{(2)}\right)\left(\mathbf{s} - \mathbf{y}^{(2)}\right) G^{(S)}\left(\mathbf{s}, t\right)\, d\mathbf{s} \qquad (6.2-20a)$$

or

$$\left[\Sigma_{ij}^{(S)}\right] = \left\langle \mathbf{y}^{(S)}\mathbf{y}^{(S)} \right\rangle \qquad (6.2-20b)$$

Straightforward calculations (Brier, 1950; Batchelor, 1952 – see also Monin and Yaglom, 1975, p.555) then show that

$$\left[\Sigma_{ij}^{(S)}\right] = 2\left(\left[\Sigma_{ij}\right] - \left[\Sigma_{ij}^{(M)}\right]\right) = 2\left[\Sigma_{ij}^{(R)}\right] \qquad (6.2-21)$$

Thus, the ensemble mean-square separation in all the pairs of diffusing particles, in an instantaneous release, is just twice their mean square distance from the center of mass of this release.

A final point to note is that in (6.2-20) $\Sigma_{ij}^{(S)}$ is defined in terms of $G^{(S)}\left(\mathbf{s}, t\right)$, which incorporates a full statistical description of the initial distribution of fluid particles. An alternative approach is to define a dispersion tensor $\Sigma_{ij}^{(2P)}$ that is conditioned on the value of the initial separation by using $G^{(2P)}$ (see Monin and Yaglom, 1975, where this approach is employed). Then

$$\Sigma_{ij}^{(S)}\left(\mathbf{s}, t\right) = \int \Sigma_{ij}^{(2P)}\left(\mathbf{s}, t | \mathbf{s}_0\right)\, q\left(\mathbf{s}_0\right) d\mathbf{s}_0 \qquad (6.2-22)$$

6.3 THE MODIFIED ADE: DISCUSSION AND JUSTIFICATION

The objectives of the present section are

(i) to discuss the character of the special transition function $G^{(R)}$ in relation to that of the inertial frame G, (equivalently: the nature of the expected concentration profile in the random meandering frame), and

(ii) to explain the nature of the assumptions leading to a representation of G and $G^{(R)}$, (or of the corresponding expected concentration fields) and of the differential evolution equations that govern these quantities, in terms of diffusivities that depend on diffusion time, showing also the connection of these representations to various common dispersion models.

6.3.1 Fixed and Meandering Frame Representations: Point Releases and Green's Functions

As it has often been repeated in this work, a fundamental assumption in the formulation of both the master and peripheral components of the TRPM is that the expected concentration fields in both a fixed and a meandering frame of reference are governed by (parabolic partial differential) equations of identical structure (differing only in the values of the diffusivities employed). In other (but equivalent) words it is assumed that G and $G^{(R)}$ are identical in form, with different parameters. We will discuss this assumption here, focusing first on our knowledge regarding the aforementioned Green's functions for ideal situations; the general structure of the governing equations is discussed in the next subsections.

Let us consider in particular a "point" release of inert material in homogeneous stationary turbulence. Confining attention to the common case of slender plumes, where downwind advection dominates turbulent dispersion in the same direction, we can equivalently consider the instantaneous puff problem: a cross section of the plume (of differential thickness) will essentially contain all the fluid particles released from the source in a given differential time interval. Thus the terms Green's function and expected concentration (for both the fixed frame and the puff or meandering frame cases) can be used interchangeably.

In the special case of homogeneous and stationary turbulence with random velocity components that obey Gaussian densities the inertial frame Green's functions G are of course Gaussian (the boundary conditions imposing appropriate finite or infinite combinations of Gaussian functions). This exact theoretical fact is indeed the first step towards the Gaussian plume approximation of actual field dispersion. However, even in the idealized case where G is exactly Gaussian for all times t, the correspondind $G^{(R)}$ is not always unambiguously known. Without delving into fine details (for which the reader is referred to Monin and Yaglom, 1975, secs.24.2, 24.3) we note that the relative motion of fluid particles undergoes a sequence of stages. Very schematically these stages are: (i) first, a *"source conditioned motion,"* dependent on the initial distribution of separations among the fluid particles, (ii) second, a so called *"quasi-asymptotic motion"* (Batchelor, 1952), where the effect of the initial conditions has become negligible, but the motions of any two particles are still correlated, (iii) third, an *"asymptotic motion,"* where the motions of different fluid particles are practically independent, and, finally, (iv) a *"large scale motion,"* where the average separation between two particles becomes very large compared with the integral scale of turbulence and relative diffusion becomes identical to absolute diffusion (and of course $G = G^{(R)}$). The common A.D.E. is relevant to this final stage. Here our interest is mainly in stages (ii) and (iii), since, on one hand, we consider "point" sources and thus in general wish to avoid introducing source parameters other than the emissions rate in our models (*), and, on the other hand, available observations show that this stage in the atmosphere lasts for only a few seconds (see, e.g., Hanna et al. 1982, p.42).

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* One must also take into account that identifying an effective initial distribution of separations for an actual source is far from being a trivial matter.

Let us consider first the stage of asymptotic motion where the trajectories of different fluid particles in the puff (i.e. of same age in the plume) are statisticaly independent. Then, if the number N of these fluid particles is large enough ($N \to \infty$), the random trajectory of the center of mass of any $N-1$ particles is practically identical to that of the center of mass of all N particles, and, further, this trajectory and that of the N-th particle are statistically independent. In other words $\mathbf{r}$ and $\overline{\mathbf{y}}\,(t)$ are independent random variables whose sum $\mathbf{x} = \mathbf{r} + \overline{\mathbf{y}}\,(t)$ has a Gaussian probability density G. This however directly implies that, according to an important theorem due to Cramér (see Papoulis, 1965, p.222), the probability densities of $\overline{\mathbf{y}}\,(t)$ and $\mathbf{r}$ (the latter being exactly $G^{(R)}$) are also Gaussian. The Gaussian character of $G^{(R)}$ for the asymptotic stage, which plays a key role in the formulation of the TRPM, was demonstrated here in a very straightforward manner (that–to our knowledge–has not appeared formally in the literature before) strictly for point releases in homogeneous stationary turbulence, but it can be considered a plausible approximation in more general cases where homogeneity and stationarity of the turbulent velocity field are not strongly violated (the mean concentration field is of course inhomogeneous).

In the stage of quasi-asymptotic motion the shape of $G^{(R)}$ (more commonly referred to as the expected concentration distribution relative to the center of gravity of a cloud) has been a subject of continuing controversy. Typically it is assumed that for a substantial fraction of the duration of the stage of quasi-asymptotic motion the instantaneous dimensions of the dispersing cloud "most probably" do not exceed the maximum scales of the inertial subrange. Inertial subrange scaling and similarity analysis for locally isotropic turbulence allow for various modeling schemes that lead to different forms of $G^{(R)}$. (see also Monin and Yaglom, 1975, p.577, and Pasquill and Smith, 1983, p.153). Among the possible admissible models (on similarity grounds) the three most widely considered and discussed are essentially equivalent to semiempirical parabolic partial differential equations for $G^{(R)}\,(\mathbf{r}, t)$, with eddy diffusivities that depend on either the dispersion time t or the distance from the center of mass $r = |\mathbf{r}|$, or both. These are

- the Batchelor-Obukhov equation (see, e.g., Monin and Yaglom, 1975, secs. 24.2, 24.3), with

$$K \sim \epsilon t^2$$

producing a Gaussian solution (that decreases at infinity as $\exp\left(-br^2\right)$, b being an appropriate constant),

- the Richardson (1926) equation with

$$K \sim \epsilon^{1/3} r^{4/3}$$

producing a solution that is more steeply peaked than the Gaussian (and decreases at infinity as $\exp\left(-br^{2/3}\right)$), and

- the Okubo (1962) equation with

$$K \sim \epsilon^{2/3} r^{2/3} t$$

producing a solution that decreases at infinity as $\exp\left(-br^{2/3}\right)$.

(Note that the average value ϵ of the actually fluctuating energy dissipation rate is used in the above equations).

Thus, in the Batchelor-Obukhov formulation – the one leading to a *linear* equation for $G^{(R)}(\mathbf{r}, t)$ – only statistics of the fluid particle positions in the meandering frame (or the two-particles separation), i.e. their variances, affect the parameters of the governing equations for relative dispersion, whereas in the nonlinear models these parameters are functions of the actual position in this frame.

Available observations have not allowed for a definite conclusion on the superiority of the above schemes. Although some sets of data show excellent agreement with the Gaussian model (e.g. Csanady, 1966; Sullivan, 1971 – see also Figure 5-1 of the previous chapter) in certain cases some researchers have found a slightly better agreement with nonlinear models (e.g. Okubo, 1962). In view of the analytical advantages of the linear model, its proven validity for times beyond those of the quasi-asymptotic stage, and supportive observational evidence, it seems very reasonable to accept it as the universal model for all dispersion times. This is in agreement with the recommendations of Monin and Yaglom (1975, pp. 562 and 578), and with practically all applied studies of instantaneous plume properties, such as Gifford's (1959) fluctuating plume model and Csanady's (1973) relative dispersion and fluctuations models.

What comes as an overall conclusion of the above discussion is that (at least in the ideal case of homogeneous stationary turbulence examined here) assuming $G(\mathbf{x}, t)$ and $G^{(R)}(\mathbf{r}, t)$ to have similar forms, and be governed by equations of similar structure, is a reasonable assumption. We will adopt this assumption as a first approximation for studying dispersion processes in more complicated turbulent fields. In the following we overview the most common equations that have been used to model G (most of which are also assumed appropriate for modeling $G^{(R)}$).

6.3.2 Master Equations and Practical Models

Obtaining the analytical form of the transition function $G(\mathbf{x}, t|\mathbf{x}_0, t_0)$ or, more generally, deriving a governing equation (a "master equation") for this probability, that, under certain simplifying assumptions, can be reduced to solvable form (analytically or numerically), constitutes the fundamental problem of the transition function Lagrangian approach.(*)

In the special case where the turbulent Lagrangian velocity field is unbounded and, beyond being homogeneous and stationary, is also Markovian and Gaussian with independent components (i.e. every component of the velocity vector is Gaussian and has an exponential autocorrelation: an Örnstein-Uhlenbeck process), and, furthermore, the fluid particle trajectories are independent, it can be directly shown, through kinematic considerations and the definition $G = \langle \psi \rangle$, that $G(\mathbf{x} - \mathbf{x}_0, t - t_0)$ is Gaussian. The details of the proof can be found in Seinfeld (1983, pp. 218-222).

Under the conditions where the common ADE is valid (briefly when the fluid

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[*] The alternative to this theoretical determination of the transition function is of course to use laboratory (e.g. Willis and Deardorff, 1978, 1981) or numerical (e.g. Deardorff, 1974; Lamb, 1978) simulations of turbulent flow fields.

particles motion can be seen as a discrete random walk that is a 1st order Markovian process with effective step lengths in space and time that are comparable to the Lagrangian space-time scales) G will correspond to the *fundamental solution* (i.e. the response to an impulse forcing term) of any linear form of the ADE (which is local in space and time).

On smaller scales, however, the equation governing G must reflect the persistence of correlation over finite space and time. Batchelor and Townsend (1956, p. 360) first suggested that this non-localness may be best expressed by an integrodifferential equation. Such an equation was first derived by Bourret (1960) who generalized a property of a simple model of turbulent diffusion due to Taylor that assumed a finite Lagrangian time, i.e., a persistence of velocity correlation over the fluid particles trajectory. Bourret's equation uses the Lagrangian velocity autocorrelation

$$R_{ij}^{L}\left(t-t_0\right)=\left\langle v_i'\left(t\right)v_j'\left(t_0\right)\right\rangle$$

and holds for homogeneous-stationary turbulence:

$$\frac{\partial G\left(\mathbf{x},t\right)}{\partial t}=\frac{\partial^2}{\partial x_i\partial x_j}\int_0^t R_{ij}^{L}\left(t-t'\right)G\left(\mathbf{x},t'\right)dt'$$

Other general integrodifferential master equations, for both one- and two-particle transition functions, utilizing Eulerian velocity autocorrelations, were subsequently derived by Roberts (1961) who employed Kraichnan's Direct Interaction Approximation to obtain closure for equation (6.2-6a).(*) Since then many interesting results of similar nature have been obtained, e.g., by Deissler (1961), Bourret (1962, 1965) Kraichnan (1966), Saffmann (1969), Knobloch (1977), Lundgren (1981), and Jiang (1984, 1985). In general the evolution of G is found to be described by nonlinear integrodifferential equations, closely resembling that of Roberts, which are closed by a truncation of a series of correlations. Recently developed methods are reviewed by Jiang (1985) who, for the dispersion of a single particle, derived an equation for G

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[*] The monograph of Leslie (1973) provides a comprehensive review of Kraichnan's methods and discusses extensively the equation of Roberts.

that, at the zeroth order, reduces to that of Roberts (while there are some differences regarding the behavior of the two-particle transition function dynamics).

From the perspective of the present discussion Roberts' equation (1961) provides a general framework of analysis that is more than adequate for practical purposes. Indeed, practically all first order operational models of (absolute and relative) turbulent dispersion, including the common ADE as well as the modified ADE adopted by the TRPM, can be derived as special cases of this equation when appropriate approximations are introduced. This procedure provides a most useful insight into the relative capabilities, limitations and relationships among the various "usable" models. So, in the following we will examine briefly the reduction of a general integrodifferential master equation into practical expressions.

The most general form of Roberts' (1961) equation (for the fixed frame G) is

$$\frac{\partial}{\partial t} G\left(\mathbf{x}, t | \mathbf{x}_0, t_0\right) = \int_{t_0}^{t'} dt' \int d\mathbf{x} R_{ij}^{E}\left(\mathbf{x}, t; \mathbf{x}', t'\right) \frac{\partial}{\partial x_i} G\left(\mathbf{x}, t | \mathbf{x}', t'\right) \frac{\partial}{\partial x_j} G\left(\mathbf{x}', t' | \mathbf{x}_0, t_0\right)$$

For homogeneous–stationary turbulence this equation becomes

$$\frac{\partial}{\partial t} G\left(\mathbf{x}, t\right) = \frac{\partial^2}{\partial x_i \partial x_j} \int_0^t dt' \int d\mathbf{x}' R_{ij}^{E}\left(\mathbf{x}', t'\right) G\left(\mathbf{x}', t'\right) G\left(\mathbf{x} - \mathbf{x}', t - t'\right) \qquad (6.3-3a)$$

Roberts (1961, p.266) replaced the product $R_{ij}^{E}\left(\mathbf{x}, t\right) G\left(\mathbf{x}, t\right)$ with a general correlation $Q_{ij}\left(\mathbf{x}, t\right)$. Hence, if Corrsin's conjecture holds, Q_{ij} is formally related to to R_{ij}^{L}, and Roberts' equation is now written as

$$\frac{\partial}{\partial t} G\left(\mathbf{x}, t\right) = \frac{\partial^2}{\partial x_i \partial x_j} \int_0^t dt' \int d\mathbf{x}' Q_{ij}\left(\mathbf{x}', t'\right) G\left(\mathbf{x} - \mathbf{x}', t - t'\right)$$

or, equivalently (for $\mathbf{x}'$ ranging from $-\infty$ to ∞),

$$\frac{\partial}{\partial t} G\left(\mathbf{x}, t\right) = \frac{\partial^2}{\partial x_i \partial x_j} \int_0^t dt' \int d\mathbf{x}' Q_{ij}\left(\mathbf{x} - \mathbf{x}', t - t'\right) G\left(\mathbf{x}', t'\right) \qquad (6.3-3b)$$

a result that is found to resemble strongly the equation of Bourret (see also following paragraphs).

Evolution equations for the special non-inertial transition functions have also been formally derived (in particular for $G^{(2P)}$). The reader is referred to Leslie (1973) and Jiang (1985) for detailed analyses. As a representative example we mention that on the basis of the analysis of Roberts (and the equivalence of $G^{(S)}$ and $G^{(R)}$ after very small times) the analog of (6.3-3a) for $G^{(R)}(\mathbf{r},t)$ becomes approximately

$$\frac{\partial}{\partial t}G^{(R)}(\mathbf{r},t)=\frac{\partial^2}{\partial r_i\partial r_j}\int_0^t dt'\int d\mathbf{r}'\left[R_{ij}^E(\mathbf{r}',t')-R_{ij}^E(\mathbf{r}-\mathbf{r}',t')\right]\times$$
$$\times G(\mathbf{x}',t')\;G^{(R)}(\mathbf{r}-\mathbf{r}',t-t')$$

One should notice the dependence of the term replacing the Eulerian velocity correlation of (6.3-3a) on both $\mathbf{r}-\mathbf{r}'$ and $\mathbf{r}'$. For the purposes of the present work it seems reasonable to assume that the last equation can be represented in general by an equation identical to (6.3-3b) but with Q_{ij} depending on t as well as on $t-t'$ to reflect the nonstationarity present in the Lagrangian velocity correlations in the non-inertial frame (to be also discussed in the next section).

Dispersion Parameters
(through the G-formalism)

Equations (6.3-3ab) – or the corresponding equations for $G^{(R)}(\mathbf{r},t)$ – can be combined directly with the definitions of the dispersion parameters Σ_{ij} etc. in order to express the latter directly in terms of the general correlation Q_{ij}. Defining the *turbulent diffusivities*

$$K_{ij}=\frac{1}{2}\frac{d}{dt}\Sigma_{ij}$$

and using definition (6.2-14a) one has

$$K_{ij}=\frac{1}{2}\int x_i x_j dx\frac{\partial^2}{\partial x_m\partial x_n}\int_0^t dt'\int d\mathbf{x}'Q_{mn}(\mathbf{x}-\mathbf{x}',t-t')\;G(\mathbf{x}',t')=$$
$$=\int_0^t dt'\int d\mathbf{x}d\mathbf{x}'Q_{ij}(\mathbf{x}-\mathbf{x}',t-t')\;G(\mathbf{x}',t')$$

and, since $\int G(\mathbf{x},t)\,d\mathbf{x}=1$,

$$K_{ij}=\int_0^t dt'\int d\mathbf{x}Q_{ij}(\mathbf{x}-\mathbf{x}',t-t') \qquad (6.3-4)$$

A similar general expression will hold for the relative turbulent diffusivities $K_{ij}^{(R)}$.

Applicable Models of Dispersion

Let us now examine the applicable models that are obtained for various choices of Q_{ij} in (6.3-3b). Without loss of generality we consider an one-dimensional situation with $Q_{ij} = Q$.

• *A.D.E.: The Classic K-Model*

If

$$Q = K\,\delta\,(x - x')\,\delta\,(t - t') \qquad (6.3-5a)$$

(with possibly $K = K\,(x,t)$) (6.3-3) reduces to the conventional K-model

$$\frac{\partial G\,(\mathbf{x},t)}{\partial t} = K \frac{\partial^2 G\,(\mathbf{x},t)}{\partial x^2} \qquad (6.3-5b)$$

Notice that condition (6.5-4a) implies that the velocity of a fluid particle is delta-correlated (i.e. "immediately forgets" its earlier values) in both space and time. This of course can be true only when the "time instants" are actually longer than the Lagrangian time scale of the flow (and the adverb "immediately" is interpreted analogously). Thus the severe limitations in the description of turbulent dispersion through the ADE, already discussed in Chapter 1, are obvious.

• *The Equation of Bourret*

If correlation is assumed only in time, i.e.

$$Q = \delta\,(x - x')\,R^L\,(t - t') \qquad (6.3-6a)$$

one obtains the (one-dimensional) form of Bourret's (1960) equation

$$\frac{\partial G\,(\mathbf{x},t)}{\partial t} = \frac{\partial^2}{\partial x^2} \int_0^t R^L\,(t - t')\,G\,(x,t')\,dt' \qquad (6.3-6b)$$

• *The Hyperbolic Telegrapher's Equation*

Assuming correlation only in time (as before) that is specifically of exponential form

$$Q = \delta\left(x - x'\right) R^L\left(t - t'\right) = \delta\left(x - x'\right) \sigma_v^2 \exp\left(-\frac{t - t'}{T^L}\right) \qquad (6.3 - 7a)$$

where T^L is the Lagrangian time scale, one obtains the well known telegrapher's equation (see, e.g., Goldstein, 1951).

$$\frac{\partial^2 G}{\partial t^2} = -\frac{1}{T^L}\frac{\partial G}{\partial t} + \sigma_v^2 \frac{\partial^2}{\partial x^2} \qquad (6.3 - 7b)$$

• *The Modified (Non-Local) A.D.E.*

The modified ADE is obtained through the same choice of Q as for the equation of Bourret (i.e. autocorrelation of fluid particle velocities only in time)

$$Q\left(x - x', t - t'\right) = \delta\left(x - x'\right) R^L\left(t - t'\right) \qquad (6.3 - 8a)$$

or

$$Q\left(r - r', t - t', t\right) = \delta\left(r - r'\right) R^L\left(t, t - t'\right) \qquad (6.3 - 7b)$$

under the additional assumption that the positions of the fluid particles constitute Markovian processes (with arbitrary step). Then, the Chapman–Kolmogorov equation for G gives (for arbitrary (x^*, t^*))

$$G\left(x - x_0, t - t_0\right) = \int\int G\left(x - x^*, t - t^*\right) G\left(x^* - x_0, t^* - t_0\right)\, dx^*\, dt^*$$

Introducing this property to the master equation one obtains

$$\frac{\partial G\left(x - x_0, t - t_0\right)}{\partial t} = \int_{t_0}^{t} dt'\, R^L\left(t - t'\right) \frac{\partial^2 G\left(x - x_0, t - t_0\right)}{\partial x^2}$$

which corresponds directly to a linear (non-local) differential dispersion equation with eddy diffusivities that depend on the travel time:

$$\frac{\partial G\left(x - x_0, t - t_0\right)}{\partial t} = K\left(t - t_0\right) \frac{\partial^2 G\left(x - x_0, t - t_0\right)}{\partial x^2} \qquad (6.3 - 8c)$$

where (for $t_0 = 0$)

$$K(t) = \int_0^t dt'\, R^L(t-t') \qquad (6.3-8d)$$

and similarly for $G^{(R)}(r,t)$ with

$$K^{(R)}(t) = \int_0^t dt'\, R^L(t, t-t')$$

- *The "Spectral Diffusivity" Model*

If one assumes correlation only in space, i.e.

$$Q = R^{\#}(x-x')\,\delta(t-t') \qquad (6.3-9a)$$

where $R^{\#}$ is an appropriate space correlation function, equation (6.3-3) reduces to

$$\frac{\partial G(x,t)}{\partial t} = \frac{\partial^2}{\partial x^2}\int dx'\, R^{\#}(x-x')\, G(x',t)$$

The r.h.s. of this equation can be writen as

$$-\frac{\partial}{\partial x}\int dx'\, R^{\#}(x'-x)\, G(x',t)$$

Integrating by parts this expression allows us to write

$$\frac{\partial G(\mathbf{x},t)}{\partial t} = \frac{\partial}{\partial x}\int R^{\#}(x-x')\,\frac{\partial G(x',t)}{\partial x'}dx' \qquad (6.3-9b)$$

This equation is essentially equivalent to the pseudo-spectral model of Berkowicz and Prahm (1979ab, 1980).

Thus now, after clarifying how the modified ADE is related to other turbulent dispersion models, we proceed to examine methods for the estimation of the (relative) dispersion parameters appearing in this equation.

6.4 RELATIVE DISPERSION ANALYSIS:
I. TIME DOMAIN METHODS

6.4.1 The Direct Kinematic Approach:
General Relations and Asymptotic Results

In this section we briefly review the fundamentals of the direct kinematic approach for estimating dispersion parameters. The general kinematic relations that describe the statistics of the fluid particle motions provide some direct information regarding these parameters in the form of asymptotic expressions; however in the case of relative dispersion this information is more limited than in the case of absolute dispersion. Further results can be obtained through dimensional/similarity analysis and on the basis of assumptions regarding the turbulent velocities correlation tensors; these results are also reviewed in the next sub-sections.

In the following exposition the turbulence is assumed (locally) homogeneous and stationary (unless it is specified otherwise). Furthermore, for simplicity (and without any loss of generality) the analysis of the present section assumes that there is no mean flow (or equivalently the equations are formulated in an inertial frame following the mean flow), i.e.

$$\langle \mathbf{u} \rangle = 0, \quad \langle \mathbf{v} \rangle = 0$$

and

$$\mathbf{u}' = \mathbf{u}, \quad \mathbf{v}' = \mathbf{v}$$

and therefore

$$\langle \overline{\mathbf{y}}\,(t) \rangle = 0, \quad \mathbf{y}'\,(t) = \mathbf{y}\,(t) = \mathbf{y}\,(0, t)$$

We further set $\mathbf{x}_0 = 0$, $\mathbf{y}\,(0,0) = 0$.

• *Review of Absolute Dispersion I*

General Relations and Definitions

Under the assumptions stated above

$$\Sigma_{ij}(t) = \langle y_i(t)\, y_j(t)\rangle = \left\langle \int_0^t v_i(t')\, dt' \int_0^t v_j(t'')\, dt'' \right\rangle =$$

$$= \int_0^t \int_0^t \langle v_i(t')\, v_j(t'')\rangle\, dt' dt''$$

or

$$\Sigma_{ij}(t) = \int_0^t \int_0^t R_{ij}^L(t' - t'')\; dt' dt'' =$$

$$= \int_0^t \int_0^{t-t'} R_{ij}^L(\tau)\, d\tau dt' \qquad (6.4-1a)$$

Equation (6.4-1a) and its differential counterpart

$$\frac{d}{dt}\langle y_i(t)\, y_j(t)\rangle = 2\int_0^t R_{ij}^L(t - t')\, dt' \qquad (6.4-1b)$$

are the well known *Taylor's relations* and constitute the basis of the direct kinematic approach (Taylor, 1921). Now, by definition $R_{ij}^L(\tau) = R_{ij}^L(-\tau)$. Hence

$$\Sigma_{ij}(t) = \int_0^t (t - \tau)\left[R_{ij}^L(\tau) + R_{ji}^L(\tau)\right] d\tau \qquad (6.4-2)$$

This relation was first obtained (in a slightly different form) by Kampé de Feriet (1939).(*)

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* At this point it seems worthy of mentioning that relations analogous to (6.4-1ab) and (6.4-2) can also be directly formulated for the case of dispersion in uniform shear flow ("second order homogeneous" turbulence); the corresponding exact expressions were first obtained by Corrsin (1953). Various (approximate) extensions of the fundamental (homogeneous-stationary turbulence) kinematic Lagrangian analysis to more realistic situations, involving wind-shear and convective motions, are also possible, but discussing them is beyond the scope of this presentation. An excellent introduction to the problems of dispersion in flows with shear and density differences can be found in Csanady (1973, Chapters V and VI); for more recent relevant reviews of kinematic methods for decribing fluid particle dispersion in complex (nonhomogeneous-nonstationary) flows one should consult Pasquill and Smith (1983) and Hunt (1985).

The (modified) eddy diffusivities K_{ij}^L are defined again as

$$K_{ij}^L(t) \equiv \frac{1}{2}\frac{\partial}{\partial t}\langle y_i(t)\, y_j(t)\rangle \tag{6.4 – 3a}$$

where the superscript L is used to note that they are derived from a Lagrangian analysis. Hence, in general

$$K_{ij}^L(t) = \frac{1}{2}\int_0^t \left[R_{ij}^L(\tau) + R_{ji}^L(\tau)\right]\delta\tau \tag{6.4 – 3b}$$

The elements of the Lagrangian time scale tensor are defined as

$$T_{ij}^L = \frac{1}{\left(\langle v_i^2\rangle\langle v_j^2\rangle\right)^{1/2}}\int_0^\infty \left[R_{ij}^L(\tau) + R_{ji}^L(\tau)\right]d\tau \tag{6.4 – 4}$$

• *Review of Absolute Dispersion II*

Asymptotic Results

The general relations (6.4-1ab) allow us to conclude directly that at very small and very large dispersion times the elements of $[\Sigma_{ij}]$ are independent of the particular form of the Lagrangian velocity correlation. Thus, for $t \to 0$

$$\Sigma_{ij}(t) = \langle v_i(0,0)\, v_j(0,0)\rangle\, t^2 \tag{6.4 – 5a}$$

or

$$K_{ij}^L(t) = \langle v_i(0,0)\, v_j(0,0)\rangle\, t \tag{6.4 – 5b}$$

whereas for $t \to \infty$

$$\Sigma_{ij}(t) = \left(\langle v_i^2\rangle\langle v_j^2\rangle\right)^{1/2}\left(T_{ij}^L + T_{ji}^L\right) t \tag{6.4 – 6a}$$

or

$$K_{ij}^L(\infty) = \frac{1}{2}\left(\langle v_i^2\rangle\langle v_j^2\rangle\right)^{1/2}\left(T_{ij}^L + T_{ji}^L\right) \tag{6.4 – 6b}$$

In particular for $i = j$ one has

$$(\text{ for } t \to 0) \quad \sigma_i^2 = \sigma_{v_i}^2 t^2, \quad K_i^L = \sigma_{v_i}^2 t \tag{6.4 – 5c}$$

$$(\text{ for } t \to \infty) \quad \sigma_i^2 = 2\sigma_{v_i}^2 T_i^L t, \quad K_i^L = \sigma_{v_i}^2 T_i^L \qquad (6.4-6c)$$

Of course for homogeneous-stationary turbulence

$$\sigma_{v_i}^2 = \sigma_{u_i}^2$$

- *Review of Absolute Dispersion III*

Extensions

As it was stated earlier, the above results were obtained for arbitrary Lagrangian velocity correlations; however, in order to calculate dispersion parameters for any (intermediate) dispersion time the shape of the above correlations has to be specified. The functional forms and properties of various permissible correlations are presented and discussed, e.g., in Monin and Yaglom (1975) and Pasquill and Smith (1983). For historical reasons the correlation of Sutton (1953), that was most extensively used for atmospheric applications, especially in the 1950's and early 1960's until it was replaced by the introduction of the Pasquill-Gifford curves, should be mentioned. Among the other possible correlations the simple exponential

$$R_{ii}^L = \sigma_{v_i}^2 \exp\left(-\frac{\tau}{T_i^L}\right)$$

has often proved to be a very useful approximation, and, as it has been pointed out by Tennekes (1977, 1979) provides also a connection between single and two-particle dispersion, that is of particular interest from the perspective of the present work (and for this it is worth mentioning). Integrating (6.4-2) (for $i = j$) for an exponential autocorrelation gives

$$\sigma_i^2(t) = 2\sigma_{v_i}^2 {T_i^L}^2 \left[\frac{t}{T_i^L} - 1 + \exp\left(-\frac{t}{T_i^L}\right)\right]$$

which reduces to the asymptotic forms (6.4-5c) and (6.4-6c) for small and large times respectively. (It is interesting to note that the lines corresponding to these asymptotic limits meet roughly at $t = 2T_i^L$). Tennekes (1979) noted that by expanding the above relation in a Taylor series near $t = 0$

$$\sigma_i^2(t) = \sigma_{v_i}^2 t^2 - \frac{1}{3}\sigma_{v_i}^2 \frac{t^3}{T_i^L} + \ldots$$

(valid for $t/T_i^L \ll 1$, i.e. for the inertial subrange of turbulence), one can associate the first, linear, term, that actually decribes random advection with persistent velocities, with the process of turbulent diffusion very close to the source, and the second term with the gradual loss of correlation of Lagrangian velocities as dispersion time increases. This process of "decorrelation" allows the separation of neighbouring particles to increase and is therefore directly related to relative dispersion in the inertial subrange.

We next proceed to discuss the kinematic analysis of relative dispersion without considering the various approximate and semiempirical or empirical methods that aim at extending and applying the preceding analusis of absolute dispersion to actual atmospheric situations, and, finally, in providing "optimal" estimates for the parameters of Gaussian plume models (as well as for other atmospheric dispersion schemes). Among the many available references that review and summarize such practical methods we specifically mention Hanna et al. (1982), Seinfeld (1983), and Pasquill and Smith (1983) (see also Irwin, 1983); a collection of relevant review papers that cover some more recent information can be found in the November 1985 issue of the *Journal of Climate and Applied Meteorology*, whereas, at a more fundamental level, current reviews on methods for treating non-ideal turbulent environmental dispersion can be found in the 1985 issue of *Annual Reviews of Fluid Mechanics.* A final note that is appropriate at this point of our discussion should concern the effect of sampling time that is implicit in the values of the (semiempirical) dispersion parameters reviewed in the above references. As it will be further discussed in Section 6.5, the distinction between relative and absolute dispersion, for given dispersion time, can be essentially associated with the choice of the proper sampling period (or equivalently the turbulent frequency band relevant to each process). On the other hand empirical expressions relating dispersion parameters for different sampling times are sometimes available. For example Gifford (1975) suggests the following formula for the horizintal crosswind dispersion parameter σ_y corresponding to sampling times $T_s^{(1)}$ and $T_s^{(2)}$:

$$\frac{\sigma_y^{(1)}}{\sigma_y^{(2)}} = \left(\frac{T_s^{(1)}}{T_s^{(2)}}\right)^q$$

where q is in the range 0.25 to 0.3 for 1 hr $< T_s^{(1)} <$ 100 hr and equals approximately 0.2 for 3 min $< T_s^{(1)} <$ 1 hr. Thus, if one can identify approximately the value of the sampling time that will produce an estimate of relative dispersion parameters (and this value is in the range of validity of the above or a similar expression), one would have a crude model for these parameters. An approach following roughly the same lines, but based on general theoretical rather than empirical relations, is pursued in detail in Section 6.5.

• *Relative Dispersion I*

General Relations

The kinematic analysis of single particle motions was extended to relative dispersion in the early 1950's by Batchelor, Brier, Obukhov, and others (see, e.g., Monin and Yaglom, 1975, for detailed references), who initially considered the statistical properties of two-particle separations and relative velocities. Here we adhere to the (almost) equivalent but more practical concept of dispersion relative to the instantaneous center of mass and examine elements of the tensor $\left[\Sigma_{ij}^{(R)}\right]$ rather than $\left[\Sigma_{ij}^{(2P)}\right]$ or $\left[\Sigma_{ij}^{(S)}\right]$, where always

$$\Sigma_{ij}^{(S)} = 2\Sigma_{ij}^{(R)}$$

Now, the fluid particle velocity in the meandering frame is

$$\mathbf{v}^{(R)} = \mathbf{v} - \overline{\mathbf{v}}$$

where

$$\overline{\mathbf{v}}(t) = \frac{d\overline{\mathbf{y}}(t)}{dt}$$

For an inertial frame that follows the mean flow $\langle \mathbf{v} \rangle = 0$, $\langle \overline{\mathbf{v}} \rangle = 0$ and therefore

$$\left\langle \mathbf{v}^{(R)} \right\rangle = 0, \quad \left(\mathbf{v}^{(R)}\right)' = \mathbf{v}^{(R)}$$

The relative displacement and velocity vectors of a diffusing particle are related by

$$\mathbf{y}^{(R)} = \int_0^t \mathbf{v}^{(R)} dt$$

and hence

$$\Sigma_{ij}^{(R)} = \left\langle y_i^{(R)}(t)\, y_j^{(R)}(t) \right\rangle = 2\int_0^t \int_0^t \left\langle v_i^{(R)}(t')\, v_j^{(R)}(t'') \right\rangle dt'dt'' \qquad (6.4-7a)$$

$$\frac{d}{dt}\left\langle y_i^{(R)}(t)\, y_j^{(R)}(t) \right\rangle = 2\int_0^t \left\langle v_i^{(R)}(t)\, v_j^{(R)}(t') \right\rangle dtdt' \qquad (6.4-7b)$$

However, even in homogeneous-stationary turbulence, the relative velocity components $v_i^{(R)}(t)$ do not constitute stationary processes. As the cloud of diffusing fluid particles grows increasingly larger eddies contribute to $\mathbf{v}^{(R)}(t)$ and the relative velocity correlation $\left\langle v_i^{(R)}(t)\, v_j^{(R)}(t') \right\rangle$ is a function of the dispersion time t as well as of the lag time $\tau = t' - t$

$$R_{ij}^{(R)}(t,\tau) = \left\langle v_i^{(R)}(t)\, v_j^{(R)}(t+\tau) \right\rangle \qquad (6.4-8)$$

(Notice that we omit the superscript L when we refer to relative diffusion properties since it is obvious that we use a Lagrangian approach for their description).

Relating the general $R_{ij}^{(R)}(t,\tau)$ to absolute velocities statistics is a rather complicated task since this will involve the Lagrangian correlation for a single particle, the Eulerian correlation referring to two particles at a given instant, and a mixed correlation referring to two particles at different instants (see, e.g., Pasquill and Smith, 1983, pp.154-155). Expressing the latter correlation in terms of more manageable quantities is a major problem that has been pursued on the basis of different assumptions; Sawford (1982a) provides a rather detailed discussion and comparison of such assumptions and the reader is referred to this work for further details. Here we limit ourselves to the examination of the relative velocity variance in the i-th direction, defined as

$$\sigma_{R,v_i}^2 = R_{ii}^{(R)}(t,0)$$

which is a function of the dispersion time. For a "point"-source release, one finds that since

$$\sigma^2_{R,v_i} = \left\langle v_i^2 \right\rangle + \left\langle \overline{v}_i^2 \right\rangle - 2\left\langle v_i \overline{v}_i \right\rangle \tag{6.4 - 9a}$$

then, in the limit of very small times, where $v_i \simeq \overline{v}_i$, it will be

$$(\text{for } t \to 0) \quad \sigma^2_{R,v_i} \simeq 0 \tag{6.4 - 9b}$$

whereas for large times, where v_i and $\overline{v}_i$ are independent

$$(\text{for } t \to \infty) \quad \sigma^2_{R,v_i} \to 2\sigma^2_{v_i} \tag{6.4 - 9c}$$

Thus we see that σ^2_{R,v_i} grows from zero to a value twice that of $\sigma^2_{v_i}$ (or $\sigma^2_{u_i}$) as the dispersion process evolves.

A most important point point has to be stressed in relation to equation (6.4-9b): the fact that the relative velocity variance is zero at the beginning of the time coordinate for a point release allows one to identify the process of relative or two-particle diffusion with the *conditioned* diffusion of a single particle, i.e. that at $t = 0$ has a deterministic velocity (zero variance); we will elaborate further on this point in the next sub-section.

The non-stationarity of $R_{ij}^{(R)}$ implies that Taylor's theorem does not hold for relative dispersion; one thus has

$$\Sigma_{ij}^{(R)} = \int_0^t \int_0^{t'} \left[R_{ij}^{(R)}(t',\tau) + R_{ji}^{(R)}(t',\tau) \right] d\tau dt' \tag{6.4 - 10a}$$

and for $i = j$

$$\Sigma_{ii}^{(R)} = \sigma^2_{R_i} = 2\int_0^t \int_0^{t'} R_{ii}^{(R)}(t',\tau)\, d\tau dt' \tag{6.4 - 10b}$$

Lagrangian time scales for relative diffusion are also functions of t:

$$T_{ij}^{(R)} = \frac{1}{\left(\sigma^2_{R,v_i}\sigma^2_{R,v_j}\right)^{1/2}} \int_0^t \left[R_{ij}^{(R)}(t,\tau) + R_{ji}^{(R)}(t,\tau) \right] d\tau \tag{6.4 - 11}$$

$T_{ij}^{(R)}(t)$ is characteristic of those eddies that contribute to relative dispersion at time t after a (point) release; these are expected to be mainly the ones comparable to the typical fluid particle separation in the dispersing cloud, i.e. approximately comparable to the cloud size (Csanady, 1973).

• *Relative Dispersion II*

General Asymptotic Results

The general relations (6.4-10ab) allow derivation of a direct asymptotic result only in the case of very large times. Using (6.4-9c) one can write for the final phase of dispersion

$$\sigma_{R_i}^2 = 2\sigma_{v_i}^2 \overline{T}_{ii}^{(R)} t \tag{6.4 – 12}$$

where

$$\overline{T}_{ii}^{(R)} = \frac{1}{\sigma_{v_i}^2} \lim_{t' \to \infty} \frac{1}{t'} \int_0^{t'} \int_0^{\infty} R_{ii}^{(R)}(t, \tau)\, d\tau dt \tag{6.4 – 13}$$

is an averaged integral time scale of relative velocities in the i-th direction. One must note that an *implicit* assumption appearing in most works relevant to two-particle dispersion is that

$$\overline{T}_{ii}^{(R)} = T_i^L$$

• *Relative Dispersion III*

Dimensional Analysis for the Inertial Subrange

For small and intermediate diffusion times Batchelor (1949, 1952) applied Kolmogorov's hypothesis and dimensional analysis to determine $\Sigma_{ii}^{(2P)}$ for dispersion taking place at scales that belong in the inertial subrange of turbulence. He argued that in this subrange $d\Sigma_{ij}^{(2P)}/dt$ depends only on the initial separation of the fluid particles, the rate of turbulent energy dissipation ϵ and the time t for "small" diffusion times ($t < t^*$), but it depends only on ϵ and t for "intermediate" times. Batchelor's analysis is summarized, for example, in Seinfeld (1975, pp.313-316) and will not be repeated here. We only state briefly its main results (formulated in the meandering frame we consider here) for ready reference:

After a "molecular phase", that will take place when the initial dimensions of the dispersing cloud are smaller than the Kolmogorov microscale $\ell_K = \left(\nu^3/\epsilon\right)^{1/3}$, and in which the species under consideration will spread only due to molecular diffusion, one has (recall also the discussion in Section 6.3.1)

(I) *the Short Time Inertial Subrange Dispersion* or simply *Initial Stage,* where

$$\sigma_{R_i}^2 = \sigma_{0_i}^2 + \beta_i^{(\mathrm{I})}(\epsilon\sigma_{0_i})^{2/3}t^2 \tag{6.4 – 14a}$$

$$K_i^{(R)} = \beta_i^{(\mathrm{I})}(\epsilon\sigma_{0_i})^{2/3}t \tag{6.4 – 14b}$$

and

(II) *the Intermediate Time Inertial Subrange Dispersion* or *Accelerated Dispersion Phase,* or simply *Inertial Stage,* where the quasi-asymptotic motion of fluid particles (Section 6.3.1) takes place in the inertial subrange and

$$\sigma_{R_i}^2 = \beta_i^{(\mathrm{II})}\epsilon(t-t^*)^3 \tag{6.4 – 15a}$$

$$K_i^{(R)} = \frac{3}{2}\beta_i^{(\mathrm{II})}\epsilon(t-t^*)^2 \tag{6.4 – 15b}$$

t^* being a (small) correction for an effective "inception of dispersion" that is often set equal to zero. Relation (6.4-15b) can also be writen as

$$K_i^{(R)} = \frac{3}{2}\left(\beta_i^{(\mathrm{II})}\epsilon\right)^{1/3}\sigma_{R_i}^{4/3} \tag{6.4 – 15c}$$

which is of course typically referred as *Richardson's 4/3 power law,* and is mentioned that it was first proposed by Richardson (1926) on purely empirical grounds. However, if we want to be precise, we must mention that Richardson proposed his 4/3-law with respect to some actual, observable (and therefore stochastic), dimension of an expanding puff, and not with respect to the deterministic statistical property σ_{R_i}; in fact the latter formulation is due to the (independent) work of Batchelor and Obukhov (see, e.g., Monin and Yaglom, 1975). The major differences of these formulations have already been discussed in sub-section 6.3.1.

• *Relative Dispersion IV*

Quasi-Asymptotic Results

Lin (1960ab) (see also Lin and Reid, 1963, p.513; Monin and Yaglom, 1975, pp.547-551) extended the 4/3 power diffusion law beyond the inertial subrange on the assumption that the mean-square relative particle acceleration is statistically homogeneous and stationary and has a short-ranged autocorrelation. Stating the homogeneity and stationarity assumptions in terms of the velocity relative to the center of mass and setting

$$\mathbf{a}^{(R)} = \frac{d\mathbf{v}^{(R)}}{dt} \qquad (6.4-16a)$$

and

$$A_{ii}^{(R)}(\tau) = \left\langle a_i^{(R)}(t+\tau)\, a_i^{(R)}(t)\right\rangle \qquad (6.4-16b)$$

one finds that

$$\Sigma_{ij}^{(R)} = \frac{1}{3}\left(t^3\int_0^t A_{ii}^{(R)}(\tau)\,d\tau - \frac{3}{2}t^2\int_0^t \tau A_{ii}^{(R)}(t)\,d\tau + \right.$$
$$\left. +\frac{1}{2}\int_0^t \tau^3 A_{ii}^{(R)}(\tau)\,d\tau\right) \qquad (6.4-17)$$

subject to the conditions of zero initial separation and

$$v_i^{(R)}(0) = 0, \quad a_i^{(R)}(0) \neq 0$$

From equation (6.4-17) one immediately has that, if $A_{ii}^{(R)}$ is effectively zero for $t > t_a$, i.e. if the acceleration covariance is sufficiently short-ranged, then for $t \gg t_a$ it follows that $\sigma_{R_i}^2 \sim t^3$. The coefficient of proportionality in this relation is easily found to be equal to the integral time scale of $a_i^{(R)}$.

One also has for sufficiently long dispersion times

$$A_{ii}^{(R)}(\tau) = 2A_{ii}^{L}(\tau)$$

where A_{ii}^{L} is the covariance of the single particle (fixed frame) acceleration.

The general behavior of both absolute and relative dispersion parameters, based on the asymptotic results of the preceding paragraphs, is summarized schematically in Figure 6-2.

• *Relative Dispersion V*

Empirical Information

Empirical information for relative dispersion parameters is very limited compared to that for absolute dispersion (see, e.g., Hanna et al. 1982, pp.41-45, and Pasquill and Smith, 1983, pp.220-232; note that these works focus on puff rather than on instantaneous plume dispersion). Thus, nothing equivalent to the Pasquill-Gifford curves (or any of the other general semiempirical, stability dependent, schemes for absolute σ_i's) is available for the estimation of σ_{R_i}'s. Nevertheless, available observations support the dimensional analysis results (6.4-14a), (6.4-15a), the latter actually for ranges extending significantly beyond the inertial subrange. Indeed, these observations suggest that (6.4-14a) is valid for dispersion times typically less than 10^2 sec (approximately 1 min) whereas (6.4-15a) is valid for times up to 10^3 to 10^4 sec, i.e. approximately of the order of 1 hr (see Hanna et al., 1982, pp.43-44, for relevant references).

The currently available information regarding the constants $\beta^{(\mathrm{I})}$, $\beta^{(\mathrm{II})}$, for atmospheric conditions, can be roughly summarized as follows (typically for neutral and unstable conditions):

$$\beta_1^{(\mathrm{I})} \simeq \beta_2^{(\mathrm{I})} \simeq \beta_3^{(\mathrm{I})} \simeq 1$$

$$\beta_2^{(\mathrm{II})} \simeq 0.4 \text{ to } 2.0, \quad \beta_3^{(\mathrm{II})} \simeq (0.5 \text{ to } 1.0)\,\beta_2^{(\mathrm{II})}$$

with $t^* = 0$ (see also Hanna, 1984, p.1099). The effect of atmospheric stability is introduced through the value of the local (average) energy dissipation rate in (6.4-14a), (6.4-15a). A typical estimate of the time after which the influence of the source size is no longer important is $t \simeq \sigma_{0_i}^{2/3}/\epsilon^{1/3}$. However it must be mentioned here that σ_{0_i} does not necessarilly correspond to an actual dimension of the source (and also reflects effects of initially enhanced dispersion due to momentum and buoyancy fluxes)

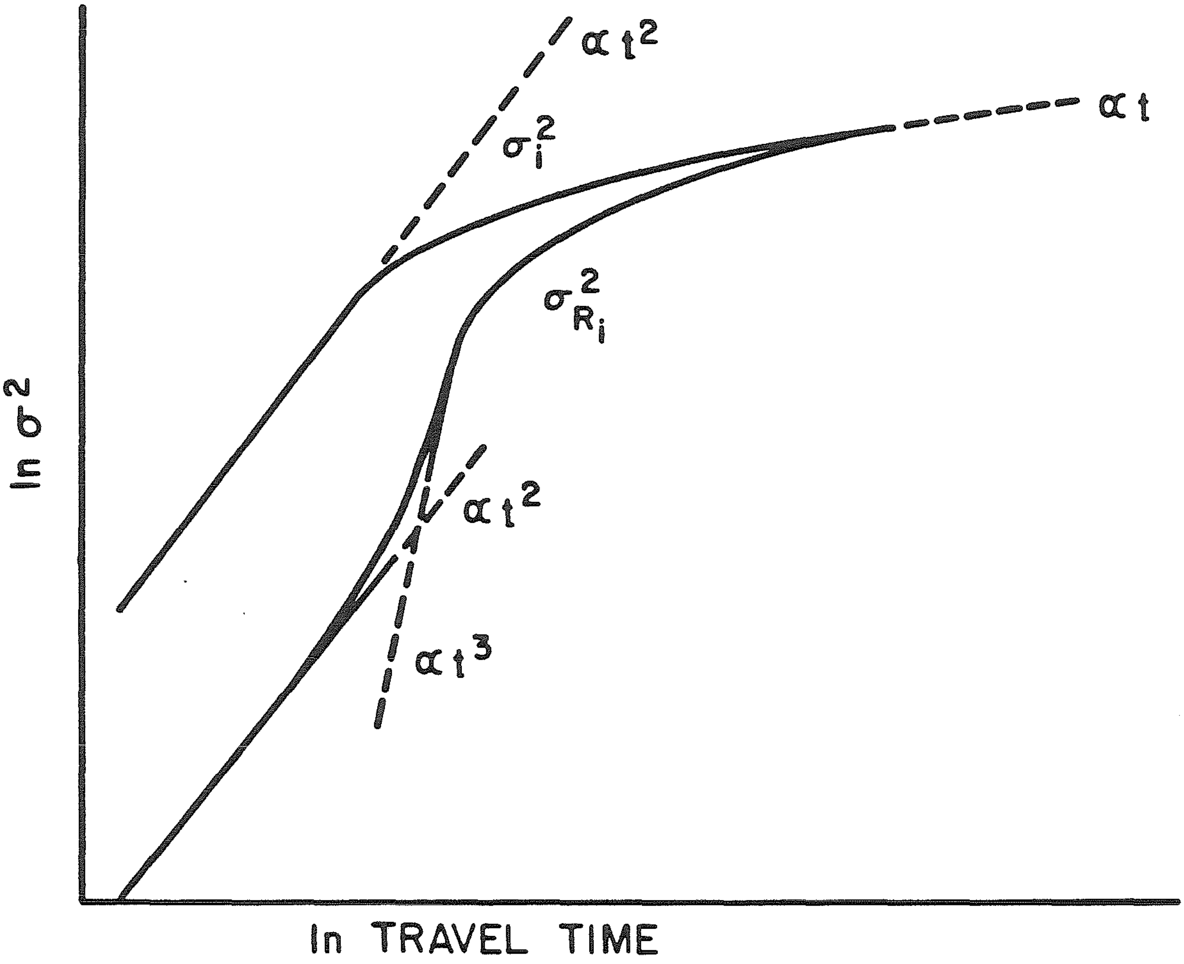

Figure 6-2

Asymptotic Behavior

of Absolute (σ_i) and Relative (σ_{R_i})Dispersion Parameters and thus is typically treated as a parameter that is fitted to the data for applying (6.4-14a); hence, a priori estimates involving this quantity are more or less meaningless. Another interesting time point is that when the relative dispersion parameter in the i-th direction equals that of meandering; according to Hanna (1984) available data show this time to vary in general from 0.5 to $1.5T_i^L$.

6.4.2 Conditioned Single Particle Motion and Its Relationship to Relative Dispersion

In this sub-section we discuss briefly the close relationship between (inertial subrange) fluid particle dispersion observed in a non-inertial frame fixed to another fluid particle (or to the center of mass of a cloud of particles) and in an inertial frame moving with a constant velocity that results from a Galilean transformation of the instantaneous initial velocity of the particle.(*) Although this relationship was derived in the early 1960's (Novikov, 1963; Lin and Reid, 1963 – see also Monin and Yaglom, 1975, p.546) and was touched upon by Smith (1968) in his analysis of the statistics of conditioned particle motion, it has only recently come in the focus of relative dispersion modeling as a means for addressing atmospheric diffusion problems, basically in the context of the Langevin equation and related Monte Carlo methods (see sub-section 6.4.3). Schemes based on this relationship, commonly referred to as "one-particle models for relative dispersion," were applied by Gifford (1982) to horizontal dispersion from a continuous point-source, and by Lee and Stone (1983ab) to diffusion from a finite-size, finite-duration source. The approach adopted in these schemes was criticized by Smith (1983), defended by Gifford (1983), discussed by Sawford (1984), and further discussed and compared with two-particle models by Lee et al. (1985).

To summarize the theoretical basis of the method let us consider the ensemble of random realizations of the initial (fixed frame) velocity of an arbitrary fluid paricle $\mathbf{v}(0,0)$. Then we consider an inertial reference frame moving with fixed in time (for a given realization) velocity $\mathbf{v}_0$ relative to $\mathbf{v}(0,0)$ in the fixed frame. Thus the velocity of the new reference frame, $\mathbf{v}(0,0) - \mathbf{v}_0$, is constant for each realization, but different from realization to realization. However, in this frame the "tagged" arbitrary fluid particle has the same initial velocity $\mathbf{v}_0$ in all realizations; thus a *conditioned* ensemble

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(*) This can equivalently be considered as the relationship between relative dispersion and conditioned absolute dispersion, i.e. dispersion of single fluid particles that are constrained to have the same initial velicity.

of fluid particle motions is defined. Let the random position vector and velocity of the particle in this frame be $\mathbf{y}^{(C)}(t)$ and $\mathbf{v}^{(C)}(t)$ respectively, where

$$\mathbf{v}^{(C)}(t) = \mathbf{v}(t) - \mathbf{v}(0) + \mathbf{v}_0$$

the superscript (C) indicating conditioned motion. Now, one can write for the elements of the tensor of fluid particle displacements in this frame (Monin and Yaglom, 1975, p.533)

$$\Sigma_{ij}^{(C)}(t) \equiv \left\langle y_i^{(C)}(t)\, y_j^{(C)}(t) \right\rangle = \int_0^t t' D_{ij}^L(t')\, dt' \qquad (6.4-19)$$

where D_{ij}^L is the Lagrangian *structure function* for homogeneous-stationary turbulence, defined in general as (see, e.g., Monin and Yaglom, 1975)

$$D_{ij}^L(\tau) \equiv D^L(\tau)\, \delta_{ij} =$$

$$= \left\langle \left(v_i^{(C)}(t+\tau) - v_i^{(C)}(t) \right) \left(v_j^{(C)}(t+\tau) - v_j^{(C)}(t) \right) \right\rangle$$

However, in every inertial frame of reference

$$D^L \tau = C_0 \epsilon \tau \qquad (6.4-20)$$

for dispersion in the inertial subrange (Monin and Yaglom, 1975, p.359), where C_0 is a universal constant. Thus (6.4-19) gives

$$\Sigma_{ij}^{(C)}(t) = \frac{1}{3} C_0 \epsilon t^3 \qquad (6.4-21)$$

which is equivalent to (6.4-15a) with $\beta^{(\mathrm{II})} = 3C_0$. Thus single-particle dispersion with fixed initial velocity is equivalent to dispersion relative to the center of mass.

Further discussion of conditioned dispersion models is presented in the next-subsection, after summarizing the fundamentals of Langevin equation methods.

6.4.2 Langevin Equation Methods

Langevin equation methods (well known through their application to Brownian motion problems) constitute "dynamic extensions" of the direct kinematic approach, described in the previous sub-sections, by introducing explicitly random force effects in the study of (fluid or other) particle motions. Langevin equations essentially are convenient models (approximations) of Newton's second law where the force (per unit mass) acting on the particle is assumed to consist of a "restoring" component, dependent on the random instantaneous velocity, and an uncorrelated part (the so called *Langevin force*).

Although generalized Langevin eqations with nonlinear restoring forces or with memory kernels (i.e. of integrodifferential form) have been used to describe the dynamics of random motions (see, e.g., van Kampen, 1981, Chapter VIII) the term "Langevin equation" is most commonly assigned to a linear stochastic differential equation whose nonhomogeneity or Langevin force (forcing term) $n(t)$ constitutes *white noise*. Its typical one-dimensional (without any loss of generality) form is

$$\frac{dv(t)}{dt} + \gamma v(t) = n(t) \qquad (6.4-22a)$$

where by definition

$$\langle n(t) \rangle = 0, \quad \langle n(t)\, n(t') \rangle = \alpha \delta (t - t')$$

Because a stochastic process with the above properties of $n(t)$ does not formally exist (in the sense of an ordinary function) many researchers prefer to use instead the integral of $n(t)$, which is the Wiener process (or Wiener-Lévy process or simply "Brownian motion") $b(t)$,

$$b(t) = \frac{1}{\sigma_b} \int_0^t n(t')\, dt'$$

with

$$\sigma_b = \sqrt{\alpha}$$

where division with σ_b produces the *standard* or *normalized* Wiener process (*), and, since the latter is nowhere (mean-square) differentiable, they write

$$dv(t) + \gamma v(t)\, dt = \sigma_b db(t) \qquad (6.4-22b)$$

where

$$\langle b(t)\rangle = t, \quad \langle b(t)\, b(t')\rangle = \min(t, t')$$

(Note that σ_b has units of acceleration).

The solution of (6.4-22ab) is given by

$$v(t) = v_0 e^{-\gamma t} + \int_0^t e^{-\gamma(t-\tau)} \sigma_b db(\tau) \qquad (6.4-23)$$

$$y(t) = y_0 + \frac{v_0}{\gamma}\left(1 - e^{-\gamma t}\right) + \frac{1}{\gamma}\int_0^t \left(1 - e^{-\gamma(t-\tau)}\right) \sigma_b db(\tau) \qquad (6.4-24)$$

Avoiding all discussion of the deep mathematical subtleties involved in the formal interpretation of the above equations and of their solutions we limit ourselves here to some brief comments concerning the physical meaning of the processes and parameters appearing in them. At first we must note that when the white noise $n(t)$ is Gaussian (which is implicitly assumed in practically all applications), then the Langevin equation is equivalent to a Fokker-Planck equation for the random *velocity* process (see, e.g., Van Kampen, 1981, for details). The latter process is Markovian, and is characterized by a Gaussian transition density, whereas the fluid particles' positions $y = \int_0^t v(t')\, dt'$ *are not* Markovian processes (although the joint vector process

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* The Wiener process is a nonstationary Markovian process – and also a martingale – with Gaussian independent increments and Gaussian transition probability density. It constitutes a model of the positions of particles undergoing Brownian motion (recall however that the Langevin equation produces non-Markovian positions) and has been studied extensively, essentially giving rise to many of the fundamental concepts of the modern theory of stochastic processes such as the Wiener measure, stochastic integration, etc. For an elementary introduction to the Wiener process one may consult, e.g., Papoulis (1965). A somewhat more advanced – but very readable – treatment can be found in Arnold (1974). From the extensive advanced mathematical literature relevant to the subject of Brownian motion, we mention the monograph of Chung (1982) and the three-volume treatise of Gihman and Skorohod (1974, 1975, 1979) – in particular volume III. Finally, the reader interested in the fractal aspects of Brownian motion can find a fascinating relevant discussion in the monograph of Mandelbrot (1983).

(v, y) is Markovian in phase space). This fact constitutes the relative advantage of this approach compared to the eddy diffusion models (with either constant or dispersion time dependent diffusivities), that result from either gradient transport hypotheses or as Fokker-Planck equations for the mean concentration (or, equivalently, the transition function). Indeed, these models (essentially all parabolic transport equations) are based on the Markovian property for the fluid particles' positions (see also our discussion in Section 6.3.2 of the present chapter, in the derivation of the modified ADE, and Seinfeld, 1975 , Chapter 6). The improvement of dispersion modeling obtained through the Langevin description lies in the fact that now velocity is allowed to change over a finite time scale, possibly comparable to the time scale over which the concentration changes (whereas, as is well known, this is not the case with equations like the ADE). This is achieved by assigning the Markov property to the derivative of the process y instead to y itself (see also Durbin, 1983).

The parameter γ is a characteristic reciprocal time scale for the v-process. Furthermore the temporal velocity correlation is found to be (for $t > t'$)

$$\langle v(t)\, v(t')\rangle = \frac{\sigma_b^2}{2\gamma}\left(1 - e^{-2\gamma t'}\right) e^{-(t-t')}$$

and letting

$$\left\langle v^2(0)\right\rangle = \left\langle v_0^2\right\rangle = \sigma_{0,v}^2$$

one obtains (setting $t' = 0$)

$$\sigma_b^2 = \alpha = 2\gamma\sigma_{0,v}^2$$

This is a significant result that relates what is essentially an initial condition to the statistical properties of the external forcing field. (Actually this last equation is the simplest form of the general *fluctuations-dissipation theorem* of statistical mechanics; see van Kampen, 1981, p.238, for a relevant discussion).

We further see that for $t \gg 1/\gamma$ the random function $v(t)$ tends to a process that besides being Gaussian-Markovian is also stationary (i.e. it is an Ōrnstein-Uhlenbeck process), independent of initial conditions, with zero mean, variance $\sigma_b^2/2\gamma$, and covariance $R(\tau) = \sigma_b^2/2\gamma \exp(-\gamma|\tau|)$. Here we must note that one can formally define the Langevin model in such a way that it directly produces a stationary $v(t)$. This can be done either by setting the initial conditions at $t = -\infty$ instead of $t = 0$, or by a suitable transformation of the time coordinate and the time scale (see, e.g., Syski, 1967). Alternatively this can be controlled by the initial conditions: if one assumes that the statistical distribution of $v(0) = v_0$ is equal to the above large-time limiting distribution, then the distribution of $v(t)$ itself is independent of t and equals the limiting distribution (a direct consequence of the Markov property).

Now, in the case of turbulent fluid particle dispersion γ is typically taken to be the inverse of the Lagrangian time scale (see, e.g., Durbin, 1983; Sawford, 1984, 1985) and thus, in a given direction, the corresponding Langevin equation can be writen as

$$dv_i(t) = -\frac{v_i(t)\, dt}{T_i^L} + \sigma_{0,v_i}\sqrt{\frac{2}{T_i^L}}\, db(t) \qquad (6.4-26)$$

Pasquill and Smith (1983, p.138) note that when the velocity autocorrelation is not of exponential form then the appropriate time scale (characteristic of the rate of exchange of momentum between fluid particle and environment) will not be equal to the Lagrangian time scale. (Recall however that in the theoretical case of an Õrnstein-Uhlenbeck proces the autocorrelation is necessarilly exponential).

Although the analogy between Brownian motion and turbulent dispersion was implicit in Taylor's (1921) concept of the "diffusion by continuous movements," and has been theoretically discussed by Obukhov (1959) and Lin and Reid (1963), it has only relatively recently (after 1975) become popular as a means for studying dispersion phenomena (and in particular atmospheric), mainly as the basis of Monte Carlo computer simulations (see also Pasquill and Smith, 1983; pp.133-141 *).

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* It must be noted here that Pasquill and Smith (1983, p. 133) refer to these approaches as "Markovian random walk methods." However it is clear from the above discussion that the Markov property is used in various other occasions in models of turbulent dispersion, typically in relevance to the trajectories of the particles; thus it must be stressed that this explicit use of the term Markovian property refers to the random velocities.

The majority of these simulations have used the Langevin equation concept (often only implicitly) to model single-particle, i.e. absolute, dispersion statistics in fixed coordinate frames and for time averaged mean concentration fields. (e.g. Reid, 1979; Durbin, 1980; Durbin and Hunt, 1980; Wilson et al., 1981; Lamb, 1982; Legg, 1983, etc. – see also Seinfeld, 1983; Sawford, 1985). Although such numerical models do not always offer significant fundamental improvements over techniques using Taylor's theorem (see, for example, Panofsky and Dutton, 1984, p.247, for relevant comments), since in both cases Lagrangian velocity correlations (or some equivalent restrictions concering the nature of the velocity field) have typically to be assumed a priori, they are much more versatile, allowing for complicated boundary conditions. Furthermore they are not restricted to homogeneous-stationary turbulence and can be used with dispersion time dependent velocity correlations (although most numerical experiments adopt stationary velocity correlations of the exponential type). For a study of applications of the Langevin equation to "non-ideal" turbulence we refer the reader to the works of Durbin (1983) and Sawford (1985).

In the numerical Monte Carlo simulations one estimates the "actual" random positions of many particles; thus not only the variance but many other statistical characteristics of the trajectories can be derived. Starting point of the numerical models is typically a linear recursive relation for $v(t)$, which in the case of one-dimensional homogeneous-stationary turbulence ($\sigma_v = \sigma_{0,v}$) has the form (Smith, 1968)

$$v(t+\tau) = \rho(\tau)\, v(t) + \hat{v}(t) \tag{6.4 - 27}$$

with

$$\rho(\tau) = \frac{R^L(\tau)}{\sigma_v^2}$$

typically assumed of exponential form. The variance of $\hat{v}$ (the latter typically assumed Gaussian) is taken to be

$$\sigma_{\hat{v}}^2 = \sigma_v^2 \left(1 - \rho^2(\tau)\right)$$

so that the variance of successive v's remains the same. Thus in practice trajectories are calculated numerically by selecting wind velocities randomly (but so that their statistics obey some restrictions imposed either by theory or by results of numerical turbulence models), choosing $\hat{v}$ from a Gaussian distribution of prescribed variance, and finally calculating successive positions y from (6.4-27). A point worthy of noting here is that (6.4-27), with the variance of $\hat{v}$ as above, constitutes a so called *First Order Autoregressive (AR1)*, Stochastic Time Series Model. It is in fact in the context of such a time series that many of the Monte Carlo models have been formulated, without explicit reference to the relation with the underlying Langevin equation (for the limit of continuous time). This relation can be shown to hold in the limit of small time lags. Indeed, for small τ (say $\tau = \tau_s$) (6.4-27) (after expanding in a series of powers of τ and discarding higher order terms) reduces to

$$\frac{dv\,(t)}{dt} + \frac{[1-\rho\,(\tau_s)]}{\tau_s} v\,(t) = \frac{\hat{v}\,(t)}{\tau_s}$$

which is an approximate Langevin equation with

$$\gamma = \frac{[1-\rho\,(\tau_s)]}{\tau_s}$$

and

$$\alpha = \frac{\sigma_v^2\left[1-\rho^2\,(\tau_s)\right]}{\tau_s}$$

One can see that for $\rho\,(\tau_s) = \exp\left(-\gamma\tau_s\right) \simeq 1 - \gamma\tau_s$ the equality $\alpha = 2\gamma\sigma_v^2$ that relates the parameters of the Langevin equation holds (approximately) for the first order autoregressive series model. Thus, for Gaussian Markovian stationary processes there is a strong connection between AR1 models and Langevin equations.

Let us now focus on the problem of relative dispersion in the perspective of the Langevin approach. As already mentioned this problem has been pursued along two different lines. One group of models considers the motion and separation of two fluid particles and is based on a set of two coupled Langevin equations governing the dynamics of each particle, that is essentially solved numerically (Durbin, 1980; Lamb, 1981; Sawford, 1982ab). The basic aspects of these models have been discussed by

Sawford (1983, 1985). As he points out, apart from points of detail, the fundamental difference between individual models lies in assumptions regarding the rate of two-particle separation: In both Sawford's and Lamb's models the instantaneous rate of separation of the pair of particles is a function of the ensemble-mean-square pair separation, with the result that the distribution of separations is Gaussian (for a Gaussian velocity distribution) and the two-particle displacement probability density is bivariate Gaussian. On the other hand in Durbin's model the instantaneous rate of separation is a function of the instantaneous separation, an assumption that leads to a non-Gaussian distribution of separations. These differences correspond respectively to the already discussed differences between Batchelor's (1952) notion that it is only the statistical tendency for particles to separate which is related to the size of the eddies, and Richardson's (1926) concept in which the probability density of separations depends on an eddy diffusivity that is a function of separation. For further details the reader is referred to the aforementioned publications and in particular to Sawford (1983, 1985). Finally we mention the more recent works of Faller and Choi (1985) and Faller (1985) who also use a two-equations Monte Carlo formalism to model relative dispersion in both the inertial subrange of three-dimensional turbulence and in the enstrophy(*) cascade of large-scale two-dimensional turbulence; however it must be noted that according to Sawford (1984, p.2408) "the Langevin equation is specifically applicable to three-dimensional turbulence" and "it is likely that ... it does not model the two-dimensional enstrophy cascade inertial range." In fact there are various unresolved problems in this area.

Another group of models for relative dispersion that use the Langevin equation is based on the equivalence between conditioned single particle dispersion and relative dispersion, that was discussed in the previous sub-section. As mentioned in that sub-section, recent interest in this conditioned dispersion method started with the

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[*] Enstrophy is defined as the mean square vorticity of turbulence (se, e.g., Lin, 1972)

proposal of Gifford (1982) of using a simple formula for both σ_i^2 and $\sigma_{R_i}^2$:

$$\frac{\sigma_i^2}{2K_i(\infty)\,T_i^L} = \frac{t}{T_i^L} - \left[1 - \exp\left(-\frac{t}{T_i^L}\right)\right] - \frac{1}{2}\left(1 - \frac{\sigma_{0,v_i}^2}{\sigma_{v_i}^2}\right)\left[1 - \exp\left(-\frac{t}{T_i^L}\right)\right]^2 \tag{6.4 – 28}$$

where σ_{0,v_i}^2 is the fluid particle velocity variance at the source, and, of course,

$$K_i(\infty) = \sigma_{v_i}^2 T_i^L$$

Thus as σ_{0,v_i}^2 approaches $\sigma_{v_i}^2$ (6.4-28) σ_i^2 is found to describe absolute diffusion, (as predicted for an exponential velocity autocorrelation),

$$\frac{\sigma_i^2}{2K_i(\infty)\,T_i^L} = \frac{t}{T_i^L} - \left[1 - \exp\left(-\frac{t}{T_i^L}\right)\right]$$

whereas as σ_{0,v_i}^0 approaches zero, i.e. as the dispersion becomes conditioned by the fixed random initial value, one obtains the 4/3 diffusion power law, appropriate for relative dispersion (without initial size effects).

Equation (6.4-28) is obtained directly from the general solution (6.4-23) of the Langevin equation after squaring and ensemble averaging. Smith (1983) has pointed out that his (1968) statistical relations may also be used to give exactly the same equation and further discussed the problem of its proper interpretation in relation to observational data, a matter that is not simple (see also Pasquill and Smith, 1983, pp.122-123, for relevant comments). Lee and Stone (1983ab) extended Gifford's model to clusters of particles from finite-size, finite-duration sources. Lee et al. (1985) further discussed this approach, also comparing their earlier calculations with results from a two-particles, two-equations scheme they developed. The validity of the conditioned dispersion approach in relevance to atmospheric relative dispersion modeling was also reviewed and discussed by Sawford (1984) who stressed the generality of the equivalence (in the sense that it does not rely a priori on a Langevin model) between conditioned single particle motion and particle pair motion in the inertial subrange of atmospheric turbulence.

Sawford (1984, 1985) also discussed in general the applicability of Langevin type equations to atmospheric relative dispersion modeling and in particular the agreement of equation (6.4-28) with atmospheric observations. Although open to some questions, his major conclusions seem to summarize the most important points of our current knowledge in this area and for this reason are briefly reproduced here:

- Langevin type equations are good models for Lagrangian velocities only in high Reynolds number three-dimensional turbulence where the particle acceleration autocorrelation is short-ranged (a typical case being the inertial subrange where the equivalence between conditioned and relative dispersion holds),
- Langevin equations seem not applicable to relative dispersion on the very large (global) scales of atmospheric turbulence, at least partly because of the quasi-two-dimensionality of motion on these scales,
- For horizontal dispersion at smaller scales the application of equations like (6.4-28) is complicated by the lack of a well defined upper limit to the scale of the turbulent kinetic energy,
- Conditioned single particle models cannot appropriately model higher moments (or the pdf) of the separation; a pair of Langevin equations is needed for this task.

In conclusion, modeling of relative dispersion through Langevin equations (either a single one or a pair) is currently an active – and relatively controversial – field of research. Although several questions remain unresolved and the interpretation of various assumptions is not always universally accepted, many useful concepts have been recently clarified (and the present sub-section attempted to further organize and relate them), and some powerful mathematical tools have been brought to the attention of those interested in environmental dispersion. From a more practical (and perhaps narrower) perspective we point out the potential of (6.4-28) as a simple model for relative dispersion for the stages of quasi-asymptotic and asymptotic fluid particle motion.

6.5 RELATIVE DISPERSION ANALYSIS:
II. SPECTRAL METHODS

In this section we present a new method for estimating relative dispersion parameters from (observed) atmospheric turbulence spectra. This method is based on the association of the relative dispersion and meandering processes with appropriately defined space-time scales. This allows the computation of specified dispersion parameters from the spectral form of Taylor's theorem after filtering out the frequencies at scales that do not contribute to the process under consideration. The parameters for the appropriate high-pass filter functions, required for the calculation of in-plume phenomena, are not assumed a priori but are determined through an iterative integral technique. The basic steps of this method were outlined briefly in Chapter 2. In the present section we explain the rationale behind these steps, discuss various relevant questions, and present some typical results obtained with this method. It must be mentioned at this point that since typically Eulerian and not Lagrangian atmospheric spectra are available with sufficient accuracy (and for a variety of atmospheric conditions), there arises the need to use a transformation tecnique in order to use the former spectra in conjuction with Taylor's theorem.

6.5.1 General Considerations

Scale of Atmospheric Motions and Plume Spread

Let us now briefly recall some aspects of the concepts of averaging and sampling times and of the associated scales, in relevance to plume dispersion (see also Appendix A6.1). A continuous plume from a point source in the atmosphere encounters a wide range of atmospheric motions associated with different scales, which we associate with the concept of eddies. Now, the very large eddies contribute to changes in the instantaneous wind vector while the smallest eddies cause slight dispersive spreading of the plume. The eddies of about the same size as the local plume width are the most effective in producing turbulent plume dispersion. Eddies larger than the instantaneous plume width but smaller than the characteristic horizontal scale of the region of interest (typically the downwind distance from the source) produce the meandering characteristic of the instantaneous plume. Thus if L_E is a characteristic eddy dimension, x is the characteristic horizontal scale of the region (typically the downwind distance) and D_P is an (ensemble) average *instantaneous* plume width, then the role of eddies in plume dispersion is given by (see, e.g., Seinfeld, 1983, p.262)

(1) $L_E \ll D_P$, slight plume dispersion; internal plume mixing
(2) $L_E \sim D_P$, most effective in plume dispersion
(3) $D_P < L_E \leq x$, produces plume meandering
(4) $L_E > x$, produces changes in the wind vector

Since $D_P = D_P(x)$, it is obvious that as the plume is advected downwind the effect (on its spread) of atmospheric motions associated with a *given* spatial scale becomes qualitatively different. Furthermore, although in general eddies of a very wide range of scales are expected to be present in the atmosphere, they are not expected to be found with the same probability (i.e. the spectrum of eddies will be more "dense" in certain scales – more precisely in frequency or wavenumber bands – and less in others) this variation also holding for different directions. It is therefore imperative, in relating relative dispersion parameters to atmospheric turbulence properties, such as turbulent energy (i.e. fluctuating velocity variance), to discern between the contributions to these properties from different scales, of motion and, furthermore, to take into account the change of this contribution with advection time.

Turbulence Spectra (versus Correlations)

Comments and Definitions

In principle correlation functions and spectral densities contain the same information regarding the distribution of the variance of a given quantity over different spatial scales and frequencies (or eddy sizes). However, in practice, spectra are more useful than correlations or other statistics because (besides possible computational advantages) they give directly the distribution of the variance of interest (in our case of turbulent energy, either total or in a given direction) with respect to frequency (or wavenumber), in a way such that the effects of particular frequency bands are independent from the effects of other frequency bands. This important advantage is shown schematically in Figure 6-3 (from Panofsky and Dutton, 1984) that shows a time series of data with an approximately linear macroscopic (i.e. low frequency) trend. The respective correlation functions and spectral densities are also given, calculated both without and with removal of this trend. One sees that whereas the values of the two correlation functions, for a given time lag, differ significantly, even for small time lags, the behavior of the spectral densities at large frequencies is independent of the slow variations (see Panofsky and Dutton, 1984, pp.174-176, for further relevant discussion).

In this work we adopt the following definitions for the frequency spectrum (*) $F_\alpha(\omega)$ of the *fluctuations* of the random quantity α (that is either Eulerian or Lagrangian with temporal autocorrelation $R_\alpha(\tau)$), following Monin and Yaglom (1975):

$$F_\alpha(\omega) = \frac{1}{\pi}\int_0^\infty R_\alpha(\tau)\cos\omega\tau d\tau \qquad (6.5-1)$$

(We will not consider specta corresponding to cross-correlations in the present work). Regarding the notation, it must be mentioned that, in the present work, when an $i = 1,2,3$ index notation is used for the velocities, then the index alone is used to specify the correlation (i.e. we write $R_i(\tau)$ instead of $R_{u_i}(\tau)$ - see previous sections).

For symmetric $R_\alpha(\tau)$ (i.e. stationary α') one can alternatively use the spectrum $E_\alpha(\omega) = 2F_\alpha(\omega)$, defined for $0 \leq \omega < \infty$ instead of $-\infty < \omega < \infty$, and thus the correlation $R_\alpha(\tau)$ will be given by

$$R_\alpha(\tau) = \int_{-\infty}^\infty F_\alpha(\omega)\exp(i\omega\tau)\,d\omega = \int_0^\infty E_\alpha(\omega)\cos\omega\tau d\omega \qquad (6.5-2)$$

We also use the absolute spectral density in terms of “arithmetic frequency” $n = \omega/2\pi$

$$S_\alpha(n) = 2\pi E_\alpha(2\pi n) \qquad (6.5-3)$$

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* The reader is reminded that there are some differences in the definitions of turbulent spectra adopted by various authors; the major of these differences are summarized in Appendix A6.1.

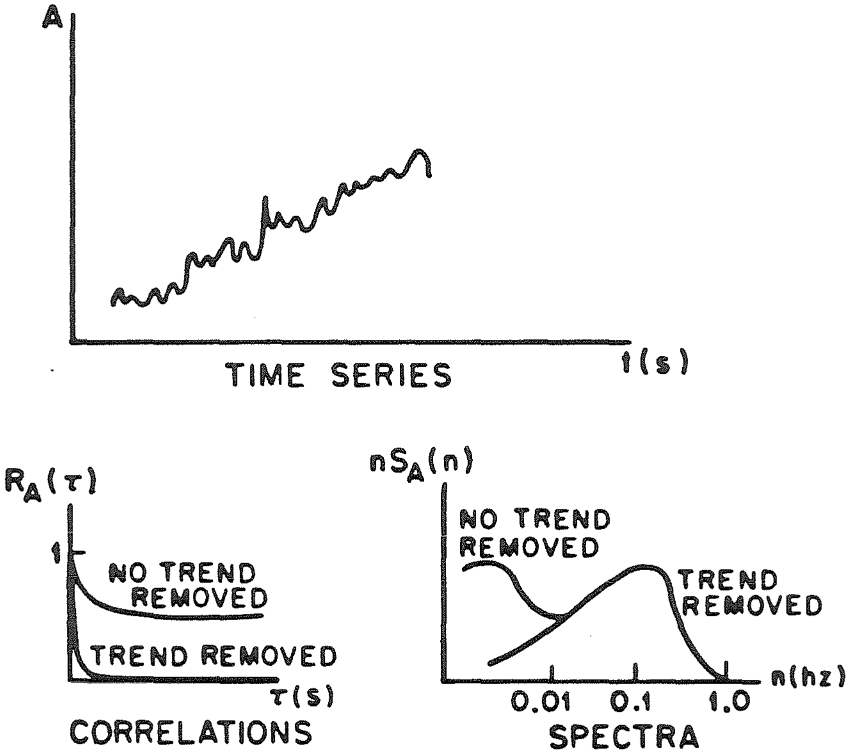

Figure 6-3

Effect of Trend Removal

on Correlation Functions and Spectral densities

(from Panofsky and Dutton, 1984)

which gives

$$\int_0^\infty S_\alpha(n)\,dn = \int_0^\infty E_\alpha(\omega)\,d\omega = \sigma_\alpha^2 \qquad (6.5-4)$$

and note the identity

$$\int_0^\infty S_\alpha(n)\,dn = \int_0^\infty nS_\alpha(n)\,d\ln n \qquad (6.5-5)$$

according to which the area under the curve defined by the function $nS_\alpha(n)$, which is often called the "logarithmic frequency spectrum," plotted against $\ln n$ represents variance and $nS_\alpha(n)$ represents the variance per unit logarithm frequency interval. This identity is useful in the computations through the iterative algorithm proposed later in this section.

We further denote with $\hat{S}_\alpha(n), \hat{R}_\alpha(\tau)$, the normalized spectral density and the temporal autocorrelation coefficient respectively

$$\hat{S}_\alpha(n) = \frac{S_\alpha(n)}{\sigma_\alpha^2}, \quad \hat{R}_\alpha(\tau) = \frac{R_\alpha(\tau)}{\sigma_\alpha^2} \qquad (6.5-6)$$

(Note also that we will use the superscripts E and L to discriminate between Eulerian and Lagrangian spectra, as we have done with the correlations).

In the following α will be identified exclusively with the fixed-point wind velocity component in the i-th direction, u_i, or with the lagrangian fluid particle component v_i. Thus the direction i will suffice in characterizing the turbulent frequency spectra $S_{ii}^E(n)$ and $S_{ii}^L(n)$. As far as (one-dimensional) spatial spectra are concerned, we assume that they are directly related to the frequency spectra through Taylor's "frozen turbulence" hypothesis, if, e.g., they are available and are to be used as a substitute of frequency spectra.

Another quantity, extensively used in atmospheric applications, also useful in our work, is the so called *meteorological frequency*, f, which is dimensionless and is defined as

$$f = n\frac{z}{\overline{u}} \qquad (6.5-7)$$

where z is the height above the ground and $\overline{u}$ is the mean wind velocity (sometimes substituted by the mean square-root-sum $\left\langle \sqrt{u_1^2 + u_2^2 + u_3^2} \right\rangle$ that is larger than the mean wind but is the quantity that is often measured in practice – see Panofsky and Dutton, 1984, p.98). The reason for using f is that, as we will briefly discuss later, on the basis of simple dimensional considerations for the surface layer, the spectra of any particular wind component are expected to scale with f (i.e. to be invariant, for given atmospheric stability conditions, when expressed in terms of f).

Spectral Form of Taylor's Theorem

Direct application of the Fourier transform to Taylor's theorem for single particle dispersion in homogeneous-stationary turbulence – equation (6.4-1a) – and for $i = j$ gives

$$\sigma_i^2(t) = \sigma_{v_i}^2 t^2 \int_0^\infty \hat{S}_{ii}^L(n) \frac{\sin^2 \pi n t}{(\pi n t)^2} dn \qquad (6.5-8)$$

It is easy to see that in the above expression, where – as always in this chapter – $\sigma_{v_i}^2$ is assumed to correspond to the theoretical value, obtained for infinite sampling time and zero averaging time, the term containing the dispersion time t essentially plays the role of a low-pass filter that cuts out the high frequencies. Indeed, t is acting as the equivalent of an averaging time T_a that "smooths out" effects of the random v_i corresponding to time scales shorter than t and thus produces the statistic σ_i^2. In the notation of Appendix A6.1, where $\sigma_\alpha^2[T_s, T_a]$ denotes the value of σ_α^2 evaluated for sampling time T_s and averaging time T_a, equation (6.5-8) can be writen as

$$\sigma_i^2 = t^2 \sigma_{v_i}^2 [\infty, t] \qquad (6.5-9)$$

The implicit sampling time is infinite, thus allowing (in principle) even the slowest variations in the turbulent field to affect the value of σ_i^2. In practice the concept of an infinite sampling time in the evaluation of turbulence statistics must correspond to intervals "long enough to accomodate all turbulent variations" but "short compared to the time scales of variations in the mean motions."

The Relation of Eulerian and Lagrangian Properties

Before proceeding to discuss the application of (6.5-8) in describing turbulent dispersion properties we must stress the (already mentioned) need to transform observed Eulerian spectra to the corresponding Lagrangian densities appearing in this equation. However, relating Eulerian and Lagrangian spectra or, equivalently, correlations, is a most complicated (and in general unresolved) problem, the detailed discussion of which is beyond the scope of this work. A brief introduction to the methods used for tackling this problem (and in general for measuring Lagrangian properties), can be found in Pasquill and Smith (1983, pp.81-87; see also pp.127-128) while for a more comprehensive analysis of such methods one may consult the report of Koper and Sadeh (1975). Some more recent dicussions of the subject can be found in Lee and Stone (1983b), Li and Meroney (1985ab) and Sadeh and Koper (1985).

In the present work we have already given equation (6.2-10), which is perhaps the most fundamental relationship among Eulerian and Lagrangian correlations, derived directly on the basis of Corrsin's (1959) independence hypothesis. The limits of the validity of this equation are discussed in Weinstock (1976). As we mentioned, the applicability of (6.2-10) to real situations is limited since it requires the a priori assumption of the transition density G. The most widely used alternative to the formal approaches based on this equation is the application of the so called ***Hay-Pasquill hypothesis*** (Hay and Pasquill, 1959) which states that Lagrangian and Eulerian correlations and spectra are similar in shape but are displaced by a scale factor β equal to the ratio of (typically the maximum) Lagrangian and Eulerian integral time scales $\beta = T^L/T^E$ (see Figure 6-4).

Thus

$$nS^L(n) = \beta n S^E(\beta n) \qquad (6.5-10a)$$

$$R^L(\beta\tau) = R^E(\tau) \qquad (6.5-10b)$$

Although this approach is strictly not valid in the high frequency range (inertial subrange), where the spectra have different limiting slopes, it appears to be a satisfactory

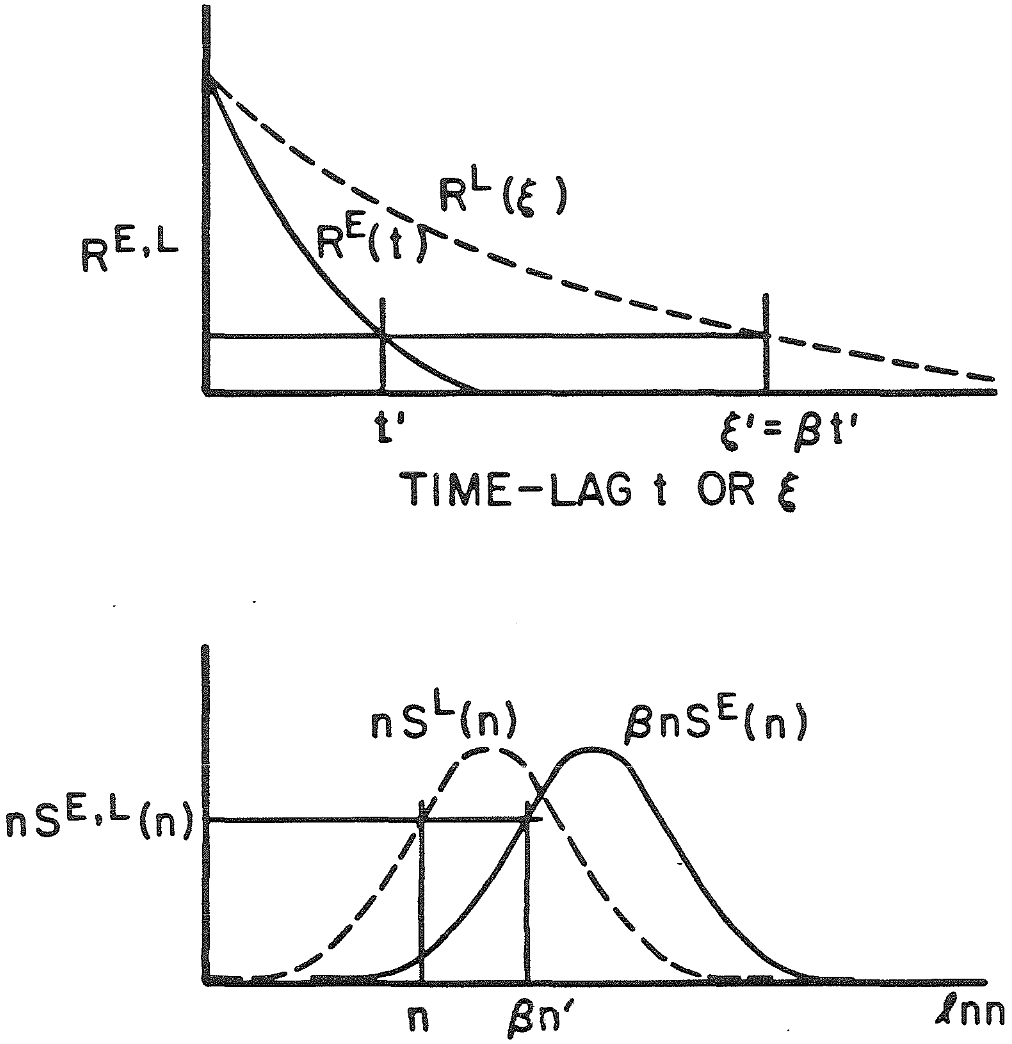

Figure 6-4

Relation of Lagrangian and Eulerian Spectra and Correlations According to the Hay-Pasquill Hypothesis approximation for the largest part of the spectrum according to available observations (see, e.g., Hanna, 1982). Thus it is adopted in the present work as the standard means for transforming observed Eulerian statistics to Lagrangian ones (especially when the calculations are relevant to the energy range).

Given the correlations or spectra, the only parameter required for applying the Hay-Pasquill hypothesis is β. Various methods have been proposed for its estimation. One approach has used equation (6.2-10) to infer some qualitative results concerning the Eulerian–Lagrangian time-scale relationship: Assuming *isotropic turbulence,* a Gaussian G with variance related to R^L through Taylor's theorem, and convenient forms of R^E, Saffman (1963) and Philip (1967) estimated the ratio of Lagrangian and Eulerian integral time scales $\beta = T^L/T^E$ as a function of the intensity of turbulence $\hat{\sigma}_{u_i} = \sigma_{u_i}/\overline{u}$, and found that, for small $\hat{\sigma}_{u_i}$,

$$\beta = \frac{T^L}{T^E} = \frac{\hat{\beta}}{\hat{\sigma}_{u_i}} \qquad (6.5-11)$$

The estimated values of the constant $\hat{\beta}$ were 0.8 (Saffman) and 0.35 (Philip).

Relation (6.5-11) was also proposed by Corrsin (1963), who, in a simplified analysis, assumed that the Eulerian and Lagrangian spectra are represented by their well known inertial subrange forms (obtained through dimensional/similarity analysis)

$$S_{ii}^{E}(n) = A_i\overline{u}^{2/3}\epsilon 2/3n^{-5/3} \qquad (6.5-12a)$$

$$S_{ii}^{L}(n) = B_i\epsilon n^{-2} \qquad (6.5-12b)$$

for $n \geq n^E = 1/T^E$ and $n \geq n^L = 1/T^L$ respectively, and are equal to zero for $n < n^E$, $n < n^L$. Indeed, integrating the above equations from 0 to ∞ and taking into account that for homogeneous turbulence $\sigma_{u_i}^2 = \sigma_{v_i}^2$, one obtains (6.5-11) again, with

$$\hat{\beta} = \left(\frac{3}{2}\right)^{3/2} \frac{A_i^{3/2}}{B_i}$$

More realistic forms of the spectra, with finite values at small frequencies, have produced similar results with $\hat{\beta}$ in general in the range 0.35–0.8 (see Pasquill and Smith, 1983, p.84). Current information regarding the value of $\hat{\beta}$ (for time scales along the mean wind direction), based on available observations, narrows the above range to 0.4–0.6, with the value 0.44 ($= \sqrt{\pi}/4$ – see Panofsky and Dutton, 1984) being the most common suggestion. Thus, typical values of β (calculated for typical values of $\hat{\sigma}_{u_i}$) wll be $\beta \simeq 4$ in neutral conditions, $\beta \simeq 2$ in the typical unstable daytime planetary boundary layer, and $\beta \simeq 10$ in stable conditions (Hanna, 1982). The value $\beta = 4$ has often been adopted as a representative average of β, independent of stability conditions.

6.5.2 An Iterative Spectral Algorithm for Estimating Relative Dispersion Parameters

General Discussion

The spectral form of Taylor's theorem for absolute dispersion, that shows explicitly the filtering role of travel time – and in particular expression (6.5-8a) which exemplifies the fact that absolute dispersion is (in principle) related to infinite sampling times – are the starting steps for developing a practical scheme for the estimation of relative dispersion parameters. The essense of our proposal is the following: at a given downwind distance (i.e. at a given dispersion time) apply the spectral formula (6.5-8) *modified so that it corresponds not to "infinite" sampling time but to a time period that is just long enough to take into account the effects of eddies of sizes smaller or comparable to a representative instantaneous "diameter" of the plume.* In this way, according to our discussion in the beginning of sub-section 6.5.1, meandering processes are excluded and the resulting σ_i^2 will be relevant only to relative dispersion processes.

In fact, the concept of finite sampling time, its effect on observed spectra, and the nature of dispersion parameters corresponding to such sampling times, have been the subject of study and discussion since the 1950's with the work of Ogura (1957, 1959) – see also Smith (1962), Hino (1968), Rowe (1979). In direct relation to relative dispersion parameter estimation, the most important work, formulated on conceptually similar grounds, has been that of Smith and Hay (1961), specifically in the context of the *growth of a finite cluster of particles.* (See also the discussion in Pasquill and Smith, 1983, pp.154-158). Their analysis, *valid exclusively for isotropic conditions* and for clusters with a priori assumed *Gaussian mean concentration distribution* about their center of mass, essentially starts from the differential form of equation (6.4-10b), makes use of the Hay-Pasquill hypothesis for the relation among Eulerian and Lagrangian correlations and spectra, and results in the following expression for the rate of growth of the isotropic cluster (with standard deviation σ_R from the center of mass)

$$\frac{d\sigma_R}{dt} = \frac{2}{3}\frac{\beta}{\overline{u}}\int_0^\infty \int_0^{\overline{u}t/\beta} E_{(3D)}(\kappa)\,\frac{\sin \kappa s}{\kappa s}\,\frac{1-\exp\left(-\sigma_R^2\kappa^2\right)}{\sigma_R}\,ds\,d\kappa \qquad (6.5-13a)$$

which for $\overline{u}t/\beta > \sigma_R$ simplifies to

$$\frac{d\sigma_R}{dt} = \frac{\pi}{3}\frac{\beta}{\overline{u}}\int_0^\infty E_{(3D)}\frac{1-\exp\left(-\sigma_R^2\kappa^2\right)}{\sigma_R\kappa}\,d\kappa \qquad (6.5-13b)$$

where $E_{(3D)}$ is the integrated three dimensional Eulerian spectrum in terms of the magnitude of the wavenumber vector κ and β is the Hay-Pasquill parameter. Based on the above expressions and making various simplifying assumptions Smith and Hay (1961) proposed a simple working approximation for the range of the expansion where the size of the cluster is of the same order of magnitude as the Eulerian integral length scale of turbulence (or – Pasquill and Smith, 1983, p.157 – where the downwind distance from the source of an initially small cloud is 10 to 80 times the Eulerian ssale):

$$\frac{1}{\overline{u}}\frac{d\sigma_R}{dt} = \frac{2}{3}\beta\hat{\sigma}_u^2 \qquad (6.5-14a)$$

or, approximately (and for $\beta = 4$) (*)

$$\frac{d\sigma_R}{dt} \simeq 0.3\sigma_u \qquad (6.5-14b)$$

---

* Note that Pasquill and Smith, 1983, p.230, suggest a factor of about 0.22 instead of 0.3 in this expression.

(which – after squaring – suggests that in this range only about a ninth of the total variance of turbulence contributes in the dispersion of the cluster). This expression corresponds to the maximum of the $d\sigma_R/dt$ slope predicted by the Smith-Hay model and requires that $\sigma_R^2 \sim t^2$. It should be observed at a "central stage" of dispersion (Panofsky and Dutton, 1984, p.252), as the exponent of t in $\sigma_{R_i}^2(t)$ drops from the value of 3.0 in the inertial stage to the value of 1.0 in the final stage of dispersion. The model of Smith and Hay (in its simplified form) was reviewed and compared with atmospheric data by Sawford (1982a) who indeed identified a certain range of agreement between predictions and observations; for further information the reader is referred to this paper and also a to a relevant discussion in Pasquill and Smith (1983, pp.230-232).

An important thing to observe at this point is that the general equation of Smith and Hay (6.5-13a) resembles the general spectral form of Taylor's single particle theorem with the additional presence of a low-pass filter function, of the form $\left[1-\exp\left(-\sigma_R^2\kappa^2\right)\right]/\sigma_R$. This particular form of this weighting function is due to assumptions concerning the two-particle velocity correlations in isotropic turbulence. In fact both the concept of isotropy and these assumptions constitute important restrictions on the generality of the Smith-Hay scheme; these restrictions are also, of course, extended to the permissible form of the spectrum that can be used in this scheme. As far as the simple approximate equation (6.5-14a) – which is actually the form of the model that has been used the most in applications – is concerned, it has been derived on the assumption of a specific, very simple (exponential type) Eulerian correlation. It is therefore obvious that the (even approximate) applicability of the Smith-Hay model to dispersion in the highly anisotropic energy range of atmospheric turbulence, with spectra that are sensitive functions of stability and height, is questionable.

So there arises naturally the problem of extending the Smith-Hay approach to more realistic situations. However, although the above approach is now twenty five years old there have not been – to our knowledge – any significant steps towards a practical generalization. An attempt to combine the theoretical scheme with information from actual atmospheric measurements was presented by Sheih (1980) who applied the approach of Smith and Hay directly to observed, Eulerian, one-dimensional, atmospheric frequency spectra. This attempt, which used isotropic theory results to model anisotropic conditions and directly substituted the one-dimensional frequency spectrum for the integrated three-dimensional wavenumber spectrum, contained some obviously serious errors and produced predictions that disagree with observations. However, it is still worth mentioning, at least because of the discussion it caused in the literature; indeed, Gifford (1981), who strongly criticized the model of Sheih, and also Mikkelsen and Troen (1981) and Rowe (1981), not only pointed out various problems and errors of Sheih's scheme but also provided some interesting comments regarding the spectral description of the relative dispersion prroblem.

Model Formulation

In the present work we avoid use of the Smith-Hay formula and propose a scheme based directly on the spectral form of Taylor's dispersion theorem, as stated in the beginning of the present subsection. The use of a theoretical result relevant to single-particle dispersion as a starting point might at first seem as an inappropriate step but in fact it is consistent with the relative dispersion concept (through the equivalence between relative-to-the-center-of-mass and two-particle dispersion). Indeed, filtering out the relatively low frequencies, that correspond to meandering, by using a small sampling time, is essentially equivalent to adopting a meandering frame (that follows the motion of the center of mass), since "an observer" moving with this frame does not "feel" exactly these frequencies.

The general relation for σ_i^2, for finite sampling time T_s (see also Appendix A6.1), is

$$\sigma_i^2\,(t;T_s) = \sigma_{v_i}^2 \int_0^\infty \hat{S}_{ii}^L\,(n)\,\frac{\sin^2 \pi n t}{(\pi n t)^2}\left(1 - \frac{\sin^2 \pi n T_s}{(\pi n T_s)^2}\right) dn \qquad (6.5-15)$$

a result that was discussed by Smith (1962).

In terms of the Eulerian spectrum (and assuming the Hay-Pasquill hypothesis is valid) equation (6.5-15) becomes

$$\sigma_i^2\left(t;T_s\right)=\sigma_{v_i}^2\int_0^\infty \hat{S}_{ii}^E\left(n\right)\frac{\sin^2\pi nt/\beta}{\left(\pi nt/\beta\right)^2}\left(1-\frac{\sin^2\pi nT_s}{\left(\pi nT_s\right)^2}\right)dn \qquad (6.5-16)$$

In order to calculate $\sigma_i^2\left(t;T_s\right)=\sigma_{R_i}^2\left(t\right)$ one must set T_s set equal to the maximum sampling time that still corresponds to the instantaneous or fluctuating plume, a typical estimate of which is

$$T_s=\frac{2\sqrt{2}\sigma_{R_i}}{\overline{u}} \qquad (6.5-17)$$

(clearly T_s will be different in the horizontal and vertical directions). An important point to note here is that the proper characteristic velocity appearing in the definition (6.5-17) does not have always to be exactly equal to the mean wind speed; in fact we define it here as being always identical to the characteristic velocity scale that appears in the definition of the meteorological frequency, and that results in invariant representations of the Eulerian spectra.

Of course T_s defined in through (6.5-17) is a function of the unknown σ_{R_i}, that is to be estimated, and hence (6.5-16) becomes a nonlinear integral equation for σ_{R_i}. The solution to this equation is obtained through an iterative algorithm as follows:

Step 1: Given the spectrum function $\hat{S}_{ii}^E\left(n\right)$ calculate the absolute diffusivity σ_i (corresponding to $T_s=\infty$) for given t:

$$\sigma_i^2\left(t\right)=\sigma_{v_i}^2t^2\int_0^\infty \hat{S}_{ii}^E\left(n\right)\frac{\sin^2\pi nt/\beta}{\left(\pi nt/\beta\right)^2}dn \qquad (6.5-18)$$

Step 2: Use σ_i as a first estimate of σ_{R_i} for given t

$$\sigma_{R_i}^{(1)}\left(t\right)=\sigma_i\left(t\right)$$

and set

$$T_{s,i}^{(1)}\left(t\right)=\frac{2\sqrt{2}\sigma_{R_i}^{(1)}}{\overline{u}}$$

to calculate

$$\left[\sigma_{R_i}^2\left(t\right)\right]^{(2)}=\sigma_{v_i}^2t^2\int_0^\infty \hat{S}_{ii}^E\left(n\right)\frac{\sin^2\pi nt/\beta}{\left(\pi nt/\beta\right)^2}\left(1-\frac{\sin^2\pi nT_{s,i}^{(1)}}{\left(\pi nT_{s,i}^{(1)}\right)^2}\right)dn \qquad (6.5-19)$$

Step 3: Use the value $\sigma^{(2)}(t)$ obtained from the previous step to calculate $T_{s,i}^{(2)}$ that improves the filter function, and introduce in the last equation above to obtain a refined estimate of $\sigma_{R_i} = \sigma_{R_i}^{(3)}$. Repeat until convergence is obtained (e.g., until two successively calculated values of σ_{R_i} do not differ by more than, say, 5%). We note here that an obvious requirement for this iterative process to converge is the absolute diffusivity to be a "sufficient" approximation for σ_{R_i}, a condition that might be violated very close to the source (in which case a fraction of σ_i might be used as a first estimate for σ_{R_i}).

Actually, numerical integration of the spectral formulas above is better performed with respect to $\ln n$ since the logarithmic frequency spectrum has a much smoother graph. Universal results (for given stability conditions) are obtained through the use of the meteorological frequency. An example of such calculations is given in the following paragraphs.

Model Application: An Example

The most important step in the implementation of the computational algorithm just described is the selection of the appropriate Eulerian spectral density. A variety of empirical and semiempirical models of $\hat{S}_{ii}^{E}(n)$ that fit extensive sets of observations have been proposed and tested during recent years. Excellent comprehensive reviews of the information and references relevant to these models can be found in Caughey (1982), Pasquill and Smith (1983, Chapter 2), Panofsky and Dutton (1984, Chapter 8), and – in a somewhat more concise form – in Jensen and Busch (1982). In particular, worthy of reference are the spectral function models proposed by Kaimal (1973) and Höjstrup (1982), for stable and neutral-unstable conditions respectively, that seem to be based on the currently most comprehensive data bases.

An extensive discussion of the spectral properties of atmospheric turbulence (which are covered satisfactorily in the works mentioned above) is beyond our present objectives. However, it is useful to recall briefly some important points: First, it must be clear that the interest here is in the spectra corresponding to the energy range of atmospheric turbulence. Observed inertial subrange spectra are in general found to follow the similarity analysis predictions, as given by equation (6.5-12a), in a satisfactory manner, the constants of this equation being approximately equal to

$$A_1 \simeq 0.15, \quad A_2 \simeq A_3 \simeq 0.20$$

Of course a sound general model for the energy range must produce the inertial subrange charactersistics at high frequencies, i.e.

$$n\hat{S}_{ii}^{E}(n) \sim n^{-2/3} \qquad (\text{large } n)$$

On the other hand, for very low frequencies $\hat{S}_{ii}^{E}(n)$ must tend to unity, i.e.

$$n\hat{S}_{ii}^{E}(n) \sim n \qquad (\text{small } n)$$

A plot of $n\hat{S}_{ii}^{E}(n)$ is expected to have these two asymptotes with a maximum (or "spectral peak") in between. This maximum is attained at a frequency n_m corresponding to the scale at which the predominant production of turbulent energy takes place. For an observer at height z above the ground this scale is expected to be proportional to $\overline{u}/z$ in the surface layer (see, e.g., Jensen and Busch, 1982, p.204). Thus the spectra $S_{ii}^{E}(n)$ of any particular velocity component are expected to scale with respect to the dimensionless meteorological frequency $f = nz/\overline{u}$, and, futhermore, $n\hat{S}_{ii}^{E}(n)$ at any height are expected to fall on a universal curve when plotted against f. (An interesting point to note is that the inertial subrange is typically always well confirmed for $f > 10$ and often for $f > 1$).

Perhaps the most simple spectral function that obeys the asymptotic rules stated above is given by

$$n\hat{S}_{ii}^{E}(n) = \frac{nS_{ii}^{E}(n)}{\sigma_{u_i}^{2}} = \frac{af}{(1+bf)^{5/3}} \qquad (6.5-20)$$

Although the above expression contains two parameters, a and b, integration from 0 to ∞ on one hand and differentiation for determining the position of the spectral extremum on the other, show immediately that

$$a = \frac{1}{f_m}, \quad b = 1.5 f_m \qquad (6.5-20a)$$

where f_m is the meteorological frequency corresponding to the maximum of the logarithmic spectrum, a parameter that is directly obtained from observations.

Introducing the spectral function (6.5-20) one calculates the ratio

$$\frac{\sigma_{R_i}^2}{\sigma_{u_i}^2}$$

as follows:

Step 1: Calculate the absolute diffusivity σ_i^2 over $\sigma_{u_i}^2$ for given dimensionless $t^* = t\overline{u}/z$:

$$\left(\frac{\overline{u}}{z}\right)^2 \frac{\sigma_i^2}{\sigma_{u_i}^2} = t^{*2} \int_0^\infty \frac{af}{(1+bf)^{5/3}} \frac{\sin^2 \pi f t^*/\beta}{(\pi f t^*/\beta)^2} d\ln f \qquad (6.5-18^*)$$

Step 2: Use $\sigma_i^2/\sigma_{u_i}^2$ as a first estimate of $\sigma_{R_i}^2/\sigma_{u_i}^2$ for given t^* and set

$$T_{s,i}^*(t) = \frac{2\sqrt{2}\sigma_{R_i}^2}{z\sigma_{u_i}^2/\overline{u}}$$

to calculate

$$\left(\frac{\overline{u}}{z}\right)^2 \frac{\sigma_{R_i}^2}{\sigma_{u_i}^2} = t^{*2} \int_0^\infty \frac{af}{(1+bf)^{5/3}} \frac{\sin^2 \pi f t^*/\beta}{(\pi f t^*/\beta)^2} \left(1 - \frac{\sin^2 \pi f T_{s,i}^*}{\left(\pi f T_{s,i}^*\right)^2}\right) d\ln f \quad (6.5-19*)$$

Step 3: Use the value of $\sigma_{R_i}^2/\sigma_{u_i}^2$ obtained from the previous step to refine the estimate of $T_{s,i}^*$, and introduce again in the last equation above to obtain a new value of $\sigma_{R_i}^2/\sigma_{u_i}^2$. Repeat until convergence is obtained.

Comments: (i) In practice a general infimum and a general supremum for the lower and upper limits of integration respectively are $f = 10^{-3}$ and $f = 10^3$; in most cases however minimum and maximum values of f equal to 10^{-2} and 10^2 are sufficient. (ii) To obtain absolute values of σ_{R_i} the relevant values of $\sigma_{u_i}^2$ are needed. Current knowledge regarding these values is reviewed in various sources, such as Nieuwstadt and van Dop (1982), Panofsky and Dutton (1984), and Weil (1985).

Given the frequency of the spectral maximum, f_m, the above procedure gives us $\sigma_{R_i}^2/\sigma_{u_i}^2$ as a function of the dispersion time t. As an example we present here calculations for both $\sigma_i^2/\sigma_{u_i}^2$ and $\sigma_{R_i}^2/\sigma_{u_i}^2$ for dispersion in the vertical ($i = 3$), with f_m given by the following equations, based on atmospheric measurements (Panofsky and Dutton, 1984, p.189):

$$f_m = 0.183 \quad \left(\frac{z}{L} < -0.7\right)$$

$$f_m = 0.482 + 0.437\frac{z}{L} \quad \left(-0.7 \leq \frac{z}{L} < 0\right)$$

$$f_m = 0.482 + 0.87\frac{z}{L} \quad \left(\frac{z}{L} > 0\right)$$

where L is the Monin-Obukhov length. Figures 6-5a, 6-5b, and 6-5c contain the results for $z/L = 0.0$ (neutral atmosphere), $z/L = -1.0$ (unstable atmosphere), and $z/L = 1.0$ (stable atmosphere). Typical values of $\beta = 4$, 2, and 10 were used respectively for these three cases.

It is easy to see that these figures show quite good agreement – at least on a qualitative basis – with the known asymptotic results from similarity theory: $\sigma_i^2 \sim t^2$ for small times and $\sigma_i^2 \sim t$ for large times; also $\sigma_{R_i}^2 \sim t^3$ in the beginning of the calculations for the σ_{R_i} and $\sigma_{R_i}^2 \sim \sigma_i^2$ at large dispersion times. (Recall that the early, source-dependent, phase of the relative dispersion process is not modeled by the present algorithm). As expected, the effect of meandering is much more profound in unstable atmospheric conditions and reduces significantly with increasing atmospheric stability. For intensely unstable atmospheres σ_i seems to be a bad first approximation for σ_{R_i} for a significant downwind distance; thus, if for an application σ_{R_i} cannot simply be neglected with respect to meandering (which dominates dispersion there), it seems that one should calculate relative dispersion from some semiempirical formula that involves an effective source size.

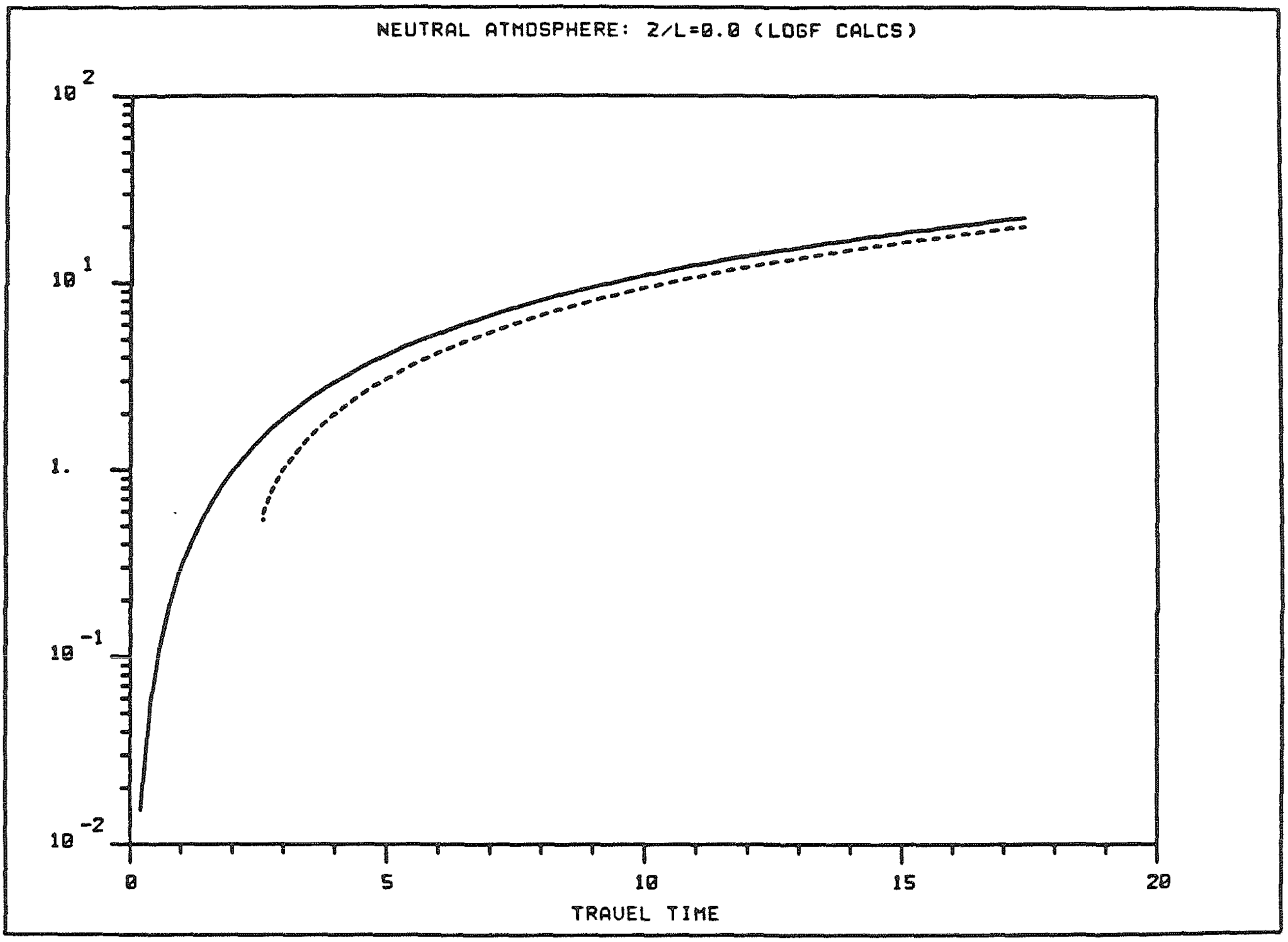

Figure 6-5a

Absolute and Relative Dispersion Parameters over $\sigma_{u_i}^2\ (z/\overline{u})^2$
(Solid and Dashed line respectively)
in the Vertical Direction, versus $t\overline{u}/z$,
for Neutral Atmospheric Conditions ($z/L = 0.0$),
Calculated through Iterative Filtering of the Turbulent Spectrum

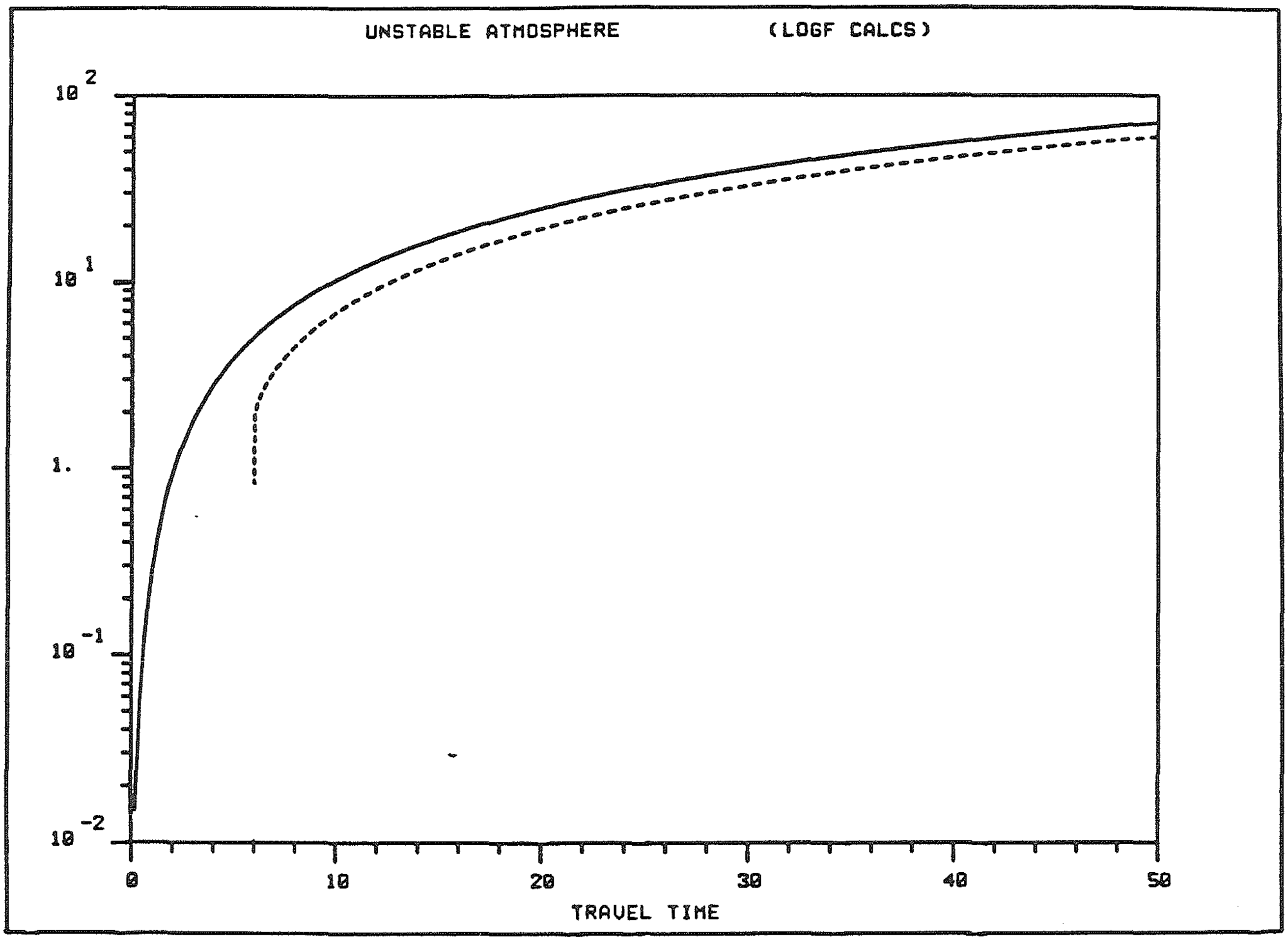

Figure 6-5b

Absolute and Relative Dispersion Parameters over $\sigma_{u_i}^2\,(z/\overline{u})^2$

(Solid and Dashed line respectively)

in the Vertical Direction, versus $t\overline{u}/z$,

for Unstable Atmospheric Conditions $(z/L = -1.0)$,

Calculated through Iterative Filtering of the Turbulent Spectrum

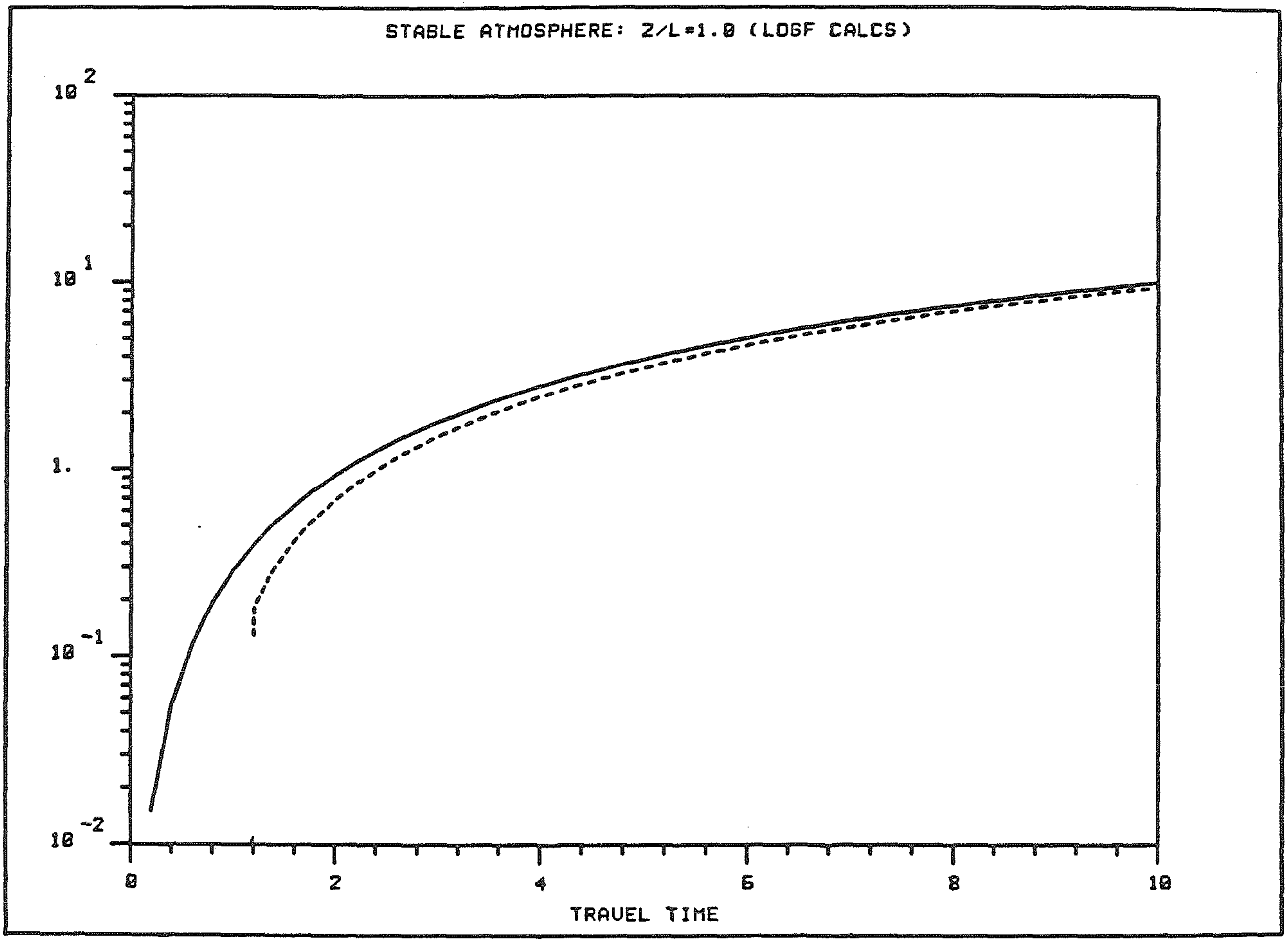

Figure 6-5c

Absolute and Relative Dispersion Parameters over $\sigma_{u_i}^2\,(z/\overline{u})^2$
(Solid and Dashed line respectively)
in the Vertical Direction, versus $t\overline{u}/z$,
for Stable Atmospheric Conditions ($z/L = 1.0$),
Calculated through Iterative Filtering of the Turbulent Spectrum

6.6 CONCLUSIONS

The discussion in this chapter attempted an overview of different concepts and methods employed in the description of relative dispersion, focusing in particular on their interrelationships. A point that was stressed here is that various important questions, regarding sometimes widely applied hypotheses, remain unresolved and waiting for definitive answers. However, the attention that is given to the subject of relative dispersion has been steadily increasing in recent years (partly due to realizing its importance in modeling short term incidental releases of hazardous gases and to the problems related to concentration fluctuations), and a better understanding of the problems involved is a certain fact. It is hoped in particular that comparison of both the underlying fundamental assumptions and of the results from different methods employed to study relative dispersion will significantly improve the insight on the ambiguous points.

Among the methods presented here, those based on stochastic ordinary differential equations (Langevin equations) and their discrete counterparts (autoregressive time series models) seem to have the potential for improving our fundamental understanding of phenomena related to relative dispersion process in a more tractable manner than formulations dealing directly with the dynamics of transition functions. Nevertheless, the generality of the formalism that is developed in connection with the dynamics of the (stochastic and deterministic) transition functions allows us to see the various practical models of dispersion from a more broad perspective, derive and classify them in an elegant and general manner, and identify the connection of the assumptions involved in their formulations. In particular the discussion in this chapter tried to show that the use of time-dependent diffusion coefficients in an ADE-type equation is not an "illogical concept," as it is often claimed, but constitutes an – admittedly artificial – compromise that turns the parabolic partial differential equation of transport into a non-local scheme, avoiding the introduction of integrodifferential models that formally account for the non-localness of the turbulent dispersion process.

From a more practical point of view, application of appropriate filtering tecniques on observed turbulent spectra seems to offer a promising method for estimating dispersion parameters, with the effects of sampling and averaging time explicitly incorporated in their estimation. In this way these parameters reflect the action of the random fuid motions associated with a particular range of temporal and spatial scales. Thus not only the nature of the different "components" of dispersion is made clear, but also a means for exactly identifying the scales relevant to "mixing" and "advection" on a quantitative basis is possible. Of course various problems associated with this method expect some future improvement in their treatment; perhaps the most important are related to the Lagrangian–Eulerian spectra relationship and to the incorporation of an effective source size in the overall scheme of calculations.

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APPENDIX A6.1

Frequency Spectra
and the Statistical Effects of
Finite Sampling and Averaging Times

The apparent statistical properties of random fluctuating aerometric quantities such as wind velocity components, temperature, concentrations etc., are implicit functions of the averaging time T_a and the sampling duration T_s involved in their measurement or estimation. In the modeling schemes of the present work we employ mainly the variances, temporal autocorrelations, and frequency spectra of such quantities. Here we focus on the effects of finite sampling and averaging time on the variance, considering its spectral representations.

Let $\sigma_\alpha^2\,[T_s, T_a]$ represent the apparent variance of the (Eulerian or Lagrangian) quantity α obtained by averaging measurements over the time interval T_a and sampling for time T_s. The fluctuation of α about its mean value is assumed to be a stationary stochastic function of time; thus the "theoretical" ensemble variance of α will be

$$\mathrm{E}\{\alpha'^2\} = \left\langle \alpha'^2 \right\rangle = \sigma_\alpha^2 = \sigma_\alpha^2\,[\infty, 0]$$

where $\alpha' = \alpha - \langle\alpha\rangle$.

Let $R_\alpha(\tau)$ be the temporal autocorrelation coefficient of α'

$$R_\alpha(\tau) = \mathrm{E}\{\alpha'(t)\,\alpha'(t+\tau)\}$$

and $F_\alpha(\omega)$ be its (cyclic) frequency spectrum. At this point it is necessary to summarize a few remarks regarding the definition of spectral functions in studies of turbulence. (It must be noted of course that although the present discussion considers temporal single-point autocorrelations and related frequency spectra these remarks also apply to cross-correlations in both space and time and to all relevant frequency or wave-number spectral functions and tensors).

The majority of works in turbulence (see,e.g.,Monin and Yaglom, 1975; Tennekes and Lumley, 1972; Townsend, 1976; Batchelor, 1953 defines $F_\alpha(\omega)$ as the non-symmetric Fourier transform of $R_\alpha(\tau)$ with the $1/2\pi$ factor in the transform partner of the pair

$$F_\alpha(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} R_\alpha(\tau)\exp(-i\omega\tau)\,d\tau \qquad (A6.1-1)$$

which for symmetric $R_\alpha(\tau)$, i.e. stationary α' (as it was assumed) becomes

$$F_\alpha(\omega) = \frac{1}{\pi}\int_{0}^{\infty} R_\alpha(\tau)\cos\omega\tau\,d\tau \qquad (A6.1-1a)$$

This allows use of the spectrum $E_\alpha(\omega) = 2F_\alpha(\omega)$, defined for $0 \le \omega < \infty$ instead of $-\infty < \omega < \infty$, and thus

$$R_\alpha(\tau) = \int_{-\infty}^{\infty} F_\alpha(\omega)\exp(i\omega\tau)\,d\omega = \int_0^\infty E_\alpha(\omega)\cos\omega\tau d\omega \qquad (A6.1-2)$$

This notation comes in contrast with the common convention of (electrical mainly) engineering literature where the $1/2\pi$ factor is included in the inverse transform partner of the pair. However notational confusion does not stop at this point. Some works which are standard references in atmospheric turbulence and atmospheric diffusion theory do not follow the majority of turbulence literature but adopt different definitions:

Pasquill and Smith (1983: third edition of the classic monograph of Pasquill) adopt the definition (also used by Hinze, 1975)

$$F_\alpha^{(PS)}(\omega) = 2\int_{-\infty}^{\infty} R_\alpha(\tau)\exp(-i\omega\tau)\,d\tau = 4\int_0^\infty R_\alpha(\tau)\cos\omega\tau d\tau$$

and therefore

$$R_\alpha(\tau) = \frac{1}{4\pi}\int_{-\infty}^{\infty} F_\alpha^{(PS)}(\omega)\exp(i\omega\tau)\,d\omega = \frac{1}{2\pi}\int_0^\infty F_\alpha^{(PS)}(\omega)\cos\omega\tau d\omega$$

whereas Panofsky and Dutton (1984) set

$$F_\alpha^{(PD)}(\omega) = \frac{1}{\pi}\int_{-\infty}^{\infty} R_\alpha(\tau)\exp(i\omega\tau)\,d\tau = \frac{2}{\pi}\int_0^\infty R_\alpha(\tau)\cos\omega\tau d\tau$$

and

$$R_\alpha(\tau) = \frac{1}{2}\int_{-\infty}^{\infty} F_\alpha^{(PD)}(\omega)\exp(-i\omega\tau)\,d\omega$$

In other words

$$F_\alpha^{(PD)}(\omega) = E_\alpha(\omega)$$

It is therefore imperative that great care is taken when, e.g., an empirical spectral function is used in calculations, to be sure to what definition it corresponds.

Here we adopt the "mainstream" definition as in Monin and Yaglom (1975), using both $F_\alpha(\omega)$ and $E_\alpha(\omega)$. We also introduce the absolute spectral density in terms of "arithmetic frequency" $n = \omega/2\pi$

$$S_\alpha(n) = 2\pi E_\alpha(2\pi n) \qquad (A6.1-3)$$

which gives

$$\int_0^\infty S_\alpha(n)\,dn = \int_0^\infty E_\alpha(\omega)\,d\omega = \sigma_\alpha^2 \qquad (A6.1-4)$$

With this definition our spectral density $S_\alpha(n)$ is identical to both the function $S(n)$ defined in Pasquill and Smith (1983, p. 23) and to the function $S(f)$ defined in Panofsky and Dutton (1984, p. 85). A useful thing to note here is the identity

$$\int_0^\infty S_\alpha(n)\,dn = \int_0^\infty nS_\alpha(n)\,d\ln n$$

Thus the area under the curve $nS_\alpha(n)$ plotted against $\ln n$ represents variance. Thus $nS_\alpha(n)$ represents the variance per unit logarithm frequency interval.

Let further $\hat{S}_\alpha(n), \hat{R}_\alpha(\tau)$, be the normalized spectral density and the temporal autocorrelation coefficient respectively

$$\hat{S}_\alpha(n) = \frac{S_\alpha(n)}{\sigma_\alpha^2}, \quad \hat{R}_\alpha(\tau) = \frac{R_\alpha(\tau)}{\sigma_\alpha^2}$$

Then it is easy to show that

$$\sigma_\alpha^2[\infty, T_a] = \frac{2\sigma_\alpha^2}{T_a}\int_0^{T_a}\left(1-\frac{\tau}{T_a}\right)\hat{R}_\alpha(\tau)\,d\tau \qquad (A6.1-6)$$

(see, e.g., Tennekes and Lumley, 1972, p. 212; see also Chapter 5).

In terms of the spectral density one has (see, e.g., Pasquill and Smith, 1983, p. 26)

$$\sigma_\alpha^2[\infty, T_a] = \sigma_\alpha^2\int_0^\infty \hat{S}_\alpha(n)\frac{\sin^2 \pi nT_a}{(\pi nT_a)^2}dn \qquad (A6.1-7)$$

Thus, as T_a is increased, more of the spectrum is cut off and $\sigma_\alpha^2[\infty, T_a]$ is reduced.

The complementary effect of sampling over finite time T_s can also be derived (Pasquill and Smith, 1985, p. 26):

$$\sigma_\alpha^2[\infty, 0] = \sigma_\alpha^2[T_s, 0] + \sigma_\alpha^2[T_s, 0]_\infty \qquad (A6.1-8)$$

where the subscript ∞ implies averaging of the variances estimated from consecutive periods T_s over infinite time. Substituting from (A6.1-7) one has

$$\sigma_\alpha^2[T_s, 0]_\infty = \sigma_\alpha^2\int_0^\infty \hat{S}_\alpha(n)\left(1-\frac{\sin^2 \pi nT_s}{(\pi nT_s)^2}\right)dn \qquad (A6.1-9)$$

For very large T_a the weighting function cuts off all but the very low frequencies, for which $\hat{S}_\alpha(n) \rightarrow 4T^*$ with $T^* = \int_0^\infty R_\alpha(\tau)\,d\tau$, effectively independent of n. Then, in (A6.1-7) $\hat{S}_\alpha(n)$ can be taken outside the integral sign and therefore

$$\lim_{T_a\rightarrow\infty}\sigma_\alpha^2[\infty, T_a]\,T_a = 2\sigma_\alpha^2 T^* \qquad (A6.1-10)$$

(A6.1-10) is also the limiting form of Taylor's relations

$$\frac{d}{dT_a}\left\{\sigma_\alpha^2[\infty, T_a]\,T_a\right\} = 2\sigma_\alpha^2\int_0^{T_a} R_\alpha(\tau)\,d\tau \qquad (A6.1-11a)$$

$$\sigma_\alpha^2\left[\infty, t\right] t^2 = 2\sigma_\alpha^2 \int_0^t \int_0^{T_a} R_\alpha\left(\tau\right) d\tau\, dT_a \qquad (A6.1-11b)$$

which are applicable to any stationary random function of time.

When available data correspond to both finite sampling and averaging time the effect of the two in combination depends on the order in which the averaging and sampling operation are carried out. The two alternative procedures are described by Pasquill and Smith (1983, p. 28):

(I) for samples of length T_s averages are taken over subintervals T_a which do not overlap (T_s/T_a must be an integer),

(II) averages are taken over intervals of length T_a and from the smoothed time series constructed in this way samples of length T_s are formed. In this case averages may be taken in an overlapping manner.

The combined effects of finite sampling and averaging times are given by the following relations (Pasquill and Smith, 1983) for procedures (I) and (II) respectively:

$$\sigma_\alpha^2\left[T_s, T_a\right]_{(\mathrm{I})} = \sigma_\alpha^2 \int_0^\infty \hat{S}_\alpha\left(n\right)\left(\frac{\sin^2 \pi n T_a}{\left(\pi n T_a\right)^2} - \frac{\sin^2 \pi n T_s}{\left(\pi n T_s\right)^2}\right) \qquad (A6.1-12a)$$

$$\sigma_\alpha^2\left[T_s, T_a\right]_{(\mathrm{II})} = \sigma_\alpha^2 \int_0^\infty \hat{S}_\alpha\left(n\right)\frac{\sin^2 \pi n T_a}{\left(\pi n T_a\right)^2}\left(1 - \frac{\sin^2 \pi n T_s}{\left(\pi n T_s\right)^2}\right) \qquad (A6.1-12b)$$

Thus, in case (I) the resultant effect is equivalent to substracting the separate weighting functions for averaging over T_a and T_s, while in case (II) it is equivalent to applying the product of the separate weighting functions.

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for Appendix A6.1

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CHAPTER 7

Chapter 7 contains

- *a discussion of the initial phases of plume dispersion, and the scales and properties that are relevant to each phase,*
- *a brief overview of methods employed to model plume rise,*
- *a presentation of the models of Briggs and Schatzmann that are suggested as the “simple” and “comprehensive” alternatives, respectively, for use with the TRPM.*

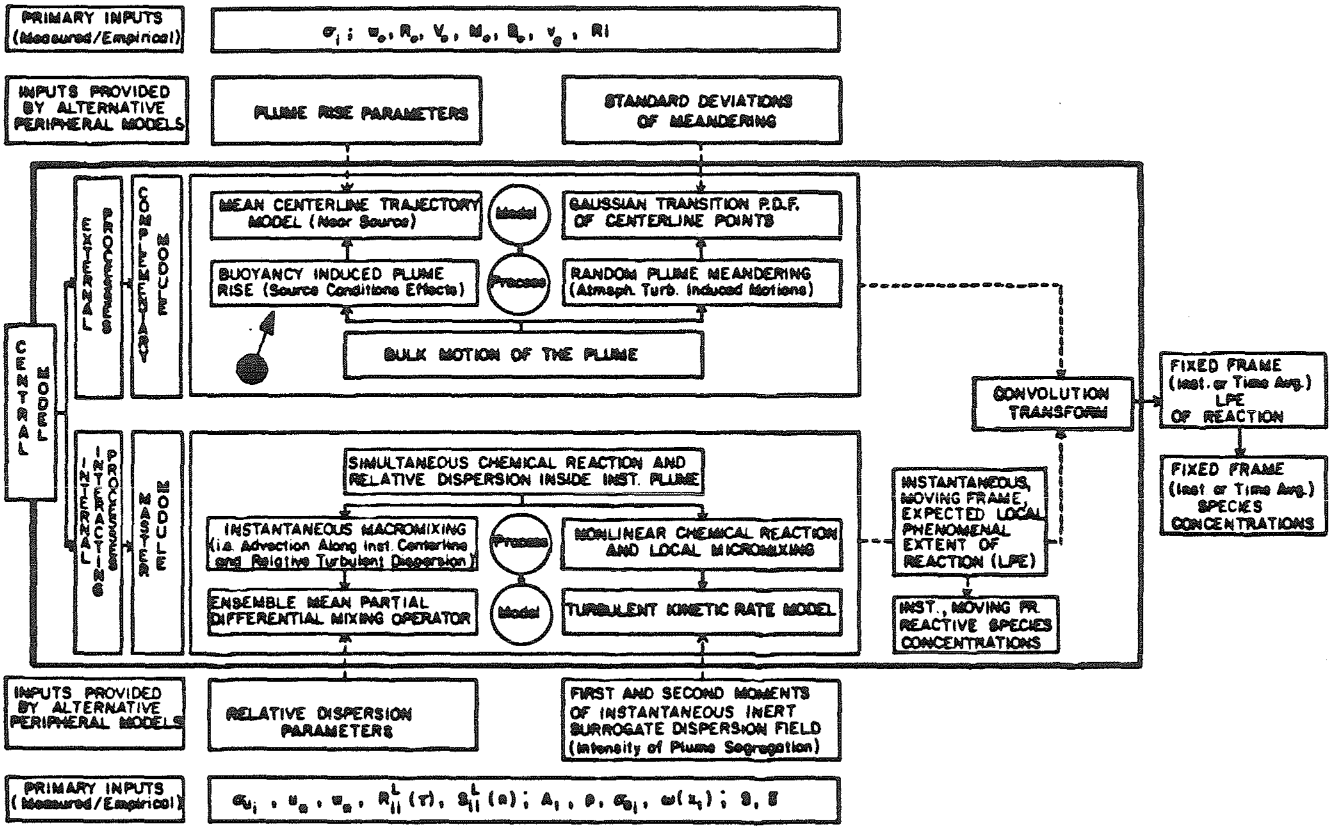

Figure 2-1d

TRPM Components Discussed in Chapter 7

CHAPTER 7

NEAR FIELD PLUME DYNAMICS

7.1 INTRODUCTION

In the development of the Turbulent Reacting Plume Model (TRPM) it was assumed that the processes of plume mixing that interact with chemistry are solely due to the action of the ambient, atmospheric, turbulence. Thus, as was mentioned in Chapters 2 and 3, the details of the early stages of plume dispersion, where the exit flow of gases from a stack (or any other "point" source) "merges" with the ambient cross-flow, are neglected (*). This was done on the basis of the argument that this process of flow merging is very fast compared to the time scales of both molecular diffusion processes and of nonlinear chemical interactions between plume and ambient species, of the type this work mainly focused on.

Nevertheless, source conditions play a significant role, not only by determining the rate and quality of early plume mixing but, more importantly, by affecting the dispersion and mixing parameters far beyond the stage where the plume exists as a separate fluid mechanical entity, distinct from the ambient flow. More specifically, initial conditions, in combination with the state of ambient stability, determine the

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(*) It must be noted that the description of mixing and dispersion in the present basic operational version of the TRPM does not involve any geometric, kinematic or thermal parameters of the source, such as stack diameter, effluent exit temperature or velocity, etc.; actually the species emission rate is the only input associated with the source that is required directly by the master module of the TRPM.

evolution of the ascending path of the mean plume centerline and its final total rise, i.e. the height where atmospheric dispersion of the emissions essentially starts. Knowledge of the position of the mean centerline is essential not only for "placing" the results of local reaction-dispersion calculations at the actual mean spatial coordinates to which they are relevant (and therefore for integrating the results of the TRPM with calculations from larger scale models), but also because the dispersion rate of the plume may depend on its actual rise. A most extreme example of this dependence is associated with the existence of elevated temperature inversions. In such a case the buoyancy of the emissions may be able to cause (at least partial) penetration of this inversion layer. This will result in a significant reduction of near ground-level concentrations as well as of plume dispersion rates just above the inversion. A more general quantitative measure of the effects of near-field plume rise on plume dispersion can be obtained by examining the maximum ground level concentration which is roughly proportional to the inverse square of the effective source height. Experience suggests that this effective height is typically 2 to 10 times the actual stack height (Hanna et al., 1982); plume rise can therefore reduce (even without causing penetration of an inversion) ground level concentration by a factor of as much as 100. One must therefore conclude that a reliable scheme for the estimation of plume rise is a required component of any "realistic" reacting plume model.

It is nevertheless clear that the problem of near field plume (or jet) dynamics can often be of overwhelming complexity as it involves the simultaneous transfer of mass, momentum and heat, coupled with boundary conditions that can be highly complicated. Thus, intricate flow patterns and mixing mechanics are to be expected, except in the most trivial of cases (see also Figure 7-1). Analytical (exact or approximate) results are available for point sources of momentum and/or heat in a calm environment, resulting in laminar jets and plumes (see, e.g., Seinfeld, 1975; Yih, 1977). Extensive information is also available regarding the internal flow structure of turbulent jets and plumes in calm backgrounds (see, e.g., Hinze, 1975). In the case of discharges in turbulent cross flows the physics of the problem become very difficult to handle and available experimental data and numerical computations reveal complex schemes of mixing and flow development (see, e.g., Moussa et al., 1977; Crabb et al., 1981). It is beyond the scope of the present work to discuss the vast range of research, both theoretical and experimental, that is relevant to turbulent jets and plumes; a relatively recent review of the current state of the field can be found in List (1982) – see also Fischer et al. (1979), Chen and Rodi (1980), Rodi (1982).

In the case of atmospheric plumes in particular, buoyancy is typically much more important than initial momentum (see next section) and hence it is mainly the former that determines plume evolution in the near field. This leads to the "line thermal analogy" for plume rise, according to which the internal motion of a point source plume resembles the convective motion induced by an instantaneous line source of heat corresponding to the projection of the mean plume centerline on the horizontal plane at source height. Csanady (1973; Chapter 6) and Scorer (1978; Chapter 10) contain informative introductions to the fundamental theory of buoyancy dominated plumes; for further analysis of the fundamentals of buoyancy effects in fluids one should consult the relevant monograph of Turner (1973); finally, useful introductions to the techniques of plume modeling can be found in Seinfeld (1975), Eskinazi (1975), Fischer et al. (1979) and Gebhard et al. (1984). Proceeding from the fundamental concepts, that are exposed in the above references, to computational models that realistically predict plume rise under atmospheric conditions (for given ambient stability) is far from being a trivial or even straightforward step. Indeed, although many models start from a common fundamental (and simplified) "picture" of the plume (see Section 7.3) they produce different working formulas (and results that vary significantly for the same inputs) as they adopt different assumptions regarding the action of atmospheric and plume turbulence.

The field of atmospheric plume rise modeling has been reviewed extensively and periodically by Briggs (see, e.g. Briggs 1969, 1975, 1984) who compared and classified

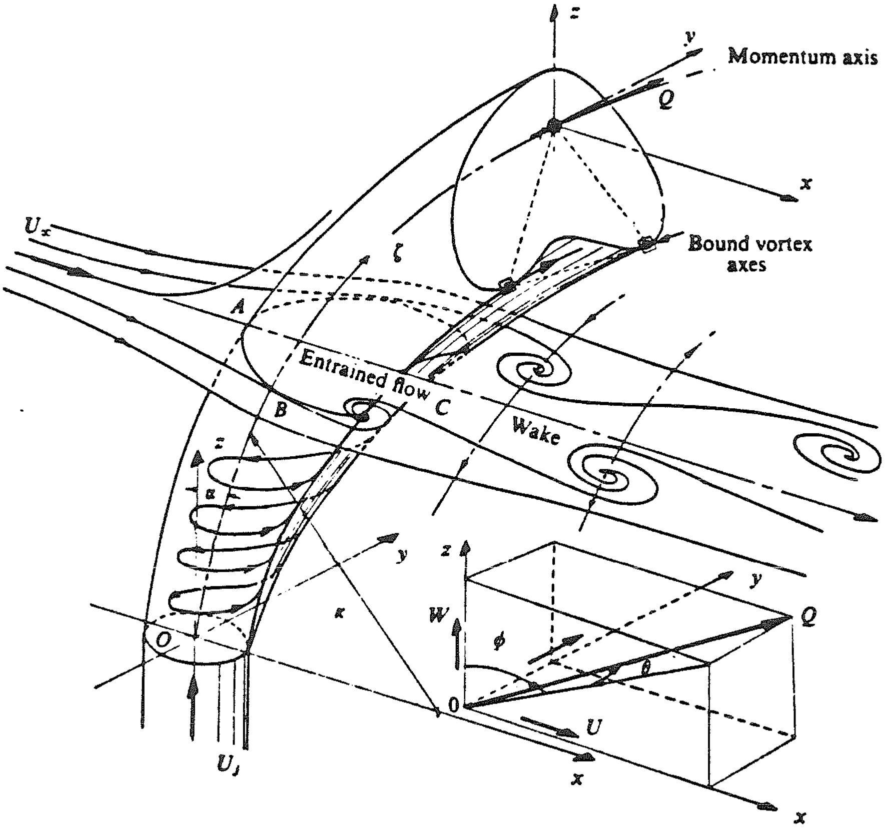

Figure 7-1

Rising Plume in a Cross-Flow

(Source: Moussa et al., 1977)

a variety of modeling approaches(*) as well as available data to finally reach a set of formulas (also periodically updated) that today are the most widely used means of calculating the rise of atmospheric plumes (see Section 7.4). Another extensive review, focusing on models for the prediction of cooling tower plume rise from natural-draft cooling towers, was presented by Carhart et al. (1982) who evaluated the theory and performance of 16 such models. Finally, a concise but general overview and discussion of the subject of plume rise modeling can be found in Schatzmann and Policastro (1984) who classify and analyze a wide range of assumptions commonly involved in this modeling.

In the present chapter, after a discussion of the main qualitative features of near field plume dynamics, and a general classification of the approaches that have employed to model these dynamics (a classification that contains some information more recent than what can be found in the latest works of Briggs), we present the two alternative options suggested for use with the TRPM. These are the widely used semiempirical algebraic equations of Briggs, and a more general scheme (a self similarity model of plume rise) resulting in a set of ordinary differential equations that require numerical solution, based on the work of Schatzmann and his coworkers; the latter is presented in relative detail in Appendix A7.2.

(*) In his 1975 review Briggs lists and discusses the basic features of about 50 models of atmospheric plume rise.

7.2 QUALITATIVE CONSIDERATIONS

7.2.1 Phases of Plume Dispersion

In order to provide perspective on the qualitative dynamics of atmospheric plumes we consider the following typical case of a plume "bent over" by the wind (Slawson and Csanady, 1967, 1971; Csanady, 1973): Effluent gases leave an industrial stack with temperature differences from the ambient environment of the order of 100-300 ^{0}C and vertical velocities w_0 of the order of 10 m s^{-1}, entering a cross wind of speed u_∞ that is of similar order of magnitude. Thus, the effluent gases from the stack "carry" both momentum and buoyancy "of their own" and therefore constitute a buoyant jet (or a forced plume) entering a turbulent atmosperic crossflow. Rapid mixing with the ambient air takes place and the plume axis bends over into the wind as the effluent gases acquire the horizontal momentum of the ambient air. Observations show that the transfer of horizontal momentum is usually essentially complete within a few stack diameters from the exit (Csanady, 1973). Thus very quickly portions of the plume start to travel horizontally at the mean speed of the ambient wind. Nevertheless, their vertical velocity relative the the ambient fluid however does not disappear so quickly, because of the continued action of the buoyancy forces.

Csanady (1973) reports that from several observations of the near-source size of chimney plumes chimney it may be inferred that the effective mass of effluent gases increases through vigorous mixing with ambient air by something like a factor of 30 within a distance of 3 to 5 source diameters. By this time the deficiency of horizontal momentum compared to ambient air is therefore a negligible 3%. The vertical velocity w_M due to initial velocity is also about 3% of the original w_0, that is for $w_0 \simeq 10$ m s^{-1} w_M is of the order of 30 cm s^{-1}. However, if the chimney diameter is not much less than say 3 m, the buoyancy force has had several seconds to act in the time the gases have moved 3 to 5 diameters (that is 9 to 15 m). A typical order of magnitude for the initial buoyant acceleration of industrial stacks is 10 m s^{-2}, and although this also reduces through mixing in the same proportion as initial momentum, it generates an appreciable vertical velocity within the first few seconds. Indeed if the average acceleration between leaving the chimney top and a 30-fold increase in mass is only 1 m s^{-2}, and if this initial adjustment phase lasts at least 1 s, the buoyant contribution to vertical velocity becomes 1 m s^{-1}, or 3 about times larger than that due to the initial momentum. Csanady (1973) notes that such a conclusion holds only for chimneys discharging substantial quantities of heat. An initial buoyancy caused acceleration of the order of 10 m s^{-2} implies an initial excess temperature of the effluent gases of the order of 300 ^{0}C. For a 3 m diameter chimney and an exit velocity w_0= 10 m s^{-1} this corresponds to a considerable rate of heat release (order of 6000 kcal s).

These conclusions will not apply to much smaller chimneys (of order 1 m in diameter or less) nor to those which discharge their gases with a small buoyant acceleration. In such non-buoyant cases plume rise is due basically to initial momentum and is usually essentially complete within 10 chimney diameters or so. However, the vast majority of large industrial point sources produce buoyancy rather than momentum dominated plumes, as in the situation described here, and most effort in the field of atmospheric modeling has focused on these cases.

From the above example it becomes obvious that in buoyancy dominated plumes neither the radius of the stack, nor the initial vertical exit velocity are dominant in determining the path of the plume beyond the earliest mixing phase (often referred to as the "jet" or "momentum phase") that lasts for a distance of the order of a few stack diameters. The factor that quickly becomes of dominant importance is the total excess heat. However, beyond the jet phase of the plume this excess heat is small enough, even in plumes generated by large heat sources, and the Boussinesq approximation seems to be a valid assumption in most of the cases. These facts suggest that it is useful to identify succesive stages in the evolution of a typical plume, where different sets of parameters are important and appropriate simplifications can be made in the analytical description of the plume. The brief discussion that follows is based on the analysis of Slawson and Csanady (1967, 1971) who identified four phases (and classified them as the zeroth, first, second and third phase of plume evolution). An actual atmospheric plume is expected to conform better to this rather idealized qualitative model of behavior in near neutral atmospheres.

The Momentum (or Jet) Phase

This initial phase of plume evolution extends a few (say 3 to 5) stack diameters downwind and its dynamics are determined by source properties (stack radius, exit speed, density of effluent) and the ambient density and mean wind speed at source height. The inherent turbulence of the exit flow is much stronger than the ambient turbulence and dominates transport processes and the internal plume flow structure.

The Thermal Phase

In this phase the effect of source diameter and exit velocity become unimportant. Mean plume dynamics are determined by the flux of buoyancy of the plume and the ambient mean wind speed and stratification (i.e. the atmospheric potential temperature gradient). Inherent plume turbulence (generated by buoyant convective motion) still dominates the ambient and determines local turbulent properties and mixing. The total downwind extent of this phase is expected to be of the order of about a hundred stack diameters.

In a neutral atmosphere, or for suitably small vertical plume displacements, the flux of buoyancy may be regarded as approximately constant in this phase. However, in a stable atmosphere the potential temperature of the environment increases as the plume rises so that the plume's excess temperature (and hence its total buoyancy decreases). The converse is the case in an unstable atmosphere. (In highly unstable atmospheric conditions the vigorous convective motions of the ambient will most probably dominate very early the inherent motions of the plume and will play a more important role in determining its rise).

The term thermal phase is usually attributed to a rather smooth phase of buoyant plume dispersion, and is commonly associated with near-neutral conditions. In these conditions most buoyancy dominated plumes retain smooth outlines and a moderate slope (about 0.2 or even less) against the horizontal for some distance during this phase, unless special ambient flow properties and source configuration cause characteristic irregularity phenomena known under the names of thermalling, downwashing (or flagging), downdraught, puffing and bifurcation (see Scorer, 1978; see also Appendix A7.1 for a brief glossary of terms describing plume behavior). It turns out to be reasonable in this phase to regard segments of the plume as if they were segments of a line thermal moving upward through quiescent surroundings (see, e.g., Turner, 1973).

The total plume rise in atmospheric crossflows during this phase is in principle predictable and the great majority of models used for this objective are relevant to the dynamics of this stage.

The Breakup Phase

Observation of buoyant plumes reveals that the relatively regular thermal phase of plume rise comes to a rather distinct end at some approximately predictable distance from the source as more vigorous mixing with the ambient air sets in and the plume often breaks up into several distinct parcels. In general, a stage, lasting for distances of the order of 100 m, where there is a distinct increase in mean plume width and mixing with the surrounding occurs mainly at large scales, is observed. This "breakup" phase of the plume is more pronounced in strong atmospheric turbulence and also occurs closer to the source when the ambient turbulence is more intense.

Obviously the large eddies which lead to the breakup are those naturally present in the wind (they are too large to be produced by the plume's own internal motion). Also their mixing action is dominant over the effects of the self-generated turbulence. When "breakup" is pronounced, it leads to an almost stepwise increase in plume diameter.

The dynamics of these phase are influenced by the scales and intensity of atmospheric turbulene (in addition to the mean wind speed and plume buoyancy flux).

The Atmospheric Diffusion Phase

A little further downwind the distinct parcels merge again into a larger, more diffuse plume, the subsequent growth of which is relatively slow. At this stage the various atmospheric diffusion theories become valid and this final phase of plume dispersion (which extends indefinitely downwind) is typically called the "atmospheric diffusion phase." Now the plume exists only in terms of the species emitted from the source; their fluctuating concentrations *define* the plume. Thus there is no separate flow structure associated with the plume phenomenon and we deal only with atmospheric fluid mechanics.

The actual height of plume rise above the actual source is affected by the randomness of the physical factors involved. The expected rise, is in general a function of the downwind distance from the source and a number of other physical parameters, different for each phase, as they were identified in the previous paragraphs. Recall that in the preceding discussion it was assumed that during the initial phases of plume dispersion no special aerodynamic phenomena such as downwash take place. It is further assumed that the source is sufficiently far above the ground so that the flow pattern within the plume is not disturbed by surface effects. Otherwise the effective height (that is the sum of plume rise plus the real source height) may influence further plume rise (see, e.g., Csanady, 1973, 6.15).

Figure 1-3 in Chapter 1 depicts schematically the downwind range relevant to the various phases that were discussed here together with the most important physical-chemical in-plume processes occurring at a given range.

Results regarding the expected plume dynamics during the "distinct" initial phases of dispersion can be obtained by simple dimensional analysis if the physical parameters recognized as important during each phase are taken into account. These simple results are summarized, together with some empirical information in List (1982). (In relation with the formulas listed there we must note that the effect of a solid boundary on the buoyant movements in a large plume has been ignored; also the atmospheric potential temperature distribution is represented through its gradients, but this in turn may be a function of height.) Finally it must be noted that the line-thermal analogy applies only to the second of the four phases of initial plume dispersion. This is the only phase for which we have a relatively adequate theory for the internal motion and concentration patterns of a buoyant plume. Appendix A7.3 summarizes the suggestions of Briggs (1975) for these internal patterns.

7.3 MODELING PLUME RISE: THE BASIC APPROACHES

Research in the field of plume rise over the past 30 years has led to a confusing proliferation of prediction schemes, that offer a variety of different answers for a specific problem, ranging from simple empirical or semiempirical formulas to complex numerical formulations. It is obvious from the discussion of Section 7.1 that compilation and discussion of a list of specific models representative of the entire spectrum of existing approaches would be a most ambitious task that certainly is beyond the scope of the present work. The reader who is seeking information of this kind is urged to consult List (1982), Briggs (1975, 1984) and Carhart et al. (1982). What is attempted here is a general classification of the various approaches on the basis of the first principles involved.

The two extreme forms of plume rise models, and in general of models of plume (or jet) dynamics, are:

(I) Simple algebraic relations giving the expansion, the trajectory (or final rise) etc., of plumes in either calm or turbulent environments, that are derived from dimensional analysis and empirical information. Typically, the construction of such relations starts with the identification of the important physical parameters involved in the problem (which may be different in the various phases of plume evolution, as discussed in Section 7.2), and, possibly, with assumptions regarding the behavior of some of these parameters. Self similarity is most commonly assumed for velocity, concentration and temperature profiles and simple self similarity laws are invoked. General correlations are then derived on dimensional grounds; qualitative consideration of the governing transport equations with an order of magnitude analysis of their terms, as well as of constraints imposed by conservation requirements, may facilitate or "enhance" this step. The correlations thus derived contain numerical parameters which must be determined on the basis of empirical information. Tutorial expositions of this approach can be found for example in Seinfeld (1975; Appendix B), Csanady (1973; sections 6.12 and 6.13) and Fisher et al. (1979; Chapter 9).

(II) Numerical schemes that solve the sets of the coupled (partial differential) equations governing the fields of mean velocity, concentration, temperature and, possibly, fields of higher order moments or correlations of these variables. The most important step in the formulation of models following this approach is the construction of appropriate closure approximations for the turbulent correlation terms; both first and higher order closure assumptions have appeared in the relevant literature. Some formulations in this area limit attention to uniform environments; others attempt to take into account the effects of ambient turbulence, crossflow and stratification which complicate the problem significantly. For examples of this approach see, e.g., Mellor and Yamada (1977), Teske et al. (1978), Yamada (1979), Chen and Nikitopoulos (1979); see also List (1982) and Liu et al. (1982; Section 4) for discussions of relevant models.

The "gap" between the approaches described above is occupied by the class of the so-called "integral type" models, widely ranging in variety and complexity, that in general attempt a description of the problem based on more "physical" grounds than models of class (I) but lead to the formulation of schemes that are more tractable than the ones contained in class (II). The key element in the various integral type models is the reduction of the set of governing partial differential equations into a set or ordinary differential equations (essentially through self similarity assumptions and appropriate closure schemes). One can discern two major lines in the development of integral approximations:

(IIIa) The governing ordinary differential equations are formulated directly by considering an appropriate control volume of the evolving plume and constructing balances of momentum, mass, energy and species concentration. This "shell balance" approach (see, e.g., Bird et al., 1960) has been adopted by the majority of investigators starting from the works of Taylor (1945), Priestley (1953), Priestley and Ball (1955) and Morton et al. (1956). Typically "top-hat" profiles of concentration, temperature, etc., are assumed inside the control volume (but more complicated self similarity is also possible). Quoting Csanady (1973), "the main idealization involved [in this approach] is that although in reality the flow and temperature patterns are continuous, an artificial distinction is introduced between an "identifiable plume" and the ambient fluid. The identifiable plume is assumed to grow by "entrainment" of the ambient fluid, the rate of entrainment being governed by an entrainment velocity at the perimeter of the plume." This constitutes the essence of what is generally referred to as the "Morton-Taylor approach" or "Taylor's entrainment hypothesis." This hypothesis replaces the "straightforward" turbulent transfer closure assumptions that are required to provide a closed set of governing equations.

The most simple models in this approach just reproduce the results of dimensional reasoning discussed earlier; more complicated models attempt detailed descriptions of plume evolution basically using more elaborate entrainment hypotheses. (For a critical discussion of the physical situation behind simple entrainment hypotheses see Netterville, 1985). A review and comparison of several models of this type can be found in Briggs (1975); Briggs' own suggestions (1969, 1975, 1984), which are summarized in Section 7.4 of this chapter, are typical simple applications of this integral approach. For an introduction to the essentials of this type of modeling one may consult the same basic references mentioned in (I). Typically, the Boussinesq approximation is invoked in application (see, e.g., Fan (1967); Abraham (1971) etc.).
(IIIb) Alternatively, the original coupled partial differential equations that govern the transport processes in the plume-ambient system are reduced into ordinary differential equations via *Prandtl's integral approximation method* and appropriate self similarity assumptions. Examples of this approach are presented by Hirst (1972) and Schatzmann (1976) and in general provide a more powerful method for describing plume dynamics, starting from a more detailed consideration of the problem and introducing simplifications not a priori but gradually, based on an explicit analysis that requires rational justification of the assumptions involved. This approach (in particular Schatzmann's schemes) is discussed in detail in the following (Section 7.5

and Appendix A7.2). Again turbulent transport closure is conveniently provided by "entrainment hypotheses." For a recent analysis and review of relevant entrainment assumptions see Chiang and Sill (1985).

Finally we close this section by pointing attention to the main subjects that seem to receive currently the major interest in the area of near-field plume dynamics modeling: these are, besides the evaluation and refinement of entrainment hypotheses (also related to their justification on physical grounds), (a) modeling of cooling tower plumes, (b) modeling of the effects related to elevated inversion penetration (see, e.g., Mannins, 1979) and (c) modeling of plume rise in the convective planetary boundary layer (see, e.g., Lamb (1982) and Willis and Deardorff (1984)).

7.4 THE MODELS OF BRIGGS

(Briggs, 1969, 1975, 1984)

The following equations for the various phenomena of plume rise (associated with the momentum and thermal phases of plume dispersion) appear in the most recent reviews of Briggs (see, e.g., Briggs, 1984) and currently they seem to be the most widely accepted working formulas relevant to these phenomena. The brief exposition presented here follows mainly the conventions and the pattern of classification adopted in the *Handbook of Atmospheric Diffusion* of the Department of Energy (Hanna et al., 1982), with some changes in the notation; it should be viewed only as a collection of common definitions and practical formulas for direct application and is included in this work for ready reference. For detailed derivations of Briggs' formulas, extensions to other cases, discussion of the assumptions involved and of the associated uncertainties, as well as for information relevant to their relation to other approaches and their evolution to the currently accepted forms one should consult Briggs (1969, 1975, 1984).

Definitions

The basic geometric (shape) parameters involved in Briggs' formulas are shown schematically in Figure 7-3; a typical "vertical" and a "bent over" plume are shown. In practice a plume will be assumed vertical or bent over when the angle of its centerline with the horizontal is respectively larger or smaller than 45^0; according to Hanna et al. (1982) a plume is "more or less vertical" if wind speed is less than about 1m/s. A "plume volume flux" is defined by Briggs as

$$\dot{V} = w\hat{R}^2 \quad \text{(vertical)} \qquad (7.4-1)$$

$$\dot{V} = u_\infty \hat{R}^2 \quad \text{(bent over)} \qquad (7.4-2)$$

where w is the vertical speed of the plume (assumed uniform in a cross-section and therefore representing an average value), u_∞ is the mean ambient wind speed and $\hat{R}$

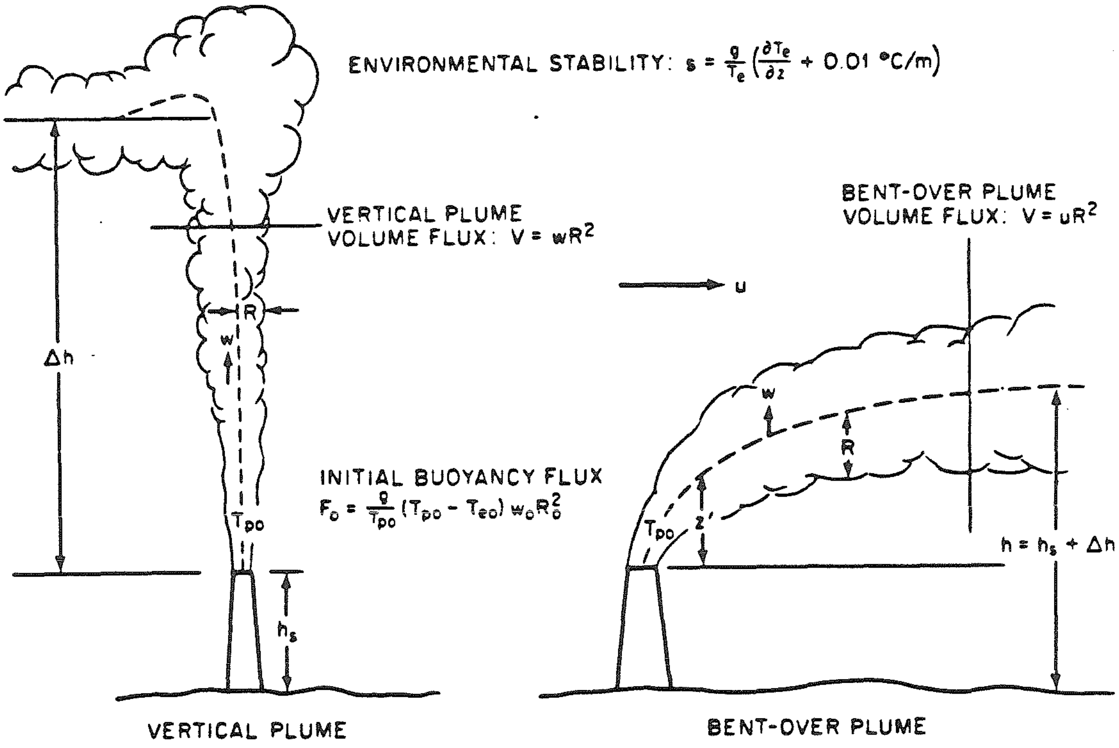

Figure 7-2

Basic Parameters of "Vertical" and "Bent Over" Plumes
Appearing in the Models of Briggs (1975, 1984)
(from Hanna et al., 1982 - the notation is that used in this ref.)

is an effective plume radius in a horizontal or vertical plane for vertical and bent over plumes respectively. (Note that in the formulation presented here the factor π does not appear explicitly anywhere; thus it is incorporated implicitly in the definition of the effective radius $\hat{R}$). Initial fluxes of volume, $\dot{V}_0$, buoyancy $\dot{B}_0$ and momentum $\dot{M}_0$ are defined as

$$\dot{V}_0 = w_0 \hat{R}_0^2 \tag{7.4 – 3}$$

$$\dot{B}_0 = \frac{g}{T_0}\left(T_0 - T_{\infty 0}\right)\dot{V}_0 \tag{7.4 – 4}$$

$$\dot{M}_0 = \frac{\rho_0}{\rho_{\infty 0}} w_0 \dot{V}_0 \tag{7.4 – 5}$$

where subscript 0 indicates stack exit values and ∞ indicates ambient properties. Thus T_0 and ρ_0 are the plume temperature and density at the stack and $T_{\infty 0}$, $\rho_{\infty 0}$ are the corresponding ambient properties at stack height. (Implicit in (7.4-4) is that the mean molecular weight of the plume gases does not differ appreciably from that of ambient air; otherwise all temperatures in (this equation must be divided by the mean plume molecular weight). At an arbitrary height buoyancy and momentum flux are defined as

$$\dot{B} = \frac{g}{T}\left(T - T_\infty\right)\dot{V} \tag{7.4 – 6}$$

$$\dot{M} = w\dot{V} \tag{7.4 – 7}$$

The environmental stability (or stratification) parameter ς is expressed in terms of the ambient potential temperature ($T_\infty^{(p)}$) gradient as

$$\varsigma = \frac{g}{T_\infty}\frac{\partial T_\infty^{(p)}}{\partial z} \simeq \frac{g}{T_\infty}\left(\frac{\partial T_\infty}{\partial z} + 0.001^{0}C/m\right) \tag{7.4 – 8}$$

(the last factor is approximately the adiabatic lapse rate; one should note that ς is also the square of the Brunt-Vaisala frequency). In many cases the appropriate field data for direct determination of ς are not available; for these situations the approximate values of temperature gradients given in Table 7-1 can be used in (7.4-8).

Another concept that appears in Brigg's formulas is the ratio of the effective area influenced by the plume momentum to the cross-sectional area of the so-called

Table 7-1

Typical Temperature Stratification
Corresponding to the Pasquill-Gifford Stability Classes

STABILITY CLASS	AMBIENT TEMPERATURE GRADIENT $\partial T/\partial z$ (^{0}C/100m)	POTENTIAL TEMPERATURE* GRADIENT $\partial \theta/\partial z$ (^{0}C/100m)
A (extremely unstable)	<-1.9	<-0.9
B (moderately unstable)	-1.9 to -1.7	-0.9 to -0.7
C (slightly unstable)	-1.7 to -1.5	-0.7 to -0.5
D (neutral)	-1.5 to -0.5	-0.5 to 0.5
E (slightly stable)	-0.5 to 1.5	0.5 to 2.5
F (moderately stable)	>1.5	>2.5

[*] Calculated by assuming $d\theta/dz \simeq dT/dz + \Gamma$, where Γ is the adiabatic lapse rate (0.986 ^{0}C/100m).

thermal plume (Briggs, 1975), S, which is approximately equal to 2.3 for bent-over plumes.

Finally, the entrainment velocity v_e that appears in the closure scheme (Taylor's entrainment hypothesis)

$$\frac{d\dot{V}}{dz} = 2\hat{R}v_e$$

is related to plume vertical speed through

$$v_e = \alpha w \quad \text{(vertical plumes)}$$

$$v_e = \beta w \quad \text{(bent-over plumes)}$$

where β is larger than α.

Governing Equations:

Vertical Plumes

(i) Conservation of buoyancy

$$\frac{d\dot{B}}{dz} = -\varsigma\dot{V} \tag{7.4 - 9}$$

(ii) Conservation of momentum

$$\frac{d\dot{M}}{dz} = \frac{\dot{B}}{w} \tag{7.4 - 10}$$

(iii) Entrainment hypothesis

$$\frac{d\dot{V}}{dz} = 2\alpha\hat{R}w = 2\alpha M^{\frac{1}{2}} \tag{7.4 - 11}$$

where $\alpha = 0.08$

Governing Equations:

Bent-Over Plumes

(i) Conservation of buoyancy

$$\frac{d\dot{B}}{dz} = -\frac{\varsigma}{S}\dot{V} \tag{7.4 - 12}$$

with $S = 2.3$

(ii) Conservation of momentum

$$\frac{d\dot{M}}{dz} = \frac{\dot{B}}{w} \tag{7.4 – 13}$$

(iii) Entrainment hypothesis

$$\frac{d\dot{V}}{dz} = 2\beta \hat{R} u_\infty \tag{7.4 – 14}$$

or, if u_∞ is constant

$$\hat{R} = \beta z \tag{7.4 – 15}$$

where $\beta = 0.6$ for a buoyant plume and $\beta = 0.4 + 1.2(u_\infty / w_0)$ for a jet.

7.4.1 Near Source Rise (Not Affected by Ambient Stability)

Typically ambient stability has little effect for dispersion times less than $\varsigma^{-1/2}$ (between 10 and 100s) and ambient turbulence is not important for distances less than about ten stack heights (Hanna et al., 1982). For these short times the following results hold:

Vertical Plumes

$$\hat{R} = 0.6z, \quad w = 6.25 \frac{M^{1/2}}{z} \quad (t < \frac{M}{\dot{B}_0}) \tag{7.4 – 16}$$

$$\hat{R} = 0.15z, \quad w = 2.3 \left(\frac{\dot{B}_0}{z} \right)^{\frac{1}{3}} \quad (t > \frac{\dot{M}}{\dot{B}_0}) \tag{7.4 – 17}$$

$\dot{M}/\dot{B}_0$ is typically less than 10 s.

Bent-Over Plumes

The plume trajectory is given by

$$\Delta z = \left(\frac{3}{\beta^2.1} \frac{\dot{M}}{{u_\infty}^2} x + \frac{3}{2\beta_2^2} \frac{\dot{B}_0}{{u_\infty}^3} x^2 \right)^{\frac{1}{3}} \quad (t < t^*) \tag{7.4 – 18}$$

where $\beta_2 = 0.6$ and $\beta_1 = 0.4 + 1.2(u_\infty / w_0)$ and

$$\Delta z = 1.6 \frac{\dot{B}_0^{\frac{1}{3}}}{u_\infty} x^{\frac{2}{3}} \quad (t > t^*) \tag{7.4 – 19}$$

with $t^* = \dot{M}/\dot{B}_0$ which is typically of the order of 5s. The coefficient 1.6 is expected to be accurate within ±40% (Hanna et al., 1982).

7.4.2 Rise Limited by Ambient Stability (Stably Stratified Atmosphere)

Vertical Plumes

In a stably stratified atmosphere vertical plumes achieve an "equilibrium rise" Δz_{eq} that is equal to

$$\Delta z_{eq} = 2.44 \left(\frac{\dot{M}}{\varsigma} \right)^{\frac{1}{4}} \qquad (7.4-20)$$

if it is dominated by buoyancy, and

$$\Delta z_{eq} = 5.3 \frac{\dot{B}_0^{1/4}}{\varsigma^{-3/8}} - 6R_0 \qquad (7.4-21)$$

Bent-Over Plumes

The final rise of a buoyant plume is

$$\Delta h = 2.6 \left(\frac{\dot{B}_0}{u_\infty \varsigma} \right)^{\frac{1}{3}} \qquad (7.4-22)$$

The wind speed u_∞ in this formula is an average value between the heights h_s and $h_s + \Delta h$.

7.4.3 Penetration of an Elevated Inversion

An elevated inversion, approximated a jump $\Delta T^{(p)}$ in a constant potential temperature at a height Δz_{el} above the stack will be penetrated if the following conditions are met:

Vertical Buoyant Plume

$$\Delta z_{el} < 4.9 \dot{B}_0^{2/5} \left(\frac{g \Delta T^{(p)}}{T^{(p)}} \right)^{-\frac{3}{5}} \qquad (7.4-23)$$

Vertical Momentum Plume

$$\Delta z_{el} < 6.2 \frac{\dot{B}_0/M^{1/2}}{\left(g/T^{(p)}\right) \Delta T^{(p)}} \qquad (7.4-24)$$

Buoyant Bent-Over Plume

$$\Delta z_{el} < 2.5 \left[\frac{\dot{B}_0}{u_\infty \left(g/T^{(p)}\right) \Delta T^{(p)}} \right]^{\frac{1}{2}} \qquad (7.4-25)$$

(Bent-over jets have little ability to penetrate inversions.)

If the final plume rise (Δh is within a factor of 2 of the inversion height above the stack (Δz_{el}), only a fraction (P) of the plume will penetrate the inversion whereas a fraction $1 - P$ is reflected off the inversion and diffuses downward. Briggs (1975) suggested the formula $P = 1.5 - \Delta z_{el}/\Delta_h$.

7.4.4 Rise Determined by Ambient Turbulence (Neutral and Unstable Atmospheres)

In this case plume rise comes to an end when the thermal phase of dispersion terminates in the breakup phase where ambient turbulence overcomes the internal turbulence of the plume. In Brigg's "breakup model" this occurs when the internal plume eddy dissipation, approximated by $1.5w^3/z$ equals the ambient eddy dissipation rate ε. The following simplified formulas for final plume rise are proposed:

Nearly Neutral Conditions

Buoyancy dominated plume

$$\Delta h = 1.54 \left(\frac{\dot{B}_0}{u_\infty u_*^2} \right)^{\frac{2}{3}} h_s^{\frac{1}{3}} \qquad (7.4-26)$$

where u_* is the friction velocity.

Momentum dominated plume

$$\Delta h = 3D \left(\frac{w_0}{u_\infty} - 1 \right) \qquad (7.4-27)$$

where D is the stack diameter

Convective Conditions

A *tentative* formula is

$$\Delta h = 3\left(\frac{\dot{B}_0}{u_\infty}\right)^{\frac{3}{5}} \mathcal{H}^{-\frac{2}{5}} \tag{7.4 – 28}$$

where $\mathcal{H}$ is the surface buoyancy flux defined as

$$\mathcal{H} = \frac{g}{T_\infty}\overline{w}'T'_\infty$$

(see, e.g., Hanna et al., 1982 – Section 1-4.4).

The formulas of Briggs are very similar to available results from dimensional analysis; as mentioned earlier, a summary of such results, together with of the empirical constants involved (according to various investigators) is given in List (1982).

7.5 THE PLUME RISE MODEL OF SCHATZMANN

(Schatzmann 1976, 1978, 1979ab; Schatzmann and Flick, 1977)

The approach of Schatzmann offers a formulation that is more comprehensive than those described in the previous section, as it takes into account the physics of the thermal phase of plume rise in much more detail. The resulting model, consists of a set of ordinary differential equations for mean centerline plume properties and other plume parameters, and has to be solved numericaly. In its most general form it holds for arbitrary ambient stratifications of temperature as well as for large density differences between the emissions and the environment (*).

Thus, temperature inversions of any slope are taken naturally into account in the model calculations. A restriction is that the ambient wind velocity field is "locally" shear free; step changes are however allowed.

A rather general situation, involving an elevated temperature inversion layer, typical of the conditions that can be directly addressed by Schatzmann's basic model is depicted schematically in Figure 7-3.

Starting point of Schatzmann's models are the fundamental Eulerian transport equations for mass, momentum and conserved scalars (inert species concentrations and temperature) formulated in an orthogonal curvilinear coordinate system that is always tangential to the mean plume centerline, as it was first introduced by Hirst (1972). Reduction of this coupled set of partial differential equations (initially corresponding to random instantaneous quantities), and of the associated boundary conditions, to an initial value problem involving a set of ordinary differential equations for mean properties and parameters, proceeds through an elaborate sequence of mathe-

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(*) The governing equations developed in this approach are reduced to a closed, solvable form without the introduction of the Boussinesq approximation. However, the currently available values of the empirical parameters appearing in the entrainment function have been determined, in both the cases of "dry" plumes (Schatzmann, 1979a) and "wet" plumes (Schatzmann and Policastro, 1984) only for conditions that are relevant to the Boussinesq approximation.

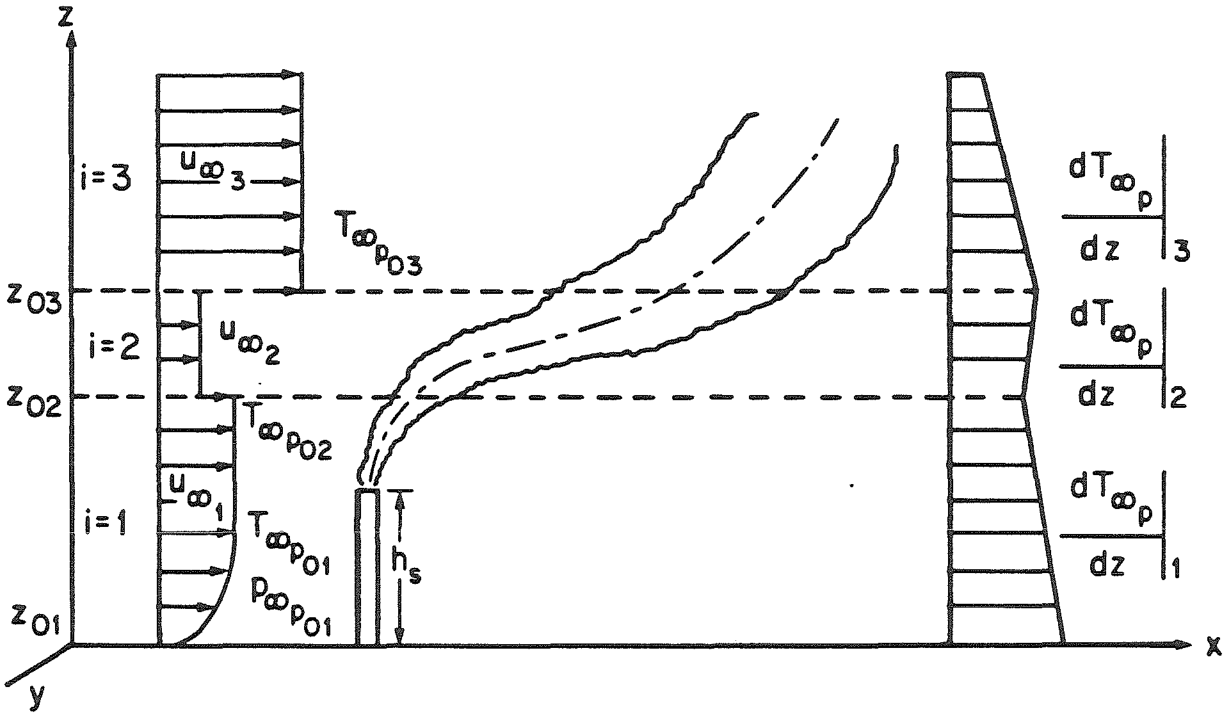

Figure 7-3

Schematic Representation of Plume Rise

in a Stratified Atmosphere,

Typical of the Conditions Addressed by Schatzmann's Model

(adapted from Schatzmann, 1977)

matical manipulations as well as of simplifying assumptions. Among these assumptions a most important one is that of self-similarity of the profiles of certain "mean excess" plume properties that finally allows integration of the governing equations into a simpler system. A complete exposition of the fundamental theory and the various assumptions involved in the aforementioned sequence can only be found scattered in a series of publications; the same holds for the determination of the empirical entrainment functions that provide closure to the turbulent transport equations and for applications and comparisons of the operational models with other approaches. For this reason, and to facilitate use of the existing models resulting from this approach (as well as in order to provide a basis for further work based on it) we present in Appendix A7.2 a concise but systematic derivation of the self-similarity ordinary differential equation system of Schatzmann (for both the two- and three-dimensional flow cases), listing in detail all the approximations involved. In the same appendix, as an additional step for providing a readily usable means for calculations, the "Schatzmann set" of equations is further reduced (from the coupled form in which it appears in the literature) into a scheme that is directly amenable to numerical treatment. All the necessary conditions and parameters for numerical application of a basic form of the model as well as a discussion relating this approach to other integral techniques can also be found there.

7.6 CONCLUSIONS

The subject of near-field plume dynamics (where plume momentum and buoyancy are significant) is a major area of atmospheric and in general fluid mechanical research and is covered by specialized monographs and an extensive literature (see, e.g., List, 1982; Briggs, 1984 for reviews). The present chapter (complemented by Appendices A7.1 to A7.4) attempted

(i) a concise overview of the physical problems and the modeling approaches in this area, and

(ii) an exposition of two alternatives (at different levels of complexity) that are appropriate for use with the TRPM model.

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APPENDIX A7.1

A Brief Glossary of Terms Describing Plume Behavior

(For further information see Scorer, 1968, 1978)

Aerodynamic Downwash or **Flagging:** *A situation in which stack effluents are brought to ground level very close to the source and in undesirably high concentrations by being entrained into the eddies in the lee of the chimney.*

It occurs in the cases of strong winds or low source exit velocities as well as for very irregular airflows where eddies in the wake of the stack entrain some of the effluent. Rapid vertical movement occurs in the separated flow region behind the source and this usually communicates with larger similar regions behind industrial buildings which are close to the source. This results to downwash. Its avoidance is achieved through proper aerodynamic design and is usually carried out the with aid of wind tunnel model studies of actual plants.

Bifurcation: *The phenomenon of a plume dividing into two distinct "branches" showing an overall cross section thar resembles a strong cylindrical thermal.*

Bifurcation occurs in cases of strongly buoyant bent-over plumes due to the pattern of intense entrainment of clear air up the middle of their boundary. Coning plumes are the ones more likely to be bifurcated.

Coning: *The situation in which the plume has a steadily widening boundary in its atmospheric diffusion phase and does not exhibit significant sinuosities. It is characteristic of neutral atmospheric conditions.*

In the case of coning plumes dispersion is due mainly to eddies of size smaller than the local instantaneous plume width. Thus relative diffusion dominates meandering.

Downdraught: *A situation similar to Aerodynamic Downwash: Effluent is entrained from time to time in the lee of the building associated with the chimney;common in dwelling houses.*

Downwash: see *Aerodynamic Downwash.*

Fanning: *A situation of limited dispersion taking place mainly in the horizontal direction. It is typical* *of stable atmospheres.*

A fanning plume achieves final rise (equilibrium level) very soon after emission. Significant concentration values are confined at this height.

Flagging: see *Aerodynamic Downwash.*

Fumigation: *A situation where the plume is dispersing downwards but not upwards. It occurs when the emission takes place below an inversion that is not penetrated.*

Lofting: *The inverse of Fumigation: The plume disperses only upwards. It occurs when the atmosphere is stable below the plume and neutral aloft.*

Lofting occurs when either the actual height of the stack is sufficient to place the effluent above the inversion (or the plume buoyancy strong enough to allow penetration of the inversion). Dominant mixing mechanism in the case of lofting plumes is the relative dispersion.

Looping: *The case where the plume exhibits large sinuosities compared to its instantaneous witdh. It occurs in unstable atmospheres.*

In the case of looping plumes the effec of meandering is most important. The averaged observed dispersion is predominantly caused by eddies with size large compared to that of the instantaneous plume.

Thermalling: *A phenomenon that takes place when thermal convection of the ambient is very strong (highly unstable atmospheres). The plume breaks up into distinct masses by the action of individual thermals of the atmosphere whose buoyancy dominates that of the plume. Another possibility is that masses from the chimney are directly entrained into natural thermals of the environment.*

References
for Appendix A7.1

Scorer, R.S. (1968) *Air Pollution*, Pergamon Press, London, 151 pp.

Scorer, R.S. (1978) *Environmental Aerodynamics*, Ellis Horwood Ltd./Halsted Press, Chichester, 488 pp.

APPENDIX A7.2

Self Similarity Modeling for the Thermal Phase of Plume Dispersion

The evolution of a buoyant plume is governed by:

(i) the continuity equation of (total) mass

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \qquad (A7.2-1)$$

(ii) the continuity equation of momentum

$$\rho \left[\frac{\partial \mathbf{u}}{\partial \mathrm{t}} + \frac{1}{2} \nabla \mathbf{u}\mathbf{u} - \mathbf{u} \times (\nabla \times \mathbf{u}) \right] = (\rho - \rho_\infty)\, \mathbf{g} - \nabla p_d \qquad (A7.2-2)$$

(iii) the continuity equation for a passive scalar

$$\frac{\partial (\rho c)}{\partial t} + \mathbf{u} \cdot \nabla (\rho c) + \rho c \nabla \cdot \mathbf{u} = 0 \qquad (A7.2-3)$$

and (iv) the continuity equation of heat

$$\frac{\partial (\rho T)}{\partial t} + \mathbf{u} \cdot \nabla (\rho \mathrm{T}) + \rho \mathrm{T} \nabla \cdot \mathbf{u} = 0 \qquad (A7.2-3)$$

To describe plume rise the (s, r, ϕ) system of orthogonal curvilinear coordinates is employed (Figure A7.2-1). The base vectors $(\mathbf{i}_s, \mathbf{i}_r, \mathbf{i}_\phi)$ of this system are expressed in terms of the base vectors $(\mathbf{i}, \mathbf{j}, \mathbf{k})$ of the *locally fixed* Cartesian (x, y, z) system, with x in the direction of the mean ambient flow(*) and z opposite to the direction of the gravity force, as follows:

$$\mathbf{i}_s = \mathbf{i} \cos\theta_1 \cos\theta_2 + \mathbf{j} \sin\theta_1 \cos\theta_2 + \mathbf{k} \sin\theta_2$$

$$\begin{aligned} \mathbf{i}_r = & \mathbf{i} \left(-\sin\theta_1 \cos\phi - \cos\theta_1 \sin\theta_2 \sin\phi \right) \\ & + \mathbf{j} \left(\cos\theta_1 \cos\phi - \sin\theta_1 \sin\theta_2 \sin\phi \right) \\ & + \mathbf{k} \cos\theta_2 \sin\phi \end{aligned}$$

(*) Note that in Schatzmann's (1978, 1979ab) notation y is set parallel to the ambient flow; however here we follow the common convention that sets x parallel to the mean ambient flow.

$$\begin{aligned}\mathbf{i}_\phi =& \mathbf{i}\left(\sin\theta_1 \sin\phi - \cos\theta_1 \sin\theta_2 \cos\phi\right)\\ &+ \mathbf{j}\left(-\cos\theta_1 \sin\phi - \sin\theta_1 \sin\theta_2 \cos\phi\right)\\ &+ \mathbf{k}\cos\theta_2 \cos\phi\end{aligned}$$

The following analysis is restricted to the two-dimensional case $(\theta_1, \theta_2) = (0, \theta)$. Letting

$$\kappa = r \sin\phi \frac{d\theta}{ds}$$

the Lamé coefficients (scale factors) become

$$h_s = 1 - \kappa, \quad h_r = 1, \quad h_\phi = r$$

and the vector operations involved in the continuity equations are

$$\nabla a = \frac{1}{1-\kappa}\frac{\partial a}{\partial s}\mathbf{i}_s + \frac{\partial \mathrm{a}}{\partial \mathrm{r}}\mathbf{i}_r + \frac{1}{\mathrm{r}}\frac{\partial \mathrm{a}}{\partial \phi}\mathbf{i}_\phi$$

$$\nabla \cdot \mathbf{a} = \frac{1}{1-\kappa}\frac{\partial \mathbf{a}_s}{\partial \mathrm{s}} + \frac{1}{\mathrm{r}}\frac{\partial(\mathrm{r}\mathbf{a}_r)}{\partial \mathrm{r}} + \frac{1}{\mathrm{r}}\frac{\partial \mathbf{a}_\phi}{\partial \phi} - \frac{\mathbf{a}_r}{1-\kappa}\frac{\kappa}{\mathrm{r}} - \frac{\mathbf{a}_\phi}{1-\kappa}\frac{1}{\mathrm{r}}\frac{\partial \kappa}{\partial \phi}$$

and

$$\begin{aligned}\nabla \times \mathbf{a} =& \frac{1}{r}\left(\frac{\partial(r a_\phi)}{\partial r} - \frac{\partial a_r}{\partial \phi}\right)\mathbf{i}_s\\ &+ \left(\frac{1}{r}\frac{\partial a_s}{\partial \phi} - \frac{a_s}{1-\kappa}\frac{1}{r}\frac{\partial \kappa}{\partial \phi} - \frac{1}{1-\kappa}\frac{\partial a_\phi}{\partial s}\right)\mathbf{i}_r\\ &+ \left(\frac{1}{1-\kappa}\frac{\partial a_r}{\partial s} - \frac{\partial a_s}{\partial r} + \frac{a_s}{1-\kappa}\frac{\kappa}{r}\right)\mathbf{i}_\phi\end{aligned}$$

In the above a is any scalar and $\mathbf{a} = \mathbf{a}_s\mathbf{i}_s + \mathbf{a}_r\mathbf{i}_r + \mathbf{a}_\phi\mathbf{i}_\phi$ is any vector.

Substituting in the continuity equations for steady state conditions one has:

(i) total mass continuity equation

$$\begin{aligned}&\rho\left[\frac{1}{1-\kappa}\frac{\partial u}{\partial s} + \frac{1}{r}\frac{\partial}{\partial r}(rv) + \frac{1}{r}\frac{\partial}{\partial \phi} - \frac{v}{1-\kappa}\frac{\kappa}{\rho} - \frac{w}{1-\kappa}\frac{1}{r}\frac{\partial \kappa}{\partial \phi}\right]\\ &\qquad + \frac{u}{1-\kappa}\frac{\partial \rho}{\partial s} + v\frac{\partial \rho}{\partial r} + \frac{w}{r}\frac{\partial \rho}{\partial \phi} = 0 \qquad (A7.2-4)\end{aligned}$$

(iia) momentum equation in the s-direction

$$\begin{aligned}&\rho\left\{u\frac{\partial u}{\partial s} + v\frac{\partial u}{\partial r}(1-\kappa) + \frac{1}{r}\left[w\frac{\partial u}{\partial \phi}(1-\kappa) - uw\frac{\partial \kappa}{\partial \phi} - uv\kappa\right]\right\} =\\ &\qquad = (1-\kappa)(\rho_\infty - \rho)\, g \sin\theta - \frac{\partial p_d}{\partial s} \qquad (A7.2-5)\end{aligned}$$

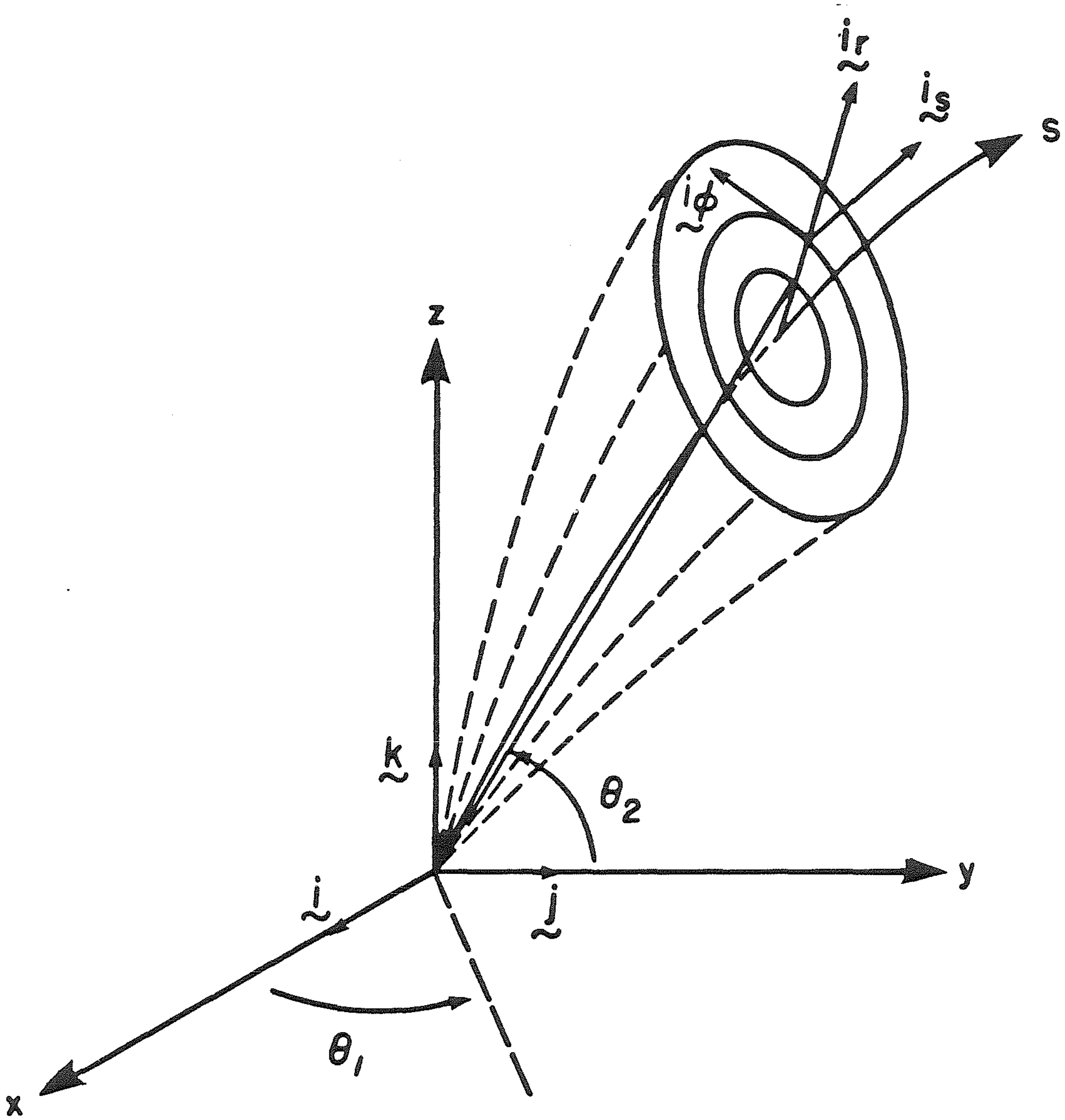

Figure A7.2-1

Cooordinate System Employed in the Plume Rise Model (iib) momentum equation in the y-direction

$$
\begin{aligned}
&\rho\left\{u\frac{\partial u}{\partial s}+v\frac{\partial u}{\partial r}\left(1-\kappa\right)+\frac{1}{r}\left[w\frac{\partial u}{\partial \phi}\left(1-\kappa\right)-uw\frac{\partial \kappa}{\partial \phi}-uv\kappa\right]\right\}\cos\theta\\
&-\rho\left\{u\frac{\partial u}{\partial s}\sin\phi+v\frac{\partial v}{\partial r}\left(1-\kappa\right)\sin\phi+u\frac{\partial w}{\partial s}\cos\phi+v\frac{\partial w}{\partial r}\left(1-\kappa\right)\cos\phi\right.\\
&+\frac{1}{r}\left[w\frac{\partial v}{\partial \phi}\left(1-\kappa\right)\sin\phi-w^2\left(1-\kappa\right)\sin\phi+u^2\kappa\sin\phi+w\frac{\partial w}{\partial \phi}\left(1-\kappa\right)\cos\phi\right.\\
&\left.\left.+\,uw\left(1-\kappa\right)\cos\phi+u^2\frac{\partial \kappa}{\partial \phi}\cos\phi\right]\right\}\sin\theta\\
&=-\frac{\partial p_d}{\partial s}\cos\theta+\frac{\partial p_d}{\partial r}\left(1-\kappa\right)\sin\phi\sin\theta+\frac{1}{r}\frac{\partial p_d}{\partial \phi}\left(1-\kappa\right)\cos\phi\cos\theta
\end{aligned}
\qquad (A7.2-5)
$$

(iic) momentum equation in the z-direction

$$
\begin{aligned}
&\rho\left\{u\frac{\partial u}{\partial s}+v\frac{\partial u}{\partial r}\left(1-\kappa\right)+\frac{1}{r}\left[w\frac{\partial u}{\partial \phi}\left(1-\kappa\right)-uw\frac{\partial \kappa}{\partial \phi}-uv\kappa\right]\right\}\sin\theta\\
&\rho\left\{u\frac{\partial v}{\partial s}\sin\phi+v\frac{\partial v}{\partial r}\left(1-\kappa\right)\sin\phi+u\frac{\partial w}{\partial s}\cos\phi+v\frac{\partial w}{\partial r}\left(1-\kappa\right)\cos\phi\right.\\
&+\frac{1}{r}\left[w\frac{\partial v}{\partial \phi}\left(1-\kappa\right)\sin\phi-w^2\left(1-\kappa\right)\sin\phi+u^2\kappa\sin\phi\right.\\
&\left.\left.+w\frac{\partial w}{\partial \phi}\left(1-\kappa\right)\cos\phi+vw\left(1-\kappa\right)\cos\phi+u^2\frac{\partial \kappa}{\partial \phi}\cos\phi\right]\right\}\cos\theta\\
&=\left(\rho_\infty-\rho\right)g\left(1-\kappa\right)-\frac{\partial p_d}{\partial s}\sin\theta-\frac{\partial p_d}{\partial r}\left(1-\kappa\right)\sin\phi\cos\theta\\
&-\frac{1}{r}\frac{\partial p_d}{\partial \phi}\left(1-\kappa\right)\cos\phi\cos\theta
\end{aligned}
\qquad (A7.2-6)
$$

(iii) continuity equation for concentration

$$
u\frac{\partial c}{\partial s}+v\frac{\partial c}{\partial r}\left(1-\kappa\right)+\frac{w}{r}\frac{\partial c}{\partial \phi}\left(1-\kappa\right)=0 \qquad (A7.2-7)
$$

(iv) continuity equation for temperature

$$
u\frac{\partial T}{\partial s}+v\frac{\partial T}{\partial r}\left(1-\kappa\right)+\frac{w}{r}\frac{\partial T}{\partial \phi}\left(1-\kappa\right)=0 \qquad (A7.2-8)
$$

Implicit in the derivation of the above steady state equations was the assumption of a divergence free flow (i.e. $\nabla\cdot\mathbf{u}=0$).

Equations for Averages

It is assumed that

(1) Reynolds averaging (i.e. decomposition in an ensemble mean and a fluctuating part) is applicable for $\mathbf{u}$, ρ, p_d, c and T, and that time averages approximate ensemble means:

$$u = \langle u \rangle + u' = \overline{u} + u', \quad \text{etc.}$$

and,

(2) the structure of turbulence is not influenced by the effects of compressibility (valid for flows with small Mach numbers) and therefore the terms containing density fluctuations ρ' are omitted.

Then, the mean quantities are decomposed into their background and excess components(*) (Figure A7.2-2):

$$\overline{u} = u_g + u_d$$

$$\overline{v} = v_g + v_d$$

$$\overline{w} = w_g + w_d$$

$$\overline{\rho} = \rho_\infty + \rho_d$$

$$\overline{T} = T_\infty + T_d$$

$$\overline{c} = c_\infty + c_d$$

where

$$u_g = u_\infty \cos\theta$$

$$v_g = -u_\infty \sin\theta \sin\phi$$

$$u_g = u_\infty \sin\theta \cos\phi$$

and the subscript ∞ denotes properties of the ambient flow field.

Introducing these assumptions in the governing equations one has:

(*) The excess components can be either positive or negative.

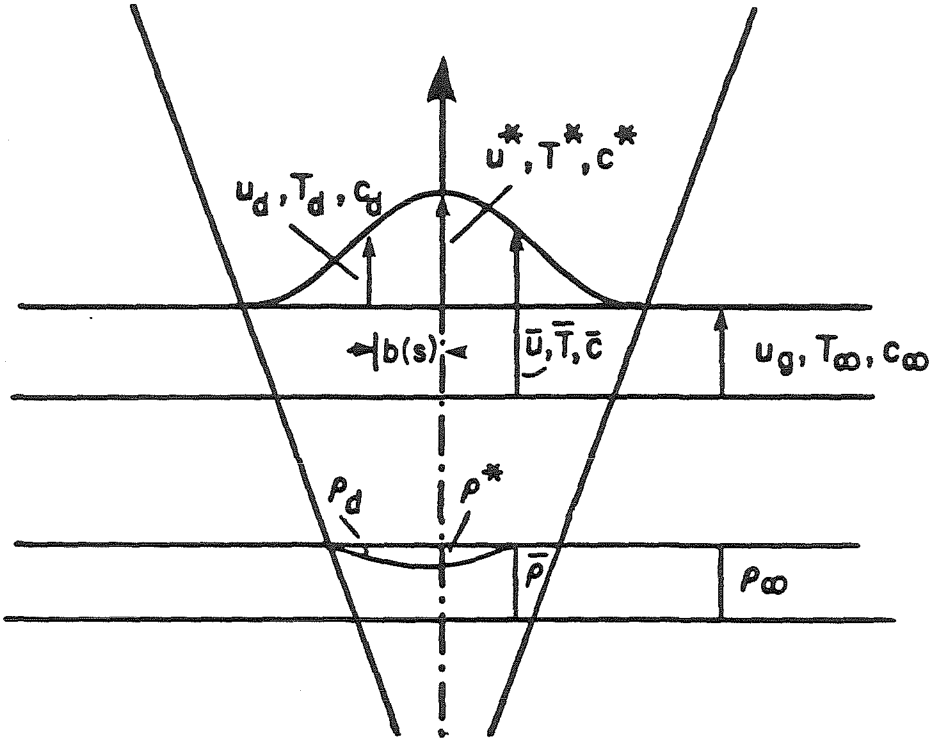

Figure A7.2-2

Definition of Background and Excess Quantities

(i) continuity of total mass

$$(\rho_\infty + \rho_d)\left\{\frac{\partial(u_g + u_d)}{\partial s} + \frac{\partial v_d}{\partial r}(1-\kappa) + \frac{1}{r}\left[\frac{\partial(w_g + w_d)}{\partial\phi}(1-\kappa) + (v_g + v_d)(1-2\kappa) - (w_g + w_d)\frac{\partial\kappa}{\partial\phi}\right]\right\}$$

$$+(u_g + u_d)\frac{\partial(\rho_\infty + \rho_d)}{\partial s} + (v_g + v_d)\frac{\partial\rho_d}{\partial r}(1-\kappa) + \frac{1}{r}(w_g + w_d)\frac{\partial\rho_d}{\partial\phi}(1-\kappa) = 0 \qquad (A7.2-9)$$

(iia) momentum equation in the s-direction

$$(\rho_\infty + \rho_d)\left\{(u_g + u_d)\frac{\partial(u_g + u_d)}{\partial s} + (v_g + v_d)\frac{\partial u_d}{\partial r}(1-\kappa)\right.$$

$$+\frac{1}{r}\left[(w_g + w_d)\frac{\partial u_d}{\partial\phi}(1-\kappa) - (u_g + u_d)(w_g + w_d)\frac{\partial\kappa}{\partial\phi} - (u_g + u_d)(v_g + v_d)\kappa\right]$$

$$\left.+\frac{\partial\overline{u'^2}}{\partial s} + \frac{1}{r}\frac{\partial\left(r\overline{u'v'}\right)}{\partial r}(1-\kappa) + \frac{1}{r}\left[\frac{\partial\overline{u'w'}}{\partial\phi}(1-\kappa) - 2\kappa\overline{u'v'} - 2\overline{u'w'}\frac{\partial\kappa}{\partial\phi}\right]\right\}$$

$$+\overline{u'^2}\frac{\partial(\rho_\infty + \rho_d)}{\partial s} + \overline{u'v'}\frac{\partial\rho_d}{\partial r}(1-\kappa) + \frac{1}{r}\overline{u'w'}\frac{\partial\rho_d}{\partial\phi}(1-\kappa) =$$

$$= -\rho_d g\,(1-\kappa)\sin\theta - \frac{\partial p_d}{\partial s} \qquad (A7.2-10)$$

(iib) momentum equation in the y-direction

$$
\begin{gathered}
(\rho_\infty + \rho_d)\Bigg\{(u_g + u_d)\frac{\partial(u_g + u_d)}{\partial s} + (v_g + v_d)\frac{\partial u_d}{\partial r}(1-\kappa) \\
+\frac{1}{r}\left[(w_g + w_d)\frac{\partial u_d}{\partial \phi}(1-\kappa) - (u_g + u_d)(w_g + w_d)\frac{\partial \kappa}{\partial \phi} - (u_g + u_d)(v_g + v_d)\kappa\right] \\
+\frac{\partial \overline{u'^2}}{\partial s}\frac{1}{r}\frac{\partial\left(r\overline{u'v'}\right)}{\partial(1-\kappa)} + \frac{1}{r}\left[\frac{\partial \overline{u'w'}}{\partial \phi}(1-\kappa) - 2\overline{u'v'}\kappa - 2\overline{u'w'}\frac{\partial \kappa}{\partial \phi}\right] \\
\frac{1}{(\rho_\infty + \rho_d)}\left[\overline{u'^2}\frac{\partial(\rho_\infty + \rho_d)}{\partial s} + \overline{u'v'}\frac{\partial \rho_d}{\partial r}(1-\kappa) + \overline{u'w'}\frac{1}{r}\frac{\partial \rho_d}{\partial \phi}(1-\kappa)\right]\Bigg\}\cos\theta \\
-(\rho_\infty + \rho_d)\Bigg\{(u_g + u_d)\frac{\partial(v_g + v_d)}{\partial s} + (v_g + v_d)\frac{\partial v_d}{\partial r}(1-\kappa) \\
+\frac{1}{r}\left[(w_g + w_d)\frac{\partial(v_g + v_d)}{\partial \phi}(1-\kappa) - (w_g + w_d)^2(1-\kappa) + (u_g + u_d)^2\kappa\right] \\
+\frac{\partial \overline{u'v'}}{\partial s} + \frac{1}{r}\frac{\partial\left(r\overline{v'^2}\right)}{\partial r}(1-\kappa) + \frac{1}{r}\left[\frac{\partial \overline{v'w'}}{\partial \phi}(1-\kappa) - \overline{w'^2}(1-\kappa) + \left(\overline{u'^2} - \overline{v'^2}\right)\kappa - \overline{v'w'}\frac{\partial \kappa}{\partial \phi}\right] \\
+\frac{1}{r}\left[\overline{u'v'}\frac{\partial(\rho_\infty + \rho_d)}{\partial s} + \overline{v'^2}\frac{\partial \rho_d}{\partial(1-\kappa)} + \overline{v'w'}\frac{1}{r}\frac{\partial \rho_d}{\partial \phi}(1-\kappa)\right]\Bigg\}\sin\phi\sin\theta \\
-(\rho_\infty + \rho_d)\Bigg\{(u_g + u_d)\frac{\partial(w_g + w_d)}{\partial s} + (v_g + v_d)\frac{\partial w_d}{\partial r}(1-\kappa) \\
+\frac{1}{r}\left[(w_g + w_d)\frac{\partial(w_g + w_d)}{\partial \phi}(1-\kappa) + (v_g + v_d)(w_g + w_d)(1-\kappa) + (u_g + u_d)^2\frac{\partial \kappa}{\partial \phi}\right] \\
+\frac{\partial \overline{u'w'}}{\partial s} + \frac{1}{r}\frac{\partial\left(r\overline{v'w'}\right)}{\partial r}(1-\kappa) + \frac{1}{r}\left[\frac{\partial \overline{w'^2}}{\partial \phi}(1-\kappa) + \overline{v'w'}(1-\kappa) + \left(\overline{u'^2} - \overline{w'^2}\right)\frac{\partial \kappa}{\partial \phi} - \overline{v'w'}\kappa\right] \\
+\frac{1}{(\rho_\infty + \rho_d)}\left[\overline{v'w'}\frac{\partial(\rho_\infty + \rho_d)}{\partial s} + \overline{v'w'}\frac{\partial \rho_d}{\partial r}(1-\kappa) + \overline{w'^2}\frac{1}{r}\frac{\partial \rho_d}{\partial \phi}(1-\kappa)\right]\Bigg\}\cos\phi\sin\theta = \\
= -\frac{\partial p_d}{\partial s}\cos\theta + \frac{\partial p_d}{\partial r}(1-\kappa)\sin\phi\sin\theta + \frac{1}{r}\frac{\partial p_d}{\partial \phi}\cos\phi\sin\theta \qquad (A7.2-11)
\end{gathered}
$$

(iic) momentum equation in the z-direction

$$(\rho_\infty + \rho_d)\Big\{(u_g + u_d)\frac{\partial(u_g + u_d)}{\partial s} + (v_g + v_d)\frac{\partial u_d}{\partial r}(1-\kappa)$$

$$+\frac{1}{r}\left[(w_g + w_d)\frac{\partial u_d}{\partial \phi}(1-\kappa) - (u_g + u_d)(w_g + w_d)\frac{\partial \kappa}{\partial \phi} - (u_g + u_d)(v_g + v_d)\kappa\right]$$

$$+\frac{\partial \overline{u'^2}}{\partial s}\frac{1}{r}\frac{\partial\left(r\overline{u'v'}\right)}{\partial(1-\kappa)} + \frac{1}{r}\left[\frac{\partial \overline{u'w'}}{\partial \phi}(1-\kappa) - 2\overline{u'v'}\kappa - 2\overline{u'w'}\frac{\partial \kappa}{\partial \phi}\right]$$

$$\frac{1}{(\rho_\infty + \rho_d)}\left[\overline{u'^2}\frac{\partial(\rho_\infty + \rho_d)}{\partial s} + \overline{u'v'}\frac{\partial \rho_d}{\partial r}(1-\kappa) + \overline{u'w'}\frac{1}{r}\frac{\partial \rho_d}{\partial \phi}(1-\kappa)\right]\Big\}\sin\theta$$

$$-(\rho_\infty + \rho_d)\Big\{(u_g + u_d)\frac{\partial(v_g + v_d)}{\partial s} + (v_g + v_d)\frac{\partial v_d}{\partial r}(1-\kappa)$$

$$+\frac{1}{r}\left[(w_g + w_d)\frac{\partial(v_g + v_d)}{\partial \phi}(1-\kappa) - (w_g + w_d)^2(1-\kappa) + (u_g + u_d)^2\kappa\right]$$

$$+\frac{\partial \overline{u'v'}}{\partial s} + \frac{1}{r}\frac{\partial\left(r\overline{v'^2}\right)}{\partial r}(1-\kappa) + \frac{1}{r}\left[\frac{\partial \overline{v'w'}}{\partial \phi}(1-\kappa) - \overline{w'^2}(1-\kappa) + \left(\overline{u'^2} - \overline{v'^2}\right)\kappa - \overline{v'w'}\frac{\partial \kappa}{\partial \phi}\right]$$

$$+\frac{1}{r}\left[\overline{u'v'}\frac{\partial(\rho_\infty + \rho_d)}{\partial s} + \overline{v'^2}\frac{\partial \rho_d}{\partial(1-\kappa)} + \overline{v'w'}\frac{1}{r}\frac{\partial \rho_d}{\partial \phi}(1-\kappa)\right]\Big\}\sin\phi\cos\theta$$

$$-(\rho_\infty + \rho_d)\Big\{(u_g + u_d)\frac{\partial(w_g + w_d)}{\partial s} + (v_g + v_d)\frac{\partial w_d}{\partial r}(1-\kappa)$$

$$+\frac{1}{r}\left[(w_g + w_d)\frac{\partial(w_g + w_d)}{\partial \phi}(1-\kappa) + (v_g + v_d)(w_g + w_d)(1-\kappa) + (u_g + u_d)^2\frac{\partial \kappa}{\partial \phi}\right]$$

$$+\frac{\partial \overline{u'w'}}{\partial s} + \frac{1}{r}\frac{\partial\left(r\overline{v'w'}\right)}{\partial r}(1-\kappa) + \frac{1}{r}\left[\frac{\partial \overline{w'^2}}{\partial \phi}(1-\kappa) + \overline{v'w'}(1-\kappa) + \left(\overline{u'^2} - \overline{w'^2}\right)\frac{\partial \kappa}{\partial \phi} - \overline{v'w'}\kappa\right]$$

$$+\frac{1}{(\rho_\infty + \rho_d)}\left[\overline{v'w'}\frac{\partial(\rho_\infty + \rho_d)}{\partial s} + \overline{v'w'}\frac{\partial \rho_d}{\partial r}(1-\kappa) + \overline{w'^2}\frac{1}{r}\frac{\partial \rho_d}{\partial \phi}(1-\kappa)\right]\Big\}\cos\phi\cos\theta =$$

$$= -\rho_d g(1-\kappa) - \frac{\partial p_d}{\partial s}\sin\theta + \frac{\partial p_d}{\partial r}(1-\kappa)\sin\phi\cos\theta + \frac{1}{r}\frac{\partial p_d}{\partial \phi}\cos\phi\cos\theta \qquad (A7.2-12)$$

(iv) continuity equation for a scalar (c or T)

$$(u_g + u_d)\frac{\partial(c_\infty + c_d)}{\partial s} + (v_g + v_d)\frac{\partial c_d}{\partial r}(1-\kappa) + (w_g + w_d)\frac{1}{r}\frac{\partial c_d}{\partial \phi}(1-\kappa)$$

$$+\frac{\partial \overline{u'c'}}{\partial s} + \frac{1}{r}\frac{\partial\left(r\overline{v'c'}\right)}{\partial r}(1-\kappa) + \frac{1}{r}\left[\frac{\partial \overline{w'c'}}{\partial \phi}(1-\kappa) - \overline{v'c'}\kappa - \overline{w'c'}\frac{\partial \kappa}{\partial \phi}\right]$$

$$\frac{1}{(\rho_\infty + \rho_d)}\left[\overline{u'c'}\frac{\partial(\rho_\infty + \rho_d)}{\partial s} + \overline{v'c'}\frac{\partial \rho_d}{\partial r}(1-\kappa) + \overline{w'c'}\frac{1}{r}\frac{\partial \rho_d}{\partial \phi}(1-\kappa)\right] = 0 \qquad (A7.2-13)$$

Simplifications

(a) The Pressure Gradients

The difficulty of estimating the complex gradients of p_d is circumvented through the following method (Fan, 1967; Schatzmann, 1978): One arbitrarily sets

$$\frac{\partial p_d}{\partial s} = \frac{\partial p_d}{\partial r} = \frac{\partial p_d}{\partial \phi} = 0$$

and assigns the effects of these gradients to an empirical "drag function" for the pressure forces per plume segment ds after integration over the angular and radial directions

$$F_D(s) = c_D \frac{1}{2} \rho_\infty(s) (u_\infty \sin\theta)^2 2R(s) \tag{A7.2 – 14}$$

where c_D is an empirical coefficient.

(b) Shear Free Assumption

The ambient mean velocity is assumed uniform in the region of interest:

$$\frac{\partial u_\infty}{\partial x} = \frac{\partial u_\infty}{\partial y} = \frac{\partial u_\infty}{\partial z} = 0 \tag{A7.2 – 15}$$

Note however that the derivatives of the background velocity components u_g, v_g and w_g with respect to s and ϕ do *not* vanish.

(c) Axisymetry Assumption

The plume flow is assumed to be axisymetric during the phase under consideration *with respect to the mean excess quantities and the turbulent correlations*:

$$\begin{gathered} w_d = 0 \\ \frac{\partial u_d}{\partial \phi} = \frac{\partial v_d}{\partial \phi} = \frac{\partial w_d}{\partial \phi} = 0 \\ \frac{\partial \overline{u'^2}}{\partial \phi} = \frac{\partial \overline{v'^2}}{\partial \phi} = \frac{\partial \overline{w'^2}}{\partial \phi} = \frac{\partial \overline{u'v'}}{\partial \phi} = \frac{\partial \overline{u'w'}}{\partial \phi} = \frac{\partial \overline{v'w'}}{\partial \phi} = 0 \\ \frac{\partial \overline{u'c'}}{\partial \phi} = \frac{\partial \overline{v'c'}}{\partial \phi} = \frac{\partial \overline{w'c'}}{\partial \phi} = \frac{\partial \overline{u'T'}}{\partial \phi} = \frac{\partial \overline{v'T'}}{\partial \phi} = \frac{\partial \overline{w'T'}}{\partial \phi} = 0 \\ \frac{\partial \rho_d}{\partial \phi} = \frac{\partial c_d}{\partial \phi} = \frac{\partial T_d}{\partial \phi} = 0 \end{gathered} \tag{A7.2 – 16}$$

The assumption of axisymmetry is expected to be valid for vertical plumes in calm environments. Deviations are expected for bent-over plumes in cross-flows, mainly due to the suppression of the counter rotating vortex pair; appropriate formulations for the entrainment function are used to compensate for this effect.

(d) Similarity Assumption

This is the most essential part of the general method described here. It allows separation of variables and subsequent integration in the radial direction that simplify the partial differential equations to ordinary differential equations. Self similarity of the profiles of mean quantities is in general expected to be valid after short distances ($s/D \simeq 6$) from the source (zone of flow establishment). Turbulent quantities in general assume fully developed profiles at larger distances, e.g. for $s/D > 50$ (Schatzmann, 1978). The following Gaussian forms are assigned to the mean excess quantities:

$$u_d(s,r) = u^*(s) \exp\left[-\left(\frac{r}{b(s)}\right)^2\right] \qquad (A7.2-17a)$$

$$T_d(s,r) = T^*(s) \exp\left[-\left(\frac{r}{\lambda b(s)}\right)^2\right] \qquad (A7.2-17b)$$

$$c_d(s,r) = c^*(s) \exp\left[-\left(\frac{r}{\lambda b(s)}\right)^2\right] \qquad (A7.2-17c)$$

$$\rho_d(s,r) = \rho^*(s) \exp\left[-\left(\frac{r}{\lambda b(s)}\right)^2\right] \qquad (A7.2-17d)$$

where the superscript * is used to denote centerline values and the "spreading ratio" λ (proportional to the turbulent Schmidt number) is introduced to account for the different rates of dispersion of momentum and of scalar quantities.

Radial Integration of the Continuity Equations

To integrate the continuity equations use is made of

(i) Prandtl's boundary layer approximation, according to which the gradients in the direction of the flow are negligible compared to gradients perpendicular to this direction, and of

(ii) The boundary conditions

$$\begin{gathered} u_d = \rho_d = c_d = T_d = 0 \\ \overline{u'v'} = \overline{v'c'} = \overline{v'T'} = 0 \\ \overline{v'^2} = \overline{v'^2_\infty} \end{gathered} \qquad (A7.2-18)$$

where the boundary is taken at $R = \sqrt{2}b$, or to $R \to \infty$ if the value of the quantity under consideration becomes zero at the nominal edge of the plume.

General Integral Forms
of the Continuity Equations

Applying the Leibniz rule

$$\int_{\alpha(s)}^{\beta(s)} \frac{\partial\left[f(s,r)\right]}{\partial s} dr = \frac{d}{ds}\int_{\alpha(s)}^{\beta(s)} f(s,r)dr = \frac{d}{ds}\left[\beta(s)\right] f(s,\beta) + \frac{d}{ds}\left[\alpha(s)\right] f(s,\alpha)$$

and combining the y and z momentum equations to describe the variability of θ with s one obtains:

(i) continuity equation for total mass

$$\frac{d}{ds}\int_0^\infty (\rho_\infty + \rho_d)u_d r dr + \frac{d}{ds}\left[u_g \int_0^\infty \rho_d r dr\right] + \frac{1}{2}R^2 u_g \frac{d\rho_\infty}{ds} = \rho_\infty E \qquad (A7.2-19)$$

(ii) momentum equation in the s direction

$$\frac{d}{ds}\int_0^\infty (\rho_\infty + \rho_d)u_d(u_g + u_d) r dr = -\int_0^\infty \rho_d g r dr \sin\theta \qquad (A7.2-20)$$

(iii) θ–equation

$$\frac{d\theta}{ds} = \frac{-\int_0^\infty \rho_d g r \cos\theta - \frac{1}{2}u_\infty \rho_\infty E \sin\theta - \left(\sqrt{2}/2\pi\right) c_D \rho_\infty b u_\infty^2 \sin^2\theta}{\int_0^\infty (\rho_\infty + \rho_d)u_d(u_g + u_d) r dr - \rho_\infty b^2 \overline{v'^2_\infty}} \qquad (A7.2-21)$$

(iv) continuity equation for a scalar (c or T)

$$\frac{d}{ds}\int_0^\infty (\rho_\infty + \rho_d) c_d (u_g + u_d) r dr = -\frac{dc_\infty}{ds}\int_0^R (\rho_\infty + \rho_d)(u_g + u_d) r dr \qquad (A7.2-22)$$

In the above equations E represents the volume of ambient air entrained into the plume due to turbulence and is defined by

$$E(s) = -\frac{1}{2\pi}\int_C v_d\,(R)\,dC = -v_d\,(R)\,R \qquad (A7.2-23)$$

Integral Forms for Gaussian Profiles

Introducing the Gaussian self similarity profiles $(A7.2-17a, b, c, d)$ the integration with respect to r can be performed, resulting in a set of five ordinary differential equations for seven unknowns $b(s)$, $\theta(s)$, $u^*(s)$, $\rho^*(s)$, $T^*(s)$, $c^*(s)$ and $E(s)$:

(i) continuity equation of total mass

$$\frac{d}{ds}\left(\rho_\infty u^* b^2\right) + 2b^2 u_\infty \cos\theta \frac{d\rho_\infty}{ds} + \lambda^2 \frac{d}{ds}\left(u_\infty \cos\theta \rho^* b^2\right) + \frac{\lambda^2}{\lambda^2+1}\frac{d}{ds}\left(\rho^* u^* b^2\right) = 2\rho_\infty E \qquad (A2.7-24)$$

(ii) momentum equation in the s-direction

$$\frac{d}{ds}\left\{u^* b^2 \left[u^*\left(\frac{1}{2}\rho_\infty + \frac{\lambda^2}{2\lambda^2+1}\rho^*\right) + u_\infty \cos\theta\left(\rho_\infty + \frac{\lambda^2}{\lambda^2+1}\rho^*\right)\right]\right\} = -\lambda^2 b^2 \rho^* g \sin\theta \qquad (A7.2-25)$$

(iii) θ-equation

$$\frac{d\theta}{ds} = -\frac{\lambda^2 b^2 \rho^* g\cos\theta + u_\infty \rho_\infty E \sin\theta + (1/\pi)\sqrt{2} c_D \rho_\infty b u_\infty^2 \sin^2\theta}{b^2 u^{*2}\left(\frac{1}{2}\rho_\infty + \frac{\lambda^2}{2\lambda^2+1}\rho^*\right) + b^2 u^{*2} u_\infty \cos\theta\left(\rho_\infty + \frac{\lambda^2}{\lambda^2+1}\rho^*\right) - 2b^2 \rho_\infty \overline{v'^2_\infty}} \qquad (A7.2-26)$$

(iv) continuity equation for an inert scalar (concentration)

$$\frac{d}{ds}\left[\lambda^2 b^2\left(u_\infty \cos\theta \rho_\infty c^* + \frac{1}{2}u_\infty \cos\theta \rho^* c^* + \frac{1}{\lambda^2+1}u^* \rho_\infty c^* + \frac{1}{\lambda^2+2}u^* \rho^* c^*\right)\right] =$$

$$= -\left(\frac{dc_\infty}{ds}\right) b^2 \left(2u_\infty \cos\theta \rho_\infty + \lambda^2 u_\infty \cos\theta \rho^* + u^* \rho_\infty + \frac{\lambda^2}{\lambda^2+1}u^* \rho^*\right) \qquad (A7.2-27)$$

(v) heat transport equation

$$\frac{d}{ds}\left[\lambda^2 b^2\left(u_\infty \cos\theta \rho_\infty T^* + \frac{1}{2}u_\infty \cos\theta \rho^* T^* + \frac{1}{\lambda^2+1}u^* \rho_\infty T^* + \frac{1}{\lambda^2+2}u^* \rho^* T^*\right)\right] =$$

$$= -\left(\frac{dT_\infty}{ds}\right) b^2 \left(2u_\infty \cos\theta \rho_\infty + \lambda^2 u_\infty \cos\theta \rho^* + u^* \rho_\infty + \frac{\lambda^2}{\lambda^2+1}u^* \rho^*\right) \qquad (A7.2-28)$$

To obtain closure one must further provide:

- an equation of state $\rho = f_1(c, T)$,
- an entrainment hypothesis $E = f_2\left(b, \theta, u^*, \rho^*, c^*, T^*\right)$, and
- ●● information concerning the variability of ambient properties T_∞, c_∞ and $\overline{v'^2_\infty}$ with the streamwise coordinate s.

Finally the initial conditions (corresponding to the end of the zone of flow establishment $s = s_0$) $b(s_0)$, $\theta(s_0)$, $u^*(s_0)$, $T^*(s_0)$ and $c^*(s_0)$ must be specified for the numerical solution of the system $(A7.2-23)$ to $(A7.2-27)$. These subjects will be discussed in following sections. An extension of the basc system of equations to three dimensions is presented next.

Generalization to Three Dimensions

The general integral form of the continuity equations for total mass, conserved scalars (c and T), and momentum in the s-direction remain unchanged in the three-dimensional case, with u_g now given by

$$u_g = u_\infty \sin\theta_1 \cos\theta_2$$

The dependence of θ_2 and θ_1 on s is given by (Schatzmann, 1979b):

$$\frac{d\theta_2}{ds} = \frac{-\int_0^\infty \rho_d g r \cos\theta_2 - \frac{1}{2} u_\infty \rho_\infty E \sin\theta_1 \sin\theta_2 - \left(\sqrt{2}/2\pi\right) c_D \rho_\infty b u_\infty^2 \sin^2\theta_1 \sin^2\theta_2}{\int_0^\infty (\rho_\infty + \rho_d) u_d (u_g + u_d) r\,dr - \rho_\infty b^2 \overline{v'^2_\infty}} \qquad (A7.2-21')$$

and

$$\frac{d\theta_1}{ds} = \frac{\frac{1}{2}\rho_\infty E u_\infty \cos\theta_1 + \left(\sqrt{2}/2\pi\right) c_D \rho_\infty \beta u_\infty^2 \cos^2\theta_1}{\int_0^\infty (\rho_\infty + \rho_d) u_d (u_g + u_d) r\,dr - \rho_\infty b^2 \overline{v'^2_\infty}} \qquad (A7.2-21'')$$

Introducing the Gaussian self similarity profiles $(A7.2-17a, b, c, d)$ the integration with respect to r gives a set of six ordinary differential equations for eight unknowns $b(s)$, $\theta_1(s)$, $\theta_2(s)$, $u^*(s)$, $\rho^*(s)$, $T^*(s)$, $c^*(s)$ and $E(s)$:

(i) continuity equation of total mass

$$\frac{d}{ds}\left(\rho_\infty u^* b^2\right) + 2b^2 u_\infty \sin\theta_1 \cos\theta_2 \frac{d\rho_\infty}{ds} + \lambda^2 \frac{d}{ds}\left(u_\infty \sin\theta_1 \cos\theta_2 \rho^* b^2\right)$$

$$+ \frac{\lambda^2}{\lambda^2 + 1}\frac{d}{ds}\left(\rho^* u^* b^2\right) = 2\rho_\infty E \qquad (A2.7-24')$$

(ii) momentum equation in the s-direction

$$\frac{d}{ds}\left\{u^* b^2\left[u^*\left(\frac{1}{2}\rho_\infty+\frac{\lambda^2}{2\lambda^2+1}\rho^*\right)\right.\right.$$

$$\left.\left.+u_\infty\sin\theta_1\cos\theta_2\left(\rho_\infty+\frac{\lambda^2}{\lambda^2+1}\rho^*\right)\right]\right\}=-\lambda^2 b^2\rho^* g\sin\theta_2 \qquad (A7.2-25')$$

(iii') θ_2-equation

$$\frac{d\theta_2}{ds}=-\frac{\lambda^2 b^2\rho^* g\cos\theta_2+u_\infty\rho_\infty E\sin\theta_1\cos\theta_2+\left(\sqrt{2}/\pi\right)c_D\rho_\infty b u_\infty^2\sin^2\theta_1\sin^2\theta_2}{b^2 u^{*2}\left(\frac{1}{2}\rho_\infty+\frac{\lambda^2}{2\lambda^2+1}\rho^*\right)+b^2u^{*2}u_\infty\sin\theta_1\cos\theta_2\left(\rho_\infty+\frac{\lambda^2}{\lambda^2+1}\rho^*\right)-2b^2\rho_\infty\overline{v'^2_\infty}}$$

$$(A7.2-26')$$

(iii") θ_1-equation

$$\frac{d\theta_1}{ds}=\frac{u_\infty\rho_\infty E\cos\theta_1+\left(\sqrt{2}/\pi\right)c_D\rho_\infty b u_\infty^2\cos^2\theta_1}{b^2 u^{*2}\left(\frac{1}{2}\rho_\infty+\frac{\lambda^2}{2\lambda^2+1}\rho^*\right)+b^2u^{*2}u_\infty\sin\theta_1\cos\theta_2\left(\rho_\infty+\frac{\lambda^2}{\lambda^2+1}\rho^*\right)-2b^2\rho_\infty\overline{v'^2_\infty}}$$

$$(A7.2-26'')$$

(iv) continuity equation for an inert scalar (concentration)

$$\frac{d}{ds}\left[\lambda^2 b^2\left(u_\infty\sin\theta_1\cos\theta_2\rho_\infty c^*+\frac{1}{2}u_\infty\sin\theta_1\cos\theta_2\rho^* c^*+\frac{1}{\lambda^2+1}u^*\rho_\infty c^*+\frac{1}{\lambda^2+2}u^*\rho^* c^*\right)\right]=$$

$$=-\left(\frac{dc_\infty}{ds}\right)b^2\left(2u_\infty\sin\theta_1\cos\theta_2\rho_\infty+\lambda^2u_\infty\sin\theta_1\cos\theta_2\rho^*+u^*\rho_\infty+\frac{\lambda^2}{\lambda^2+1}u^*\rho^*\right) \qquad (A7.2-27')$$

(v) heat transport equation

$$\frac{d}{ds}\left[\lambda^2 b^2\left(u_\infty\sin\theta_1\cos\theta_2\rho_\infty T^*+\frac{1}{2}u_\infty\sin\theta_1\cos\theta_2\rho^* T^*+\frac{1}{\lambda^2+1}u^*\rho_\infty T^*+\frac{1}{\lambda^2+2}u^*\rho^* T^*\right)\right]=$$

$$=-\left(\frac{dT_\infty}{ds}\right)b^2\left(2u_\infty\sin\theta_1\cos\theta_2\rho_\infty+\lambda^2u_\infty\sin\theta_1\cos\theta_2\rho^*+u^*\rho_\infty+\frac{\lambda^2}{\lambda^2+1}u^*\rho^*\right) \qquad (A7.2-28')$$

Closure Assumptions

Ambient Properties

A typical case of an atmosphere with three distinct layers (the middle one corresponding to an elevated inversion) is depicted schematically in Figure 7-3. Left subscripts (01), (02), and (03) refer to properties at the bases of these three layers; thus ${}_{(01)}T_{p\infty}$ and ${}_{(01)}\rho_{p\infty}$ are respectively the ground values of potential ambient temperature and density (all potential properties being denoted with the use of subscript p). Mean ambient velocities and turbulent intensities are typically assumed uniform inside each layer; the distributions of ambient temperature and concentration are assumed known. In the following discussion focuses on the two dimensional case $(\theta_1, \theta_2) = (0, \theta)$.

Equations of State

The (potential) local density defect at the plume axis is given by

$$\rho_p^* = -\rho_{p\infty} \frac{T_{p\infty}}{T_{p\infty} + T_p^*} \qquad (A7.2-29)$$

and its along axis variation will be

$$\frac{d}{ds}\rho_p^* = -\left[\frac{\rho_{p\infty} + \rho_p^*}{T_{p\infty} + T_p}\right]\left[\frac{d}{ds}T_p^* + \frac{dT_{p\infty}}{dz}\sin\theta\right.$$
$$\left. + \frac{\rho_{p\infty}}{T_{p\infty}}\frac{dT_{p\infty}}{dz}\sin\theta \right] \qquad (A7.2-30)$$

The ambient potential density at height z from the ground is given by

$$\rho_{p\infty}(z) = {}_{(01)}\rho_{p\infty} \frac{{}_{(01)}T_{p\infty}}{T_{p\infty}(z)} \qquad (A7.2-31)$$

and will vary along the plume centerline according to

$$\frac{d}{ds}\rho_{p\infty} = -\frac{\rho_{p\infty}}{T_{p\infty}}\frac{dT_{p\infty}}{dz}\sin\theta \qquad (A7.2-32)$$

The potential temperature gradient is related to the actual atmospheric temperature gradient through

$$\frac{dT_{p\infty}}{dz} = \frac{T_{p\infty}(z)}{T_\infty(z)}\left(\frac{dT_\infty}{dz} + \frac{g}{C_P}\right)$$

and the quotient of the potential and actual temperature is

$$\frac{T_{p\infty}(z)}{T_\infty(z)} = \left(\frac{p_{p\infty}}{p_\infty(z)}\right)^{\frac{R_g}{C_P}}$$

Entrainment Hypothesis

(Turbulent Transport Closure)

Schatzmann (1979a) developed an entrainment function approximation starting from the integral equation for the mean kinetic energy of the plume

$$\frac{d}{ds}\left[u^{*2}b^2\left(u^* + \frac{3}{2}u_g\right)\right] =$$

$$= -\frac{6}{\lambda^2+1}u^{*3}b\frac{\lambda^2 \sin\theta}{\mathcal{F}^2} - 24u^*\frac{1}{b^2}\int_0^\infty \overline{u'v'}\exp\left(-\frac{r}{b}\right)^2 r^2\,dr$$

where $\mathcal{F}$ is the local densimetric Froude number, defined by

$$\mathcal{F}^2 = \frac{u^{*2}}{\dfrac{\rho^*}{\rho_\infty}gb}$$

The cross correlation $\overline{u'v'}$ was expressed in terms of empirical function of $\eta = r/b$ and the Boussinesq approximation was invoked to obtain $\hat{E} = E/(u^*b)$ as

$$\hat{E} = \frac{\frac{d}{ds}b + \left(\frac{\lambda^2-2}{\lambda^2+1} - 12I_2\right)\frac{\lambda^2\sin\theta}{\mathcal{F}^2} + \left[\left(\frac{1}{4} - 12I_4\right)\sin\theta\beta\frac{d}{ds}\theta + \frac{3}{2}\frac{d}{ds}b\right]\frac{u_\infty}{u^*}}{1 + 12I_1 + (1+24I_3)\frac{u_\infty}{u^*}\cos\theta} \qquad (A7.2-33)$$

where the I_i's are dimensionless integration constants. Schatzmann (1979a) considered limiting cases of the above expression, introduced an additional entrainment term to compensate for the suppression of the action of the vortex pair by the assumption of axisymmetry, and used available experimental data bases and numerical experiments to fit parameters and to simplify equations. Thus he finally obtained the semi-empirical expression

$$\hat{E} = \frac{A_1 + A_2\dfrac{\sin\theta}{\mathcal{F}^2}}{1 + 0.5A_3\dfrac{u_\infty}{u^*}\cos\theta}\left(1 + A_4\frac{u_\infty}{u^*}\sin\theta\right) + A_5\frac{L_\infty}{b}\frac{\sqrt{\overline{v'^2_\infty}}}{u^*} \qquad (A7.2-34)$$

The factor containing the A_4 parameter is the term accounting for the additional entrainment mentioned above; the last term represents the interaction of the energy-containing eddies of atmospheric turbulence with the large scale structure of the plume turbulence (L_∞ stands for the value of an appropriate macroscale of these energy containing eddies) and will be significant only in some relatively far-field phase of dispersion. For the near field a reasonable approximation is $A_5 = 0$. The empirical constants A_1 to A_4 suggested by Schatzmann (1979a) are

$$A1 = 0.057$$

$$A2 = 0.67$$

$$A3 = 10.0$$

$$A4 = 2.0$$

Preparation of the Continuity Equations for Numerical Solution

Equations (A7.2-23) to (A7.2-29), (A7.2-31) and (A7.2-34) provide a closed system for the evaluation of the eight unknowns $b(s)$, $\theta(s)$, $u^*(s)$, $T^*(s)$, $c^*(s)$, $\rho^*(s)$, $\rho_\infty(s)$ and $\hat{E}(s)$. To solve this system numerically it is transformed in the final form

$$\frac{dq}{ds} = f_i\left(s; q_1, q_2, \ldots, q_n\right); \quad i = 1, 2, \ldots, n$$

which (after non-dimensionalization) is ready for numerical solution.

First the above equations are transformed into explicit equations with respect to the unknown variables and their gradients. It can be shown that the variation of u^*, b and ρ^* with s does not depend on the gradients of T^* and neither on c^* or its gradients. Thus, finally, one has to solve simultaneously the system

$$\mathbf{A}\frac{d\mathbf{q}}{ds} = \mathbf{f}$$

and the equation

$$\frac{dT^*}{ds} = \frac{1}{a_{41}}\left(\frac{d\rho^*}{ds} - a_{42}\right)$$

where

$$\mathbf{q} = \left(\frac{du^*}{ds}\ \frac{db}{ds}\ \frac{d\rho^*}{ds}\right)^{\mathrm{T}}$$

$$\mathbf{f} = \left(f_1\ f_2\ f_3\right)^{\mathrm{T}}$$

and

$$\mathbf{A} = \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix}$$

with

$$a_{11} = \frac{b}{u^*}\left(1 + \lambda^2\frac{\rho^*}{\rho_\infty}\right)$$

$$a_{12} = 2\left(1 + \frac{\lambda^2}{\lambda^2+1}\frac{\rho^*}{\rho_\infty} + \lambda^2\frac{\rho^*}{\rho_\infty}\frac{u_\infty}{u^*}\cos\theta\right)$$

$$a_{13} = \frac{\lambda^2 b}{\rho_\infty}\left(\frac{u_\infty}{u^*}\cos\theta + \frac{1}{\lambda^2+1}\right)$$

$$a_{21} = \frac{b}{u^*}\left(1 + \frac{u_\infty}{u^*}\cos\theta + \frac{2\lambda^2}{2\lambda^2+1}\frac{\rho^*}{\rho_\infty} + \frac{\lambda^2}{\lambda^2+1}\frac{\rho^*}{\rho_\infty}\frac{u_\infty}{u^*}\cos\theta\right)$$

$$a_{22} = 1 + 2\frac{u_\infty}{u^*}\cos\theta + \frac{2\lambda^2}{1\lambda^2+1}\frac{\rho^*}{\rho_\infty} + \frac{2\lambda^2}{\lambda^2+1}\frac{\rho^*}{\rho_\infty}\cos\theta$$

$$a_{23} = \frac{b}{\rho_\infty}\left(\frac{\lambda^2}{2\lambda^2+1}\frac{\lambda^2}{\lambda^2+1}\frac{u_\infty}{u^*}\cos\theta\right)$$

$$a_{31} = -\frac{T^*}{u^*}\left(\frac{1}{\lambda^2+1}+\frac{1}{\lambda^2+2}\frac{\rho^*}{\rho_\infty}\right)$$

$$a_{32} = -\frac{T^*}{u^*}\left[2\left(\frac{1}{\lambda^2+1}+\frac{u_\infty}{u^*}\cos\theta\right)+\left(\frac{2}{\lambda^2+2}+\frac{u_\infty}{u^*}\cos\theta\right)\frac{\rho^*}{\rho_\infty}\right]$$

$$a_{33} = -\frac{T^*}{2\rho_\infty}\left(\frac{2}{\lambda^2+2}+\frac{u_\infty}{u^*}\cos\theta\right)$$

$$+\frac{\frac{1}{\lambda^2+1}+\frac{u_\infty}{u^*}\cos\theta+\frac{1}{2}\left(\frac{2}{\lambda^2+2}+\frac{u_\infty}{u^*}\cos\theta\right)\frac{\rho^*}{\rho_\infty}}{\frac{\rho_\infty}{T_\infty}\left(\frac{T_\infty}{Tin+T^*}\right)\left(1+\frac{\rho^*}{\rho_\infty}\right)}$$

$$f_1 = \frac{2\hat{E}}{u^*b}-\left(1+2\frac{u_\infty}{u^*}\cos\theta\right)\frac{b}{\rho_\infty}\frac{d\,\rho_\infty}{ds}+\lambda^2\frac{\rho^*}{\rho_\infty}\frac{u_\infty}{u^*}\sin\theta b\frac{d\,\theta}{ds}$$

$$f_2 = -\lambda^2\frac{\rho^*}{\rho_\infty}gb\frac{1}{u^{*2}}\sin\theta-\frac{1}{2}\left(1+2\frac{u_\infty}{u^*}\cos\theta\right)\frac{b}{\rho_\infty}\frac{d\,\rho_\infty}{ds}+\left(1+\frac{\lambda^2}{\lambda^2+1}\frac{\rho^*}{\rho_\infty}\right)\frac{u_\infty}{u^*}b\sin\theta\frac{d\,\theta}{ds}$$

$$f_3 = \frac{T_\infty}{\rho_\infty}\left(\frac{1}{\lambda^2+1}+\frac{u_\infty}{u^*}\cos\theta\right)\frac{d\,\rho_\infty}{ds}-T^*\frac{u_\infty}{u^*}\sin\theta\left(1+\frac{1}{2}\frac{\rho^*}{\rho_\infty}\right)\frac{d\,\theta}{ds}$$

$$-\frac{\frac{1}{\lambda^2+1}+\frac{u_\infty}{u^*}\cos\theta+\frac{1}{2}\left(\frac{2}{\lambda^2+2}+\frac{u_\infty}{u^*}\cos\theta\right)\frac{\rho^*}{\rho_\infty}}{\frac{\rho_\infty}{T_\infty}\left(\frac{T_\infty}{T_\infty+T^*}\right)\left(1+\frac{\rho^*}{\rho_\infty}\right)}\left[\frac{b}{T_\infty+T^*}\left(1+\frac{\rho^*}{\rho_\infty}\right)\frac{dT_\infty}{dz}\sin\theta+\frac{b}{\rho_\infty}\frac{d\,\rho_\infty}{ds}\right]$$

$$a_{41} = -\rho_\infty\frac{1}{T_\infty+T^*}\left(1+\frac{\rho^*}{\rho_\infty}\right)$$

$$a_{42} = -\left[\frac{b}{T_\infty+T^*}\left(1+\frac{\rho^*}{\rho_\infty}\right)\frac{dT_\infty}{dz}\sin\theta+\frac{b}{\rho_\infty}\frac{d\,\rho_\infty}{ds}\right]$$

Finally, c^* is calculated from

$$\frac{d\,c^*}{ds} = \frac{1}{a_{51}}\left(a_{52}\frac{d\,c_\infty}{ds}+a_{53}\frac{d\,u^*}{ds}+a_{54}\frac{d\,b}{ds}+a_{55}\frac{d\,\theta}{ds}+a_{56}\frac{d\,\rho^*}{ds}+a_{57}\frac{d\,\rho_\infty}{ds}\right)$$

where

$$a_{51} = \frac{1}{\lambda^2+1}+\frac{u_\infty}{u^*}\cos\theta+\frac{1}{2}\left(\frac{2}{\lambda^2+2}+\frac{u_\infty}{u^*}\cos\theta\right)\frac{\rho^*}{\rho_\infty}$$

$$a_{52} = -\left[\frac{1}{\lambda^2}\left(1+2\frac{u_\infty}{u^*}\cos\theta\right)+\left(\frac{1}{\lambda^2+1}+\frac{u_\infty}{u^*}\cos\theta\right)\frac{\rho^*}{\rho_\infty}\right]$$

$$a_{53} = -\frac{c^*}{u^*}\left(\frac{1}{\lambda^2+1}+\frac{1}{\lambda^2+2}\frac{\rho^*}{\rho_\infty}\right)$$

$$a_{54} = -\frac{c^*}{b}\left[2\left(\frac{1}{\lambda^2+1}+\frac{u_\infty}{u^*}\cos\theta\right)+\left(\frac{2}{\lambda^2+2}+\frac{u_\infty}{u^*}\cos\theta\right)\frac{\rho^*}{\rho_\infty}\right]$$

$$a_{55} = c^* \frac{u_\infty}{u^*} \sin\theta \left(1 + \frac{1}{2}\frac{\rho^*}{\rho_\infty}\right)$$

$$a_{56} = -\frac{c^*}{1\rho_\infty} \left(\frac{2}{\lambda^2 + 2} + \frac{u_\infty}{u^*}\cos\theta\right)$$

$$a_{57} = -\frac{c^*}{\rho_\infty} \left(\frac{1}{\lambda^2 + 1} + \frac{u_\infty}{u^*}\cos\theta\right)$$

(Note: in the above equations temperatures and densities represent potential quantities; the subscript p has been neglected for simplicity.)

Position

of the Mean Plume Centerline

Finally, the position (x, z) of the plume centerline in fixed Cartesian coordinates, for a given s, is determined through the parametric equations

$$x(s) = \int_{s_0}^{s} \cos\theta(s)\, ds$$

$$z(s) = \int_{s_0}^{s} \sin\theta(s)\, ds$$

which must be integrated numerically.

Initial Conditions

Schatzmann (1976) and Schatzmann and Flick (1977) suggested the following relationships (initial conditions) between centerline quantities at the end of the zone of flow establishment (subscript 0) and their corresponding values at the source (subscript j):

$$u_0^* = u_j^* \tag{A7.2 - 35}$$

$$\theta_0 = \theta_j \left(1 - 1.22 \frac{u_\infty}{u_j^*}\right) \quad \text{for } \theta_j = 90^0,\ \frac{u_\infty}{u_j^*} < 0.7 \tag{A7.2 - 36a}$$

$$\theta_0 = 0.167 \theta_j \quad \text{for } \theta_j = 90^0,\ \frac{u_\infty}{u_j^*} \geq 0.7 \tag{A7.2 - 36b}$$

$$b_0 = D_s \sqrt{\frac{1}{2} \frac{\left(u_j^* + u_\infty \cos\theta_0\right)}{\left(u_j^* + 2u_\infty \cos\theta_0\right)}} \tag{A7.2 - 37}$$

where D_s is the source diameter,

$$T_0^* = T_j^* \frac{\lambda^2 + 1}{2\lambda^2} \frac{u_j^* + 2u_\infty \cos\theta_0}{u_j^* + (\lambda^2 + 1)\, u_\infty \cos\theta_0} \tag{A7.2 - 38}$$

$$c_0^* = c_j^* \frac{\lambda^2 + 1}{2\lambda^2} \frac{u_j^* + 2u_\infty \cos\theta_0}{u_j^* + (\lambda^2 + 1)\, u_\infty \cos\theta_0} \tag{A7.2 - 39}$$

and

$$s_0 = 0 \quad \text{if } \frac{u_\infty}{u_j^*} > 0.3 \tag{A7.2 - 40a}$$

$$s_0 = D_s \left(6.2 - 20 \frac{u_\infty}{u_j^*}\right) \quad \text{if} u_\infty u_j^* < 0.3 \tag{A7.2 - 40b}$$

Simplifications through the Boussinesq Approximation

Introduction of the Boussinesq approximation in the continuity equations (A7.2-24) to (A7.2-28) gives the following reduced forms

(i) continuity equation of total mass

$$\frac{d}{ds}\left(u^{*}b^{2}\right)=2E \qquad (A2.7-24a)$$

(ii) momentum equation in the s-direction

$$\frac{d}{ds}\left[u^{*}b^{2}\left(u^{*}\left(+2u_{\infty}\cos\theta\right)\right)\right]=-\lambda^{2}b^{2}\frac{\rho^{*}}{\rho_{0}}g\sin\theta \qquad (A7.2-25a)$$

(iii) θ-equation

$$\frac{d\theta}{ds}=-2\left[\frac{\lambda^{2}b^{2}\frac{\rho^{*}}{\rho_{0}}g\cos\theta+u_{\infty}E\sin\theta+\left(\sqrt{2}1/\pi\right)c_{D}bu_{\infty}^{2}\sin^{2}\theta}{b^{2}u^{*}\left(u^{*}+2u_{\infty}\cos\theta\right)-4b^{2}\overline{v'^{2}_{\infty}}}\right] \qquad (A7.2-26a)$$

(iv) continuity equation for an inert scalar (concentration)

$$\frac{d}{ds}\left\{b^{2}c^{*}\left[u^{*}\left(\lambda^{2}+1\right)u_{\infty}\cos\theta\right]\right\}=-\left(\frac{\lambda^{2}+1}{\lambda^{2}}\right)\frac{dc_{\infty}}{ds}\left[b^{2}\left(u^{*}+2u_{\infty}\cos\theta\right)\right] \qquad (A7.2-27a)$$

(v) heat transport equation

$$\frac{d}{ds}\left\{b^{2}T^{*}\left[u^{*}\left(\lambda^{2}+1\right)u_{\infty}\cos\theta\right]\right\}=-\left(\frac{\lambda^{2}+1}{\lambda^{2}}\right)\frac{dT_{\infty}}{ds}\left[b^{2}\left(u^{*}+2u_{\infty}\cos\theta\right)\right] \qquad (A7.2-28a)$$

Comments

Using the Boussinesq approximation, and assuming the ambient fluid to be free of turbulence and of density stratification, the equations of Schatzmann can be compared directly with those published by Abraham (1971), Chan and Kennedy (1972), Fan (1967), Hoult, Fay and Forney (1969), Keffer and Baines (1963), Hirst (1972) and others, who also applied the integral method. Comparison, however, shows that the equations of these authors are not in general identical with the formulas presented here. According to Schatzmann (1978, 1979a) the differences are due to the following:

(i) Hirst, in deriving his mathematical model, applied the Leibniz rule (for the differentiation of an integral with variable limits) in an erroneous way.

(ii) All other above-mentioned investigators, who basically followed the classical vertical plume analysis of Morton, Taylor and Turner (1956) for plumes in a cross-flow, balanced the fluxes through the control surface incompletely.

Both errors lead to the same results. For example, the integral form of the continuity equation of mass becomes

$$\frac{d}{ds}\int_0^R (u_g + u_d) r\, dr = \frac{1}{2}\frac{d}{ds}\left[b^2\left(u^* + 2u_\infty \cos\theta\right)\right] = E \qquad (A7.2-41)$$

instead of the correct relation

$$\frac{d}{ds}\int_0^R u_d r\, dr = \frac{1}{2}\frac{d}{ds}\left(b^2 u^*\right) = E \qquad (A7.2-41a)$$

Figure A7.2-3 shows the difference between (A7.2-41) and (A7.41a) for a plume in a co-flowing stream. The flux of ambient fluid $E = -v_d(R)\, R = -v_d(R_\kappa)\, R_\kappa$, which flows into the control volume due to turbulent fluctuations inside the plume, only increases the excess velocity section, marked by A. What equation (A7.2-41) suggests is that Section B of the velocity profile would also be enlarged by the entrainment process, which is obviously not correct. The same error occurs by using a cone-shaped control volume, if the coaxial mass flux through the circumferential area is not taken into account. Uniquely in the special case $u_\infty = 0$ both equations are identical.

The momentum equations developed by Schatzmann also differ from those developed previously for similar reasons: When Hirst's or Fan's momentum equations are applied to a momentum plume in a co-flowing stream they fail to conserve the excess momentum flux. Nevertheless, Hirst, Fan etc. obtained reasonable agreement between theory and development. This is explained according to Schatzmann (1978, 1979a) by the empirical nature of the entrainment hypothesis. This empirical input to the mathematical model, together with skillful data fitting in order to fix the constants, may explain why models with internal inconsistencies managed to achieve the aforementioned agreement.

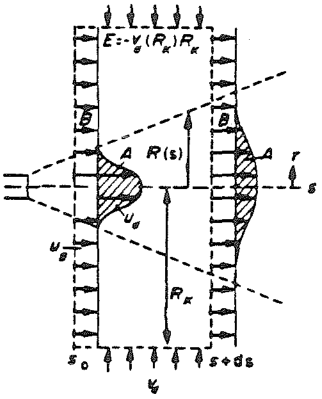

Figure A7.2-3

The Concept of Entrainment
for a Plume in a Co-Flowing Stream
(Source: Schatzmann, 1979a)

The scheme that was summarized in this appendix was tested by Schatzmann and his co-workers against approximately eighty different sets of data, from both laboratory and field measurements, with very satisfactory results; some representative comparisons are reproduced here, in Figures A7.2-4 and A7.2-5 (see Schatzmann, 1979a, for details). An extension of this scheme to "moist" plumes has also been developed (Schatzmann and Policastro, 1984).

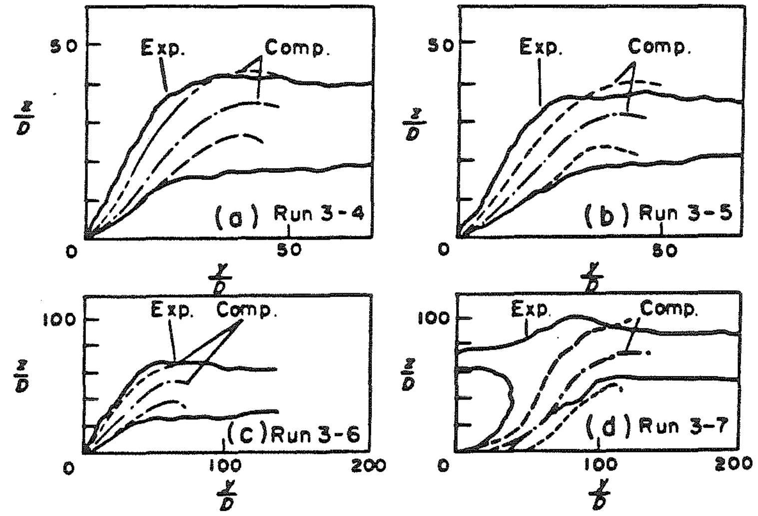

Figure A7.2-4

Buoyant Plumes Discharged at Various Angles into a Stably Stratified Ambient.

Calculations from the Model of Schatzmann

Compared with Laboratory Data of Fan (1967)

(D: plume diameter; z: height from source; y: downstream distance)

(Source: Schatzmann, 1979a)

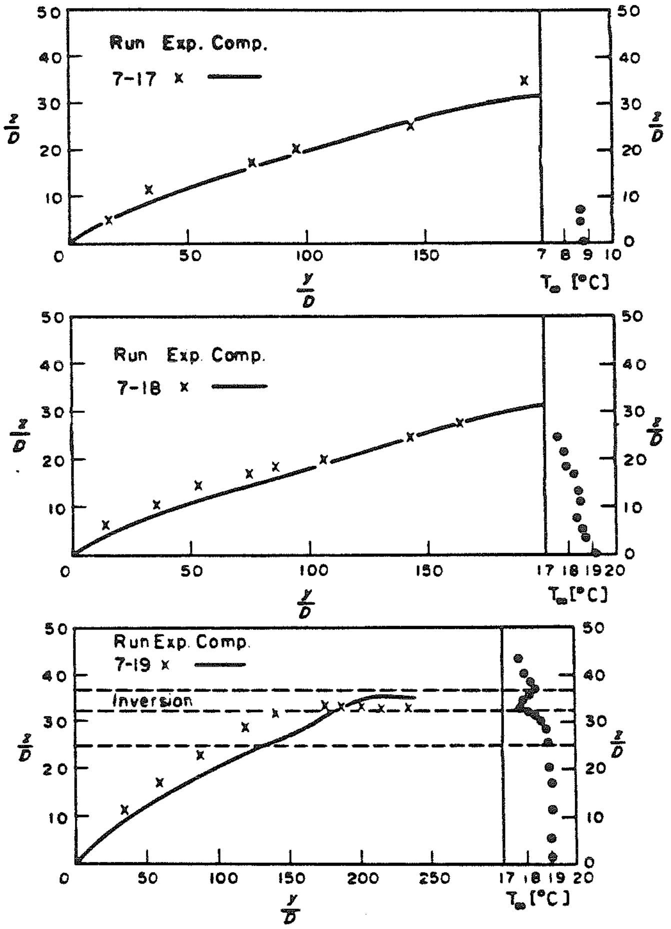

Figure A7.2-5

Trajectories of Buoyant Plumes Discharged into Stratified Ambient Cross-Winds with and without Temperature Inversion.

Calculations from the Model of Schatzmann

Compared with Field Data of Slawson and Csanady(1971)

(D: plume diameter; z: height from source; y: downstream distance)

(Source: Schatzmann, 1979a)

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APPENDIX A7.3

The Internal Structure of Buoyant Plumes in the Near Field

(Briggs, 1975)

The properties of the internal structure of a rising plume can be of great interest since they determine mixing in the early stages of plume evolution. Some of the details of structure within a rising plume have been studied through laboratory experiments on horizontal thermals, which closely resemble bent-over plumes in cross-section. Based on available data from the streamline measurements of Richards (1963), the vorticity measurements of Tsang (1971), and the concentration measurements in a bent-over laboratory plume of Fan (1967) Briggs (1975) summarized the following conclusions about bent over plume structure (see Figure A7.3-1):

First, the measurements show that almost all of the entrainment occurs across the top part of the plume. Part of the rise is due to mean vertical motion, but basically it is due to turbulent entrainment (almost by a factor of 75%). A secondary zone of entrainment exists under the middle of the plume, where induced velocities are very much higher than anywhere else around the boundary. This may be due to the low hydrostatic pressure underneath the buoyant fluid, and might not be so pronounced in a bent-over jet. Turbulence is generated here due to a strong shear of the vertical motion, evidenced by closeness of the streamlines near the center and by the flanking areas of high vorticity. This turbulence is advected upward through the middle of the plume, where it bisects the concentration maximum. The intensity it develops as it spreads across the top of the plume is partly due to horizontal divergence, which stretches vortex filaments in a direction almost tangent to the upper surface, thereby intensifying turbulent velocities perpendicular to the surface. In a buoyant plume, turbulence is also generated due to unstable internal density stratification above the concentration maxima, which are density minima. The marked decrease in turbulent entrainment around the lower flanks of the plume is probably due to the small amount of shear with the ambient at these points (it appears that the plume almost "rolls" up an imaginary inclined plane tangent to these points), and also is due to the proximity of the larger regions of high mean vorticity.

For a plume entering a a fluid having ambient turbulence, Briggs (1975) suggests that it is likely that the ambient turbulence must first mix its way into the plume by means of a "frontside attack." Also, there is a strong convergence of ambient streamlines under the plume, which tends to relax

Figure A7.3-1

Structure of a Bent Over Buoyant Plume

(adapted from Briggs, 1975)

Dashed and solid lines show the shape of a plume cross section at two successive times. Arrows show streamlines of mean motion. Horizontal hatching shows high vorticity regions. Dotted areas correspond to concentration maxima.

turbulence velocities that are perpendicular to the surface.

If this analysis is true, and ambient turbulence must first break into the plume in the frontal region, then its effectiveness will be delayed due to the relatively high plume turbulence in this same region. In effect, the plume will at first advance into the ambient faster than the ambient can advance into the plume. Once the balance is reversed, as the plume motions weaken, it is quite easy to conceive that the ambient turbulence may move downward and destroy the stable double vortex structure from within, making the plume vulnerable from all sides. In other words, plume "breakup" may occur relatively quickly, as has been suggested by Csanady (1973) and others and this must be taken into account for the correct formulation of entrainment hypotheses.

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for Appendix A7.3

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PART II

STATISTICAL METHODS AND MODELS: A DISTRIBUTION BASED APPROACH

Distributions, Order Statistics, and Applications

CHAPTER 8

STATISTICAL DISTRIBUTIONS OF AIR POLLUTANT CONCENTRATIONS

8.1 INTRODUCTION

Statistical analysis of monitored aerometric data aims to extract and organize information useful for the better treatment of problems related to establishing and evaluating air quality standards. Air pollutant concentrations are inherently random variables because of their dependence on the random fluctuations of a variety of meteorological and emission variables. When sets of air quality data are available certain distributional characteristics can be determined, under some simplifying assumptions, and assigned to the air pollutant concentrations. Sections 8.2 and 8.3 are devoted to the investigation of the nature, the limitations and the methodology of the description of air quality through statistical distributions of air pollutant concentrations. The most popular functional forms of such distributions are presented and studied there.

In the field of air pollution modeling and control of extreme events are usually of most interest; this is evidenced by the content of air quality standards which establish acceptable upper limits of air pollution concentrations and acceptable frequencies with which these limits can be exceeded. The proper description of these events requires consideration of characteristic random variables such as maximum concentrations, frequencies of exceedances of critical levels, etc. The tools appropriate for a relevant analysis are provided by the Order (or Extreme) Statistics and

Level Crossing theories; the key results of these theories, in relation to air pollution modeling, are summarized in Sections 8.4 and 8.5. Applications of the fundamental theoretical results in the evaluation of alternative forms of air quality standards are given in Section 8.6. Finally, it is shown how statistical distribution theory complies with simple rollback calculations for emission control and with the use of classical Gaussian plume models.

8.2 THE STATISTICAL TREATMENT OF AIR QUALITY DATA

Air quality data are usually available as sets of successive observations that represent concentrations measured sequentially in time at some specific location, and (usually) averaged over successive equal non-overlapping time periods. These data constitute statistical (nondeterministic) time series of the discrete form

$$x_\tau(t_1), x_\tau(t_2), \ldots, x_\tau(t_n); t_1 < t_2 < \ldots < t_n$$

where $\tau = t_2 - t_1 = t_3 - t_2 = \ldots = t_n - t_{n-1}$ is the averaging time, and t_i is the index for the time period over which the averaging is done, arbitrarily set equal to the beginning of the period.

The above time series is in fact a *sample realization* from an infinite population of random concentrations generated by a continuous state-discrete time stochastic process (see, for example, Seinfeld and Lapidus, 1973). (*)

The time series of measurements under consideration $\{x_\tau(t_i)\}$, and the underlying stochastic process $\{c_\tau(t_i)\}$, may have been constructed by averaging over initial samples that are either discrete or continuous time series, corresponding to the discrete or continuous measurement of concentration which is a continuous state-continuous time stochastic process $c(t)$ at may fixed point in space.

The parameters that appear in the construction of $\{x_\tau(t_i)\}$ are the averaging time τ , and, possibly, (in the case of non-continuous initial measurements) the sampling interval Δt between successive initial measurements. The significance of Δt has been discussed extensively elsewhere (Saltzman, 1970; Hunt, 1972); the selection of the appropriate Δt is a standard problem in data processing (e.g. Seinfeld and Lapidus, 1973, p. 93). The selection of the averaging time τ is closely related to the

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* Random variables are ordinarily denoted by capital letters and the values they may assume by lower case letters. This convention will not be followed here; rather lower case c will be used to denote the random concentration.

formulation of air quality standards (Section 8.6) and is often governed by regulatory considerations. As far as the statistical properties of aerometric data $\{x_\tau(t_i)\}$ are concerned, the length of τ affects the degree of correlation of successive data points $x_\tau(t_i)$ (concentrations averaged over long periods of time tend to be less correlated than concentrations averaged over shorter successive intervals), as well as the values of the parameters of probability distribution functions that may be attributed to these data.

The information, relevant to air quality, that is carried by the time series $\{x_\tau(t_i)\}$ can be organized in forms useful to the study of questions related to pollution forecasting, evaluation of air quality standards, validation of numerical dispersion models etc., by various methods of statistical analysis. These include regression analysis, time series modeling approaches, spectral methods, etc. (see, for example, the Proceedings of the Symposium of Statistical Aspects of Air Quality Data, EPA, 1974, and Merz et al., 1974; Myrabo et al., 1975). The monograph of Essenwager (1976) provides useful introductory information relevant to many of these topics; for comprehensive overviews of current developments in the area one may consult the proceedings of the regular series of *Conferences in Probability and Statistics in Atmospheric Sciences*, sponsored by the A.M.S., that are held every two years (the 8th in 1983).

The objective of the present work is to study the cases where the statistical information relevant to aerometric data, available in the form discussed above,(*) can be embodied in a probability density function (pdf) – equivalently: in the respective cumulative distribution function – or, in general, in a set of probability density functions.

Naturally, in order that a time invariant probability density, common for all the members of the process $\{c_\tau(t_i)\}$, exist, $\{c_\tau(t_i)\}$ must be a *strictly stationary process.*

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* Sometimes only appropriate characteristic subsequences of the complete time series are considered in a statistical analysis. For example, the daily maxima of hourly average concentrations of a pollutant are often considered instead of the whole set of data when the behavior of high concentrations is under question. However the results from the reduced set of data are not always equivalent to the ones from the complete set, as is discussed later, in Section 8.6.

Further, in order that the parameters of this pdf can be estimated from just one sample realization of the process (the available time series), it has also to be *ergodic*. The ergodicity property implies that the ensemble mean of $c_r(t_i)$ – independent of i – will be approximated by the time average (mean value) of the observations $x_r(t_i)$ as their number tends to infinity. In practice what one has to confirm is the "sufficiently stationary" character of the data (or of an appropriate transformation of the data with respect to time). Although various criteria can be set to define the meaning of the adverb "sufficiently" above, it must be realized that this step is essentially a matter of engineering judgment and will not be elaborated any further here. Then ergodicity is always implicitly assumed.

The case most suitable for analysis would be that of a set of independent, identically distributed variates, $c_r(t_i)$ ("i.i.d. variates"), which of course is strictly stationary. Then the data form what is called in statistics a "random sample" from which statistical inference is especially convenient. This case is amenable to extensive theoretical treatment (Sections 8.4 and 8.5); this treatment can be extended, in special cases, to autocorrelated and even nonidentically distributed data (Appendix A8.2). Nevertheless, it is a fortunate fact that application of theoretical results concerning i.i.d. concentrations to real situations often leads to satisfactory agreement with experimental observations (Section 8.6). Thus, although the assumption of independence for air pollutant data is not strictly a valid one, it can be often applied in simplified statistical analysis.

Nonstationary time series (with independent or dependent non-identically distributed members) can often be treated in this perspective in cases of "well-behaved" nonstationarity where definite deterministic trends or periodic variation of air quality data can be incorporated in the statistical analysis, reducing the problem finally into one of stationary data (e.g. Horowitz and Barakat, 1979).

Another fact that has to be pointed out is the possibility that different distributions (or, usually, the "same" distribution with different parameters) fit different ranges of the concentration better; in such a case one may wish to have an optimal fit for a particular range of concentrations that are of the most interest) and thus decide to disregard the rest of the data (or fit another distribution to them). Here the focus will be mainly on the case where the statistical properties of the available data are described adequately by a single distribution; however the entire analysis that follows applies directly to cases where a distribution is itended to describe only a particular range of concentrations.

With the assumed distribution one will be able to make statistical inferences about, for example, the expected number of occurrences of certain concentration levels. However but one will not be able to predict when these occurrences will take place; all information concerning the time evolution of the process is disregarded.

Before examining the specific forms of pds's that fit actual aerometric data it is interesting to "visualize" the "genesis" of such a distribution from the data. Thus, in Figure 8-1(a) a histogram is presented in which the frequency of occurrence of time-averaged concentrations is plotted as a function of the time-averaged concentration for some hypothetical situation. Such a histogram would generally exhibit irregular behavior for small numbers of observations (in general for finite samples). The irregularities disappear as this number increases and finally, for infinite samples, the histogram tends to a smooth curve of the form shown in Figure 8-1(b). The distribution of this figure, under the conditions of stationarity and ergodicity is invariably valid for all the observations (but will be different for different averaging times). One should note that, typically, very low and very high concentrations occur only rarely and that the concentration occurring most frequently (the mode) need not be the average or mean concentration. From a practical point of view the width or variance of a distribution such as that of Figure 8-1(b) is a measure of how variable the concentration is from one averaging period to another.

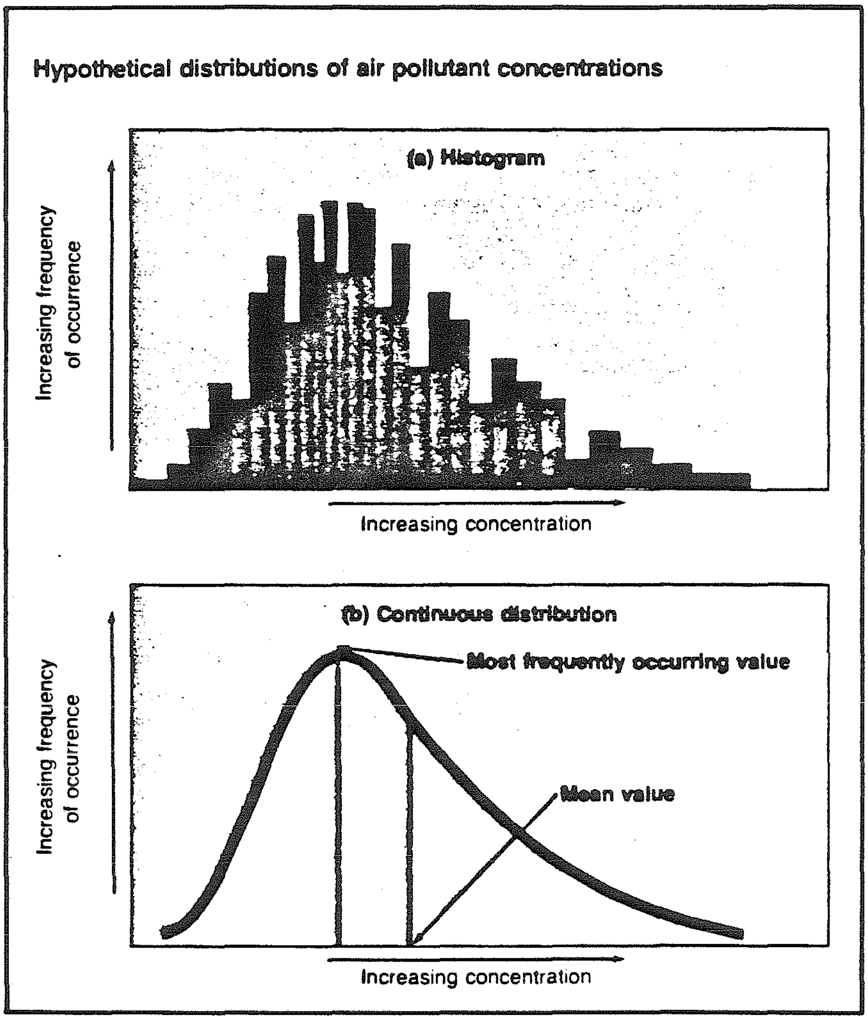


Figure 8-1

Typical Probability Densities

of Air Pollutant Concentrations:

(a) Histogram,

(b) Continuous Distribution

8.3 STATISTICAL DISTRIBUTIONS OF AEROMETRIC DATA

While there is no a priori reason to expect that air pollutant concentration distributions would adhere to a specific statistical distribution, a number of pdf's have been proven particularly useful in representing air quality data. All these pdf's have the general features of the curve shown in Figure 8-1(b); they correspond to a nonnegative random variable c_r that has probabilities of occurrence approaching zero as $c_r \rightarrow 0$ and as $c_r \rightarrow \infty$. Table 8-1 summarizes the functional form of several of these pdf's. Naturally, the larger the number of parameters in the functional form of the distribution, the greater is their flexibility of fitting sets of observed data.

The two-parameter distributions in Table 8-1 (lognormal, Weibull and gamma) assume that the random variable admits all nonnegative values. The three-parameter lognormal, Weibull and gamma distributions assume that the random variable is restricted to values greater than the parameter γ. The beta distribution is extremely flexible: it is symmetrical when $\alpha = \beta$, skewed to the right if $\alpha < \beta$, and skewed to the left if $\alpha > \beta$. The beta distribution also assumes an upper bound θ on the random variable and may or may not include a lower bound γ. The beta and gamma distributions in fact are members of the general Pearson system of probability density curves that includes twelve types of functions, most of them applicable to the description of air quality data (see, for example, Lynn, 1974).

There exists a substantial literature in which various distributions have been fit to air quality data (see, for example, the Proceedings of the Symposium of Statistical Aspects of Air Quality Data, EPA, 1974, as well as Hillyer, 1978, and Tsukatani and Shigemitsu, 1980). In addition, Holland and Fitz-Simmons (1982) have developed a computer program for fitting statistical distributions to air pollutant data.

The answer to the question of which distribution should fit best air quality data has been shown to depend in general on the pollutant, the time period of interest,

Table 8-1

Probability Density Functions

Useful in Representing Atmospheric Concentrations

Distribution	Probability density function $p(x)$
Log-normal	$\frac{1}{x\sigma(2\pi)^{1/2}} \exp\left[-\frac{(\ln x - \mu)^2}{2\sigma^2}\right]$ $x > 0; \quad \sigma > 0, -\infty < \mu < \infty$
Weibull	$\frac{\lambda}{\sigma}\left(\frac{x}{\sigma}\right)^{\lambda-1} \exp\left[-\left(\frac{x}{\sigma}\right)^{\lambda}\right]$ $x \geq 0; \quad \sigma, \lambda > 0$
Gamma	$\frac{1}{\sigma\Gamma(\lambda)}\left(\frac{x}{\sigma}\right)^{\lambda-1} \exp\left(-\frac{x}{\sigma}\right)$ $x \geq 0; \quad \sigma, \lambda > 0$
Three-parameter log-normal	$\frac{1}{(x-\gamma)\sigma(2\pi)^{1/2}} \exp\left[-\frac{[\ln(x-\gamma)-\mu]^2}{2\sigma^2}\right]$ $x > \gamma; \quad \sigma > 0; \quad -\infty < \mu < \infty$
Three-parameter gamma	$\frac{1}{\sigma\Gamma(\lambda)}\left(\frac{x-\gamma}{\sigma}\right)^{\lambda-1} \exp\left(-\frac{x-\gamma}{\sigma}\right]$ $x > \gamma; \quad \sigma, \lambda > 0$
Three-parameter Weibull	$\frac{\lambda}{\sigma}\left(\frac{x-\gamma}{\sigma}\right)^{\gamma-1} \exp\left[-\left(\frac{x-\gamma}{\sigma}\right)^{\lambda}\right]$ $x > \gamma; \quad \sigma, \lambda > 0$
Three-parameter beta	$\frac{\Gamma(\alpha+\beta)}{\Gamma(\alpha)\Gamma(\beta)} \theta^{1-\alpha-\beta} x^{\alpha-1} (\theta - x)^{\beta-1}$ $0 \leq x \leq \theta$
Four-parameter beta	$\frac{\Gamma(\alpha+\beta)}{\Gamma(\alpha)\Gamma(\beta)} (\theta-\gamma)^{1-\alpha-\beta} (x-\gamma)^{\alpha-1} (\theta - x)^{\beta-1}$ $\gamma < x < \theta; \quad \alpha, \beta > 0$

the averaging time τ of the data, the location, and other factors. Thus, because there appears to exist no "universal" distribution, that most appropriate for the particular data set must be selected by employing standard statistical methods of analysis. In general, a computer program, such as that of Holland and Fitz-Simmons (1982), should be used. Of course data with "anomalous" behavior (e.g., data that are described by a mixture of distributions for different ranges of concentration, etc.) must be treated with special appropriate techniques. We must also note here that, as pointed out by many investigators (see, for example, Gifford, 1974), there are differences between the frequency distribution of urban air pollution, resulting from the combined effects of many sources, and that of concentrations from a single isolated source. Experimental studies (Barry, 1971) suggest that usually a semi-logarithmic distribution provides the best fit to data for isolated point sources (see Chapter 5 for a more detailed discussion of this problem).

Among the distributions of Table 8-1, the two-parameter lognormal has been the most popular in representing urban air pollutant concentration data. The conformity of this representation with field measurements, as well as various other aspects concerning lognormally distributed aerometric data, has been discussed extensively elsewhere (see, for example, Larsen, 1971; Proceedings of the Symposium of Statistical Aspects of Air Quality Data, EPA, 1974; Bencala and Seinfeld, 1976). As far as analytical manipulations are concerned, the lognormal distribution, being a monotone transformation of the Gaussian distribution, offers a direct utilization of various results concerning normally distributed variables. Further, it has the advantage that variates with the simple time series model

$$c_\tau\left(t_i\right)=c_\tau\left(t_{i-1}\right)+y_\tau\left(t_i\right) c_\tau\left(t_{i-1}\right)$$

where the members of the sequence $y_\tau\left(t_i\right)$ are independent and arbitrarily distributed (i.e. $y_\tau(t)$ is an white noise process) are lognormally distributed. Indeed, if

$$y_\tau\left(t_i\right)=\frac{c_\tau\left(t_i\right)-c_\tau\left(t_{i-1}\right)}{c_\tau\left(t_{i-1}\right)}$$

then

$$\sum_{i=1}^{n} y_\tau(t_i) = \sum_{i=1}^{n} \frac{c_\tau(t_i) - c_\tau(t_{i_1})}{c_\tau(t_{i-1})}$$

and by the central limit theorem $\sum_{i=1}^{n} y_\tau(t_i)$ will be normally distributed for large n (strictly for $n \to \infty$). Further, for $t_i - t_{i-1} \to 0$ the right-hand-side of the above equality tends to

$$\int_{c_\tau(t_1)}^{c_\tau(t_n)} \frac{dc_\tau(t)}{c_\tau(t)} = \ln \frac{c_\tau(t_n)}{c_\tau(t_1)}$$

Thus $c_\tau(t_n)$ is in fact lognormally distributed. (This is a particularization of the general Kapteyn scheme for generation of skew distributions; see, e.g., Hald, 1952).

For most practical applications the two most popular of the distributions of Table 8-1, that is, the two-parameter (or ordinary) lognormal and the two-parameter Weibull, are adequate and the following analysis will focus on them. (Nevertheless, virtually all of what will be presented here is directly extendable to the other distributions of Table 8-1.)

Some basic properties of these two distributions are discussed briefly next. (For further details and for relevant material concerning other distributions, one may consult standard references on statistical distributions, as, for example, the extensive treatises of Johnson and Kotz, 1970, and Elderton and Johnson, 1969.)

8.3.1 The Two-Parameter Lognormal Distribution

If a concentration c is lognormally distributed, its pdf is(*)

$$p_L(c) = \frac{1}{c\sigma\sqrt{2\pi}} \exp\left[-\frac{(\ln c - \mu)^2}{2\sigma^2}\right] \qquad (8.3-1)$$

where μ and σ are parameters that depend on the particular situation. The logarithm of the concentration, when described by (8.3-1), has expected value and variance $\mathrm{E}\{\ln c\} = \mu$, and $\mathrm{Var}\{\ln c\} = \sigma^2$. The corresponding mean and variance of c are

$$\mathrm{E}\{c\} = \exp\left(\mu + \frac{\sigma^2}{2}\right) \qquad (8.3-2a)$$

---

* The subscript for the averaging time is omitted here for convenience; however, it should always be kept in mind that all data and parameters are related to a fixed averaging time.

$$\mathrm{Var}\{c\} = \left\{\exp\left(2\mu + \sigma^2\right)\right\}\left[\exp\left(\sigma^2\right) - 1\right] \tag{8.3 – 2b}$$

The lognormal distribution is also commonly expressed in the form

$$p_L(c) = \frac{1}{c \ln \sigma_g \sqrt{2\pi}} \exp\left[-\frac{(\ln c - \ln \mu_g)^2}{2(\ln \sigma_g)^2}\right] \tag{8.3 – 3}$$

where $\mu_g = \exp \mu$ and $\sigma_g = \exp \sigma$. μ_g and σ_g are termed the *geometric mean* and the *standard geometric deviation*, respectively. One should note that

$$\ln \mathrm{E}\{c\} = \ln \mu_g + \frac{1}{2}(\ln \sigma_g) \tag{8.3 – 4}$$

The probability that a lognormally distributed variable c exceeds the value χ is given by the complementary distribution function

$$\overline{F}_L(\chi) = \Pr\{c > \chi\} = 1 - \Phi\left(\frac{\ln \chi - \mu}{\sigma}\right) \tag{8.3 – 5}$$

where

$$\Phi(\eta) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\eta} \exp\left(-\frac{t^2}{2}\right) dt \tag{8.3 – 6}$$

is the cumulative distribution function for the unit normal distribution, i.e. with mean zero and unit standard deviation. (Recall that the cumulative distribution function is defined as $F(\chi) = \Pr\{c \leq \chi\}$, whereas the complementary distribution function is $\overline{F}_L(\chi) = 1 - F(\chi)$.) Tables of $\Phi(\eta)$ are readily available so that the probability of c exceeding a given value χ can be easily calculated from (8.3-5). One must note that if $\ln \chi = \mu$, or $\chi = \mu_g$, the argument of Φ equals zero so that $\Pr\{c > \exp \mu\} = \Pr\{\ln c > \mu\} = 0.5$. Thus, $\mu_g = \exp \mu$ is the median value of a lognormally distributed variable.

The lognormal distribution has the useful property that when the complementary distribution function $\overline{F}_L(\chi)$ is plotted versus the logarithm of the concentration on "normal curve graph paper" a straight line results. The point where $\eta = 0.0$ ($\overline{F}_L(\chi) = 0.5$) occurs where $\ln \chi = \ln \mu_g$. The point where $\eta = 1.0$ ($\overline{F}_L(\chi) = 0.16$) lies where $\ln \chi = \ln \sigma_g + \ln \mu_g$ or $\chi = \sigma_g \mu_g$.

Figure 8-2 shows the distribution of one-hour average SO_2 concentrations equal to or in excess of the stated values for Washington, D.C., for the seven-year period from December 1, 1961, to December 1, 1968 (Larsen, 1971). A lognormal distribution has been fitted to the high-concentration range of these data.

The lognormal distribution is completely characterized by two parameters, the geometric mean μ_g and the standard geometric deviation σ_g. The geometric mean or median is the concentration where the straight line plot crosses the 50th percentile. The slope of the line is related to the standard geometric deviation, which can be calculated from the plot by dividing the 16th percentile concentration, i.e. the geometric mean. (This is the 16th percentile of the complementary distribution function $\overline{F}_L(\chi)$; equivalently it is the 84th percentile of $F_L(\chi)$.) For the distribution of Figure 8-2, $\mu_g = 0.042$ ppm and $\sigma_g = 1.96$ ppm^2. Plots such as Figure 8-2 are widely used in air quality analysis to assess the frequency with which concentrations equal or exceed certain values.

8.3.2 The Two-Parameter Weibull Distribution

The Weibull pdf is given in Table 8-1. If a set of data conforms to a Weibull distribution, then the data, when plotted on "extreme-value probability paper", i.e. with coordinates $\log\chi$ and $\log\left[\ln\left(1/\overline{F}_L(\chi)\right)\right]$, should lie on a straight line. The complementary distribution function for the Weibull distribution is

$$\overline{F}_W(\chi) = \exp\left[-\left(\frac{\chi}{\sigma}\right)^{\lambda}\right] \qquad (8.3-7)$$

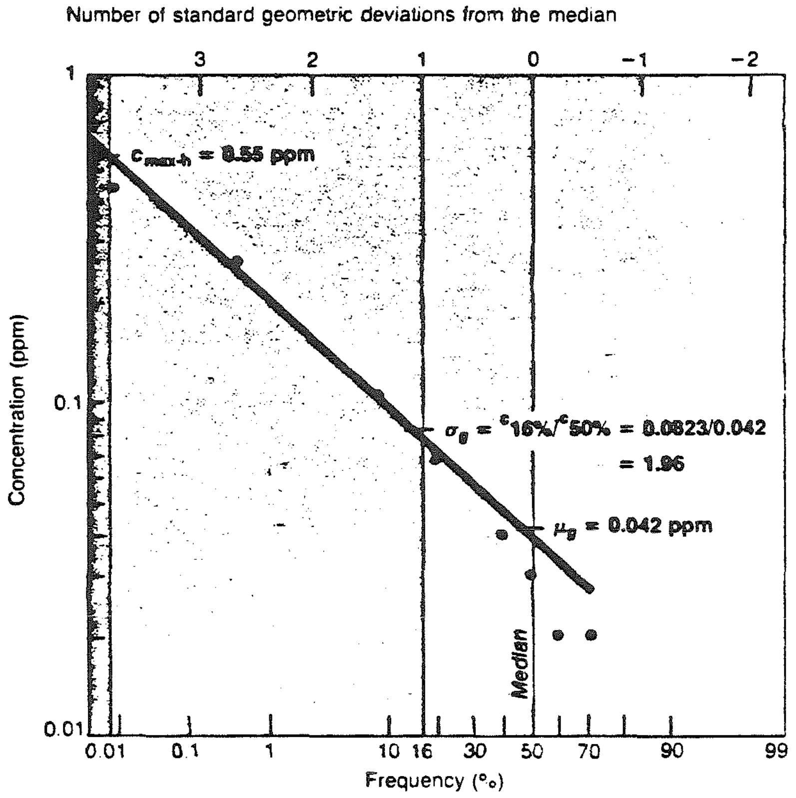
Taking logarithms and changing sign one has

$$\ln\left[\frac{1}{\overline{F}_W(\chi)}\right] = \left(\frac{\chi}{\sigma}\right)^{\lambda} \qquad (8.3-8)$$

Taking the logarithm (base 10) of both sides of (8.3-8),

$$\log\left[\ln\left(\frac{1}{\overline{F}_W(\chi)}\right)\right] = \lambda\left(\log\chi - \log\sigma\right) \qquad (8.3-9)$$

Frequency of 1-hour average SO_2 concentrations equal to, or in excess of stated values[a]



[a] At Washington D.C. Dec. 1, 1961–Dec. 1, 1968 (after Larsen, 1971)

Note: Quantile values of c refer to the complementary distribution function

Figure 8-2

Frequency of 1-hour Average SO_2 Concentrations Equal to, or in Excess of, Stated Values for Washington, D.C., December 1, 1961 – December 1, 1968 (source: Larsen, 1971) (Note: quantile values of c refer to the complementary distribution function.)

Therefore one can plot $\log\left[\left(1/\overline{F}_W(\chi)\right)\right]$ vs. $\log\chi$ and expect a straight line if the data fit a Weibull distribution. The values $\log\left[\left(1/\overline{F}_W(\chi)\right)\right]$ are the values on the ordinate scale of Figure 8-3.

σ is obtained by letting the left-hand side of (8.3-9) equal zero. This corresponds to $\overline{F}_W(\chi) = e^{-1} = 0.368$. At this $\overline{F}_W(\chi)$, the corresponding value of χ will equal σ. The parameter λ, which is the slope of the straight line, can be found by using any other point on the line and solving (8.3-9) for λ:

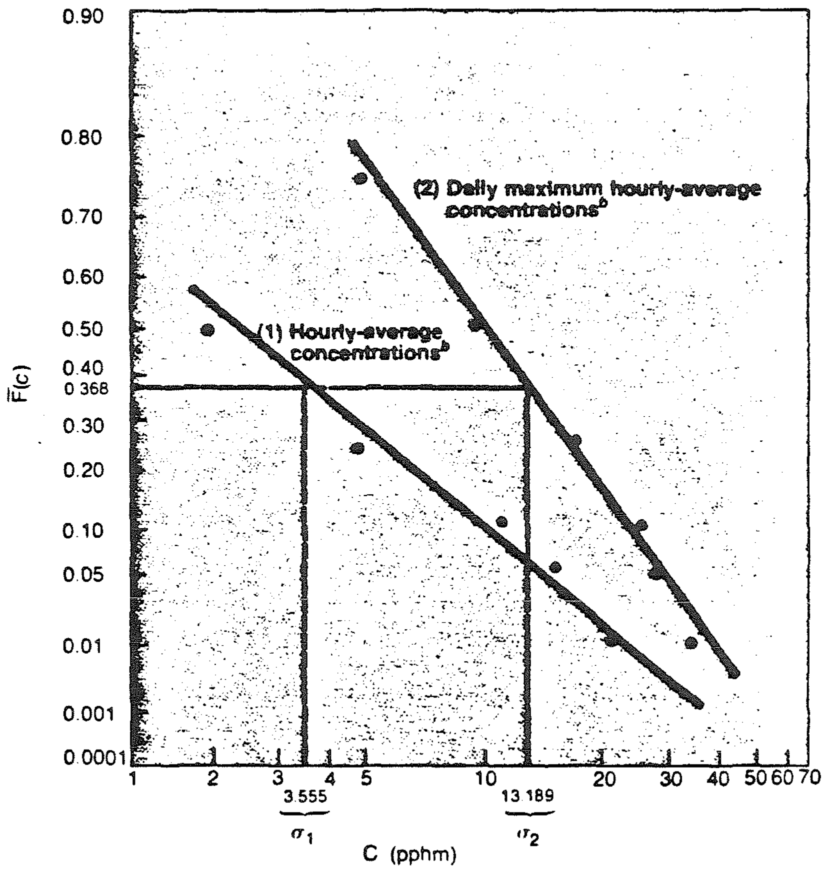
$$\lambda = \frac{\log\left[\ln\left(\frac{1}{\overline{F}_W(\chi)}\right)\right]}{\log\chi - \log\sigma} \tag{8.3-10}$$

Using for a second point that point on the line that crosses $\overline{F}_W(\chi) = 0.01$ one obtains

$$\lambda = \frac{0.663}{\log\chi_{0.01} - \log\sigma}$$

8.3.3 Estimation of Parameters in the Distributions

Each of the two distributions discussed in subsections 8.3.1 and 8.3.2 is characterized by two parameters. The fitting of a distribution to a set of data involves determining the values of the parameters of the distribution so that the fit is "optimal" in some manner. Ideally, this fitting is best carried out using a systematic optimization routine (such as that developed by Holland and Fitz-Simmons (1982)) that estimates the parameters for several distributions from the given set of data and then compares how these distributions comply to these data using various criteria of "goodness of fit". If however such a routine is not available, or one desires a quick means of parameter estimation, the following three alternative methods are appropriate: The first is the method of moments, which in general requires the computation of the first n (where n equals the number of the parameters of the distribution) sample moments of the data. Next is the method of maximum likelihood, which gives estimates that are optimal in a certain statistical sense, but may require more calculations than the method of moments. Finally, for quick calculations one can employ



Weibull distribution fits of the 1971 hourly-average, and daily maximum hourly-average oxidant concentration[a]

[a] At Pasadena Calif

[b] Points represent the values listed in Table 2

Figure 8-3

Weibull distribution fittings of the 1971 hourly-average and daily maximum hourly-average oxidant concentrations at Pasadena, CA. Distribution (1) is that for the hourly average concentrations, whereas (2) is for the daily maximum hourly-average concentrations. The points shown here represent only selected data from the 8303 and 365 data values that were respectively used to determine the distributions.

the method of quantiles which is very versatile and can (usually) be formulated in a manner especially convenient for a specific problem. These three methods are briefly discussed next. A practical procedure suggested for the estimation, if sample distributions such as the lognormal and the Weibull are to be tried, should start with the construction of a plot of the available data on the appropriate paper (that gives a straight line for the theoretical distribution), in order to get a preliminary notion of the goodness of fit. If the fit is acceptable for a given distribution one proceeds to estimate its parameters.

(a) The Method of Moments

Estimates for the values for the moments are obtained from the data, and the equations relating the moments to the parameters of the distribution are solved for the parameters. (For a two-parameter distribution, estimators for the first two moments are needed.)

The r-th non-central moment of a random variable X with pdf $p(x)$ is defined by

$$\mu_r' = \int_0^\infty x^r p(x)\,dx$$

and the r-th central moment is

$$\mu_r = \int_0^\infty (x - \mu_1')^r p(x)\,dx$$

(The mean value of the random variable x is μ_1', and the variance is μ_2.)

The estimation of μ and σ for the lognormal distribution by the method of moments is considered first. The first and second non-central moments of this distribution are

$$\mu_1' = \exp\left(\mu + \frac{\sigma^2}{2}\right) \qquad (8.3-11)$$

$$\mu_2' = \exp\left(2\mu + 2\sigma^2\right) \qquad (8.3-12)$$

Solving (8.3-11) and (8.3-12) for μ and σ^2, one has

$$\mu = 2\ln\mu_1' - \frac{1}{2}\ln\mu_2' \qquad (8.3-13)$$

$$\sigma^2 = \ln \mu_2' - 2 \ln \mu_1' \tag{8.3 - 14}$$

μ_1', μ_2' and μ_2 are related through $\mu_2 = \mu_2' - \mu_1^2$ and are estimated from the data by

$$M_1' = \frac{1}{n} \sum_{i=1}^{n} x_i \tag{8.3 - 15}$$

$$M_2' = \frac{1}{n} \sum_{i=1}^{n} x_i^2 \, ; \quad M_2 = \frac{1}{n-1} \sum_{i=1}^{n} (x_i - M_1')^2 \tag{8.3 - 16}$$

where n is the number of data points. Thus, the moment estimates of the parameters of the lognormal distribution are given by

$$\hat{\mu} = 2 \ln M_1' - \frac{1}{2} \ln M_2' \tag{8.3 - 17}$$

$$\hat{\sigma}^2 = \ln M_2' - 2 \ln M_1' \tag{8.3 - 18}$$

For the Weibull distribution, the mean and variance are given by

$$\mu_1' = \sigma \Gamma \left(1 + \frac{1}{\lambda}\right) \tag{8.3 - 19}$$

and

$$\mu_2 = \sigma^2 \left[\Gamma \left(1 + \frac{2}{\lambda}\right) - \Gamma^2 \left(1 + \frac{1}{\lambda}\right)\right] \tag{8.3 - 20}$$

In solving these equations for σ and λ, onee can conveniently use the coefficient of variation given by $\sqrt{\mu_2}/\mu_1'$. Then the moment estimators of the sample correspond to $\lambda = \hat{\lambda}$ such that

$$\left[\frac{\Gamma \left(1 + \frac{2}{\hat{\lambda}}\right)}{\Gamma^2 \left(1 + \frac{1}{\hat{\lambda}}\right)} - 1\right]^{\frac{1}{2}} = \frac{M_2^{\frac{1}{2}}}{M_1'} \tag{8.3 - 21}$$

$$\hat{\sigma} = \frac{M_1'}{\Gamma \left(1 + \frac{1}{\hat{\lambda}}\right)} \tag{8.3 - 22}$$

(b) The Method of Maximum Likelihood.

Optimal estimates of parameters for a distribution (of given functional form) can be obtained by employing the method of maximum likelihood, which usually involves more complicated computations than the method of movements. The method consists in evaluating the parameters θ_1, θ_2, …, θ_k of a k-parameter distribution so as to maximize the likelihood function, defined as the joint pdf of the observations in a random sample of size n

$$L(\theta_1, \ldots, \theta_k) = \prod_{i=1}^{n} p(x_i; \theta_1, \ldots, \theta_k)$$

The maximum likelihood is obtained by taking the partial derivatives of L with respect to each parameter, setting them equal to zero and solving the resulting k equations simultaneously. It is convenient to take the derivative of the logarithm of L; thus the maximum likelihood equations are

$$\frac{\partial}{\partial \theta_i} \ln L(x_1, \ldots, \chi_n; \theta_1, \ldots, \theta_k) = 0 \qquad (8.3-23)$$

For the two-parameter lognormal distribution one finds that the maximum likelihood estimates $\hat{\mu}$ and $\hat{\sigma}$ of the parameters μ and σ are given by

$$\hat{\mu} = \frac{1}{n} \sum_{i=1}^{n} \ln x_i \qquad (8.3-24)$$

and

$$\hat{\sigma}^2 = \frac{i}{n} \sum_{i=1}^{n} (\ln x_i - \hat{\mu})^2 \qquad (8.3-25)$$

For the Weibull distribution it can be shown that the maximum likelihood estimates $\hat{\lambda}$ and $\hat{\sigma}$ of λ and σ satisfy the set of equations

$$\hat{\lambda} = \left[\left(\sum_{i=1}^{n} x_i^{\hat{\lambda}} \ln x_i \right) \left(\sum_{i=1}^{n} x_i^{\hat{\lambda}} \right)^{-1} - \frac{1}{n} \sum_{i=1}^{n} \ln x_i \right] \qquad (8.3-26)$$

$$\hat{\sigma} = \left[\frac{1}{n} \sum_{i=1}^{n} x_i^{\hat{\lambda}} \right]^{\frac{1}{\hat{\lambda}}} \qquad (8.3-27)$$

(For details see Johnson and Kotz (1970), Vol. 1). It should be noted here that the maximum likelihood method can also be used as a criterion for evaluating goodness of fit of different distributions; among various distributions that fit a given set of data, the one with maximum L is considered optimal.

(c) The Method of Quantiles

Through this method the parameters of a distribution can be estimated so that the theoretical distribution fits optimally (for example in the least square sense) a set of points (x_{q_i}, q_i) where the x_{q_i}'s are quantiles of the sample (or empirical) distribution function. For a given probability distribution the quantile x_q is defined by the equation

$$\int_0^{x_q} p(x)\, dx = q \quad (0 < q < 1) \qquad (8.3-28)$$

For a sample of size n the empirical cumulative distribution function is

$$\hat{F} = \frac{1}{n} \times (\text{number of } x_i \text{ less than or equal to } \hat{x}_q)$$

and the quantile x_q is chosen so as to satisfy $\hat{F}(x_q) = q$. For the two-parameter lognormal and Weibull distributions one can employ the transformations of coordinates used in the graphs of the Figures 8-2 and 8-3 respectively, so that a straight line should fit the data. In the case that inspection of a plot of the data in such coordinates shows that a good linear fit exists (at least for a region of concentrations that is of interest), and a very quick (and approximate) estimation of the parameters is wanted, it is sufficient to use only two quantiles of the empirical distribution to obtain two relations that can be solved simultaneously to determine the parameters of the theoretical distribution. Usually quantiles corresponding to high values of q will be used since the region of high concentrations is of the most interest.

For the lognormal distribution, for example, it was earlier shown how μ_g and σ_g are estimated from the concentrations at the 50% and 84% quantiles, i.e.,

$$\ln \hat{x}_{0.95} - \ln \hat{\mu}_g = 0$$

$$\ln \hat{x}_{0.84} - \ln \hat{\mu}_g = \ln \hat{\sigma}_g$$

Choosing, as a further illustration, the 95% and 99% quantiles, one obtains

$$\ln \hat{x}_{0.95} - \ln \hat{\mu}_g = 1.645 \ln \hat{\sigma}_g$$

$$\ln \hat{x}_{0.99} - \ln \hat{\mu}_g = 2.326 \ln \hat{\sigma}_g$$

For the Weibull distribution, the quantile concentration is given by

$$x_{q_i} = \sigma \left[\ln \left(\frac{1}{1 - q_i} \right) \right]^{\frac{1}{\lambda}}$$

Using the 0.80 and 0.98 quantiles, for example, one obtains the estimates for the parameters λ and σ as

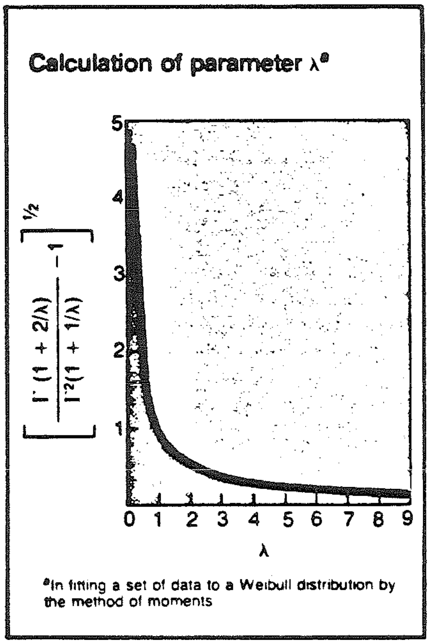
$$\hat{\lambda} = \frac{0.88817}{\ln x_{0.98} - \ln x_{0.80}}$$

$$\hat{\sigma} = \exp\left(1.53580 \ln x_{0.80} - 0.53580 \ln x_{0.98}\right)$$

8.3.4 Example:
Fitting of 1971 Pasadena, CA, Oxidant Data to a Weibull Distribution

As an example, consider the fitting of a Weibull distribution to 1971 hourly-average oxidant data from Pasadena, CA (State of California Air Resources Board, 1974). The data consist of 8303 hourly values (there are 8760 hours in a year). The maximum hourly value reported was 53 pphm. The arithmetic mean and standard deviation of the data are $M_1' = 4.0$ pphm and $M_2^{1/2} = 5.0$ pphm, and the geometric mean and standard geometric deviation are 2.4 and 2.6 pphm, respectively.

Assuming that the hourly-average oxidant concentrations fit a Weibull distribution, the parameters of the distribution can be estimated from (8.3-21) and (8.3-22) to give $\hat{\lambda} = 0.808$ and $\hat{\sigma} = 3.555$ pphm. For the determination of λ in fitting a set of data to the Weibull distribution, one can use Figure 8-4, where the left-hand side of (8.3-21) is shown as a function of λ for $0 < \lambda < 9$.



Calculation of parameter λ[a]

[a]In fitting a set of data to a Weibull distribution by the method of moments

Figure 8-4

Curve for the Calculation of the Parameter λ in Fitting a Set of Data to a Weibull Distribution by the Method of Moments.

It is interesting also to fit only the daily maximum hourly-average oxidant values to a Weibull distribution. For these measurements there exist 365 data points, the maximum value of which is, as already noted, 53 pphm. The arithmetic mean and standard deviation of the data are $M_1' = 12.0$ pphm and $M_2^{1/2} = 8.6$ pphm, and the geometric mean and standard geometric deviation are 9.1 and 2.2 pphm, respectively. Table 8-2 gives a comparison of the data and the Weibull distribution concentration frequencies in the two cases. Both fits are very good, the fit to the daily maximum values being slightly better. Figure 8-3 shows the two distributions plotted on extreme-value probability paper.

Table 8-2

1971 Hourly-Average Pasadena, CA Oxidant Data
Fitted to a Weibull Distribution

	Concentration (pphm) equalled or exceeded by the stated percent of observations								
	1%	2%	3%	4%	5%	10%	25%	50%	75%
Data (hourly-average)	24	20	18	16	15	11	5	2	1
Weibull distribution	23.5	19.2	16.8	15.1	13.8	10	5.3	2.3	0.76
Data (daily max.)	34	33	32	30	28	25	17	10	5
Weibull distribution	38.8	34.6	32	30.1	28.6	24.8	16.6	10.2	5.5

8.4 ORDER STATISTICS OF AIR QUALITY DATA: DISTRIBUTION THEORY

One of the major uses of statistical distributions of pollutant concentrations is to assess the degree of compliance of a region with ambient air quality standards. These standards define acceptable upper limits of pollutant concentrations and acceptable frequencies with which such concentrations can be exceeded. The probability that a particular concentration level, χ, will be exceeded in a single observation is given by the complementary distribution function

$$\overline{F}(\chi) = \text{Prob}\{c > \chi\} = 1 - F(\chi)$$

where

$$F(\chi) = \text{Prob}\{c \leq \chi\}$$

The larger the concentration level x, the smaller is $\overline{F}(\chi)$.

When treating sets of air quality data, available as successive observations that form time series, we may be interested in certain random variables, as, for example:

- the highest (or, in general, the r-th highest) concentration in a finite sample of size m,
- the number of exceedances of a given concentration level in a number of measurements or in a given time period,
- the number of observations (waiting time or "return period") between exceedances of a given concentration level,

all of which are useful in describing and evaluating ambient air quality.

The distributions and pdf's, as well as certain statistical properties of these random variables, can be determined by applying the methods and results of *order statistics* (or statistics of extremes). The classic reference on order statistics is Gumbel (1958). Relevant useful material can also be found in Sarhan and Greenberg (1962), whereas a recent comprehensive treatment of the subject is David (1981) which includes extensive bibliographic information. (See also Singpurwalla, 1972; Barlow and Singpurwalla, 1974; Roberts, 1979ab; Horowitz and Barakat, 1979, for applications in the field of air pollution data processing.)

This section contains a brief exposition of fundamental results from the distribution theory for order statistics that can be applied directly to air quality data. Related facts are included in the next section where the problem of critical concentration level exceedances and connected waiting times is studied.

8.4.1 Basic Notions and Terminology

Consider the m random unordered variates, $c_\tau(t_{t_1})$, $c_\tau(t_{t_2})$, ..., $c_\tau(t_m)$, that are members of the stochastic process $c_\tau(t_{t_i})$ that generates the time series $x_\tau(t_{t_1})$, $x_\tau(t_{t_2}), \ldots$, $x_\tau(t_m)$, of available air quality data. If we arrange the time series $x_\tau(t_{t_i})$ by order of magnitude, $x_{1;m} \geq x_{2;m} \cdots \geq x_{m;m}$, then a "new" random sequence of ordered variates $c_{1;m} \geq c_{2;m} \cdots \geq c_{m;m}$, is formed corresponding to sequence $\{x_{i;m}\}$; $i = 1, 2, \ldots m$. We call $c_{i;m}$ the *i-th highest order statistic* $(i = 1, 2, \ldots, m)$ or *i-th extreme statistic* (or $(m - 1 + 1)$-th order statistic) of this random sequence of size m.

In the exposition that follows it is in general assumed that:

(a) the concentration levels $x_\tau(t_i)$ measured in successive non-overlapping periods–and hence the unordered random variates $c_\tau(t_i)$–are independent of one another, and

(b) the random variables $c_\tau(t_i)$ are identically distributed (that is, the distribution of pollutant concentrations is independent of time–or can be reduced to a form independent of time by some transformation).

It is also assumed that the theoretical distribution function $F(\chi)$ as well as the pdf $p(\chi)$, corresponding to the total number of available measurements are known. They are called the *parent* (or initial) distribution and pdf, respectively. Some results of more general character (that is, without the above restrictions) will also be presented whenever they are available in usable form. These will be results concerning dependent and/or non-identically distributed variates as well as results of distribution-free form, that is, facts which hold regardless of the form (known or not) of the parent distribution. An important thing to note here is that even when the unordered variates $c_T(t_i)$ are independent, dependence is induced by the ordering process, and thus the ordered variates are always dependent (David, 1981).

8.4.2 Distribution and Parameters of Order Statistics. The Case of Extreme Values.

The probability density function $p_{r;m}(\chi)$ and the distribution function $F_{r;m}(\chi)$ of the r-th highest concentration out of samples of size m are evaluated directly from the parent pdf $p(\chi)$ and the parent distribution function $F(\chi)$ as follows.

The probability that $c_{r;m} = \chi$ equals the probability of $m - r$ trials producing concentration levels above χ, times the probability density of attaining a concentration equal to χ, multiplied by the total number of combinations of arranging these events (assuming complete independence of the data). In other words, the pdf of the r-th highest concentration has the trinomial form

$$p_{r;m}(\chi) = \frac{m!}{(r-1)!\,(m-r)!}[F(\chi)]^{m-r}\left[\overline{F}(\chi)\right]^{r-1} p(\chi) =$$

$$\frac{1}{B(r, m-r+1)}[F(\chi)]^{m-r}\left[\overline{F}(\chi)\right]^{r-1} p(\chi) \qquad (8.4-1)$$

where B is the beta function. In particular, for the highest and second highest concentration values ($r = 1, 2$) one has

$$p_{1;m}(\chi) = m[F(\chi)]^{m-1} p(\chi) \qquad (8.4-2)$$

$$p_{2;m}(\chi) = m(m-1)\,[F(\chi)]^{m-2}\left[\overline{F}(\chi)\right]^{p}(\chi) \qquad (8.4-3)$$

The probability $F_{r;m}(\chi)$ that $c_{r;m} < \chi$ is identical to the probability that no more than $r - 1$ measurements out of m result in $c_{r;m} > \chi$. Every observation is considered as a Bernoulli trial with probabilities of "success" and "failure" $F(\chi)$ and $1 - F(\chi)$, respectively. Thus,

$$F_{r;m}(\chi) = \sum_{k=0}^{r-1} \binom{m}{k} [\overline{F}(\chi)]^k [F(\chi)]^{m-k} \qquad (8.4-4)$$

It can further be shown (Feller, 1968, p. 173) that

$$F_{r;m}(\chi) = r\binom{m}{r} \int_0^{F(\chi)} t^{m-r}[1-t]^{r-1}\,dt \qquad (8.4-5)$$

(The integral in this expression is the incomplete beta function and is tabulated for various values of m, r and $F(\chi)$. See for example Pearson, 1934.) For the particular cases of the highest and the second highest values $(r = 1, 2)$ (8.4-4) becomes

$$F_{1;m}(\chi) = [F(\chi)]^m \qquad (8.4-6)$$

$$F_{2;m}(\chi) = m[F(\chi)]^{m-1} - (m-1)[F(\chi)]^m \qquad (8.4-7)$$

Relations (8.4-1) – (8.4-7) are not practically useful from a computational point of view, especially for very large values of m. In this case the asymptotic theory of extremes can be used (see Section 8.4.4). It is worthwhile to note the dependence of the probability of the largest value on the sample size. From (8.4-6) one obtains

$$F_{1;n}(\chi) = [F_{1;m}(\chi)]^{\frac{n}{m}} \qquad (8.4-8)$$

Thus, if the distribution of the extreme value is known for one sample size, it is known for all sample sizes.

The joint density function of $c_{r;m}$ and $c_{s;m}$ $(1 < s < r < m)$ is

$$p_{rs;m} = \frac{m!}{(m-r)!\,(r-s-1)!\,(s-1)!}[F(\chi)]^{m-r} p(\chi)\,[F(y) - F(\chi)]^{r-s-1} p(y)\,[1 - F(y)]^{s-1} \qquad (8.4-9)$$

The joint distribution function of $c_{r;m}$ and $c_{s;m}$ is

$$F_{rs;m}(\chi, y) = \text{Prob}\,\{(\text{at least } (m-r+1)\ c_i \le \chi, \text{ at least } (m-s+1)\ c_i \le y)\} =$$

$$\sum_{j=m-s+1}^{m} \sum_{i=m-r+1}^{i} \text{Prob}\{\text{exactly } i \ c_i \leq \chi, \ \text{ exactly } i \ c_i \leq y\} =$$

$$\sum_{j=m-s+1}^{m} \sum_{i=m-r+1}^{i} \frac{m!}{i!\,(j-1)!\,(m-j)!} [F(\chi)]^{i} [F(y) - F(\chi)]^{j-i} [1 - F(y)]^{m-j} \tag{8.4 - 10}$$

From the joint pdf of k-th order statistics one can (by standard transformation methods) derive the pdf of any well behaved function of the order statistics. (For example, to find the pdf of $w_{rs} = c_{r;m} - c_{s;m}$ one should set $w_{rs} = y - \chi$ and note that the transformation from χ, y to χ, w_{rs} has unity Jacobian.) Finally, the conditional pdf of $c_{m-s+1;m}$ given $c_{m-r+1;m} = \chi$ is represented, for $\chi < y$, by

$$f_{\text{cond}}\left(c_{m-s+1;m} = y | c_{m-r+1;m} = \chi\right) =$$

$$= \frac{(m-s)}{(r-s-1)!\,(m-r)!} \frac{[F(y) - F(\chi)]^{r-s-1} p(y) [1 - F(\chi)(y)]^{s-1}}{[1 - F(\chi)]^{r-1}} \tag{8.4 - 11}$$

Now, once the pdf of the r-th highest concentration is known, all statistical properties of this random variable are determined in principle. For example, the k-th non-central moment of the r-th highest concentration out of a sample of m measurements is

$$\mathrm{E}\{c_{r;m}^{k}\} = \int_{0}^{\infty} \chi^{k} p_{r;m}(\chi)\, d\chi \tag{8.4 - 12}$$

Thus, the expected value of $c_{r;m}$ is

$$\mu_{r;m} \equiv \mathrm{E}\{c_{r;m}\} = m \binom{m-1}{m-r} \int_{-\infty}^{\infty} \chi [F(\chi)]^{m-r} \left[\overline{F}(\chi)\right]^{r-1} dF(\chi) \tag{8.4 - 13}$$

Since $0 \leq F(\chi) \leq 1$ it follows that

$$|\mu_{r;m}| \leq m \binom{m-1}{m-r} \int_{-\infty}^{\infty} |\chi|\, dF(\chi)$$

showing that $\mu_{r;m}$ exists provided $\mathrm{E}\{c\}$ exists (the converse not being necessarily true; see David, 1981).

The variance of $c_{r;m}$ is

$$\sigma^2_{r;m} = \int_0^\infty (\chi - \mu_{r;m})^2 p_{r;m}(\chi)\, d\chi \tag{8.4 – 14}$$

and the covariance of $c_{r;m}$, $c_{s;m}$

$$\sigma_{rs;m} = \mathrm{E}\{(c_{r;m} - \mu_{r;m})(c_{s;m} - \mu_{s;m})\}$$

is, for $r < s$

$$\sigma_{rs;m} = \int_0^\infty \int_0^\infty (\chi - \mu_{r;m})(y - \mu_{s;m})\, p_{rs;m}(\chi, y)\, d\chi dy$$

In evaluating moments of order statistics recurrence relations can be used to reduce the number of independent calculations required. Thus, for an arbitrary distribution

$$(m-1)\,\mu^{(k)}_{m-r+1;m} + (m-r+1)\,\mu^{(k)}_{m-r;m} = m\mu^{(k)}_{m-r+1;m-1} \tag{8.4 – 15}$$

and

$$\mu^{(k)}_{m-r+1;m} = \sum_{i=r}^{m} \binom{m-1}{m-r} \binom{m}{m-i+1} (-1)^{i-r} \mu_{1;i} \tag{8.4 – 16}$$

The same recurrence relations also link the pdf's, distribution functions and in fact the expected values of any function of $c_{r;m}$ (see David, 1981, for detailed derivations and other relevant results).

It is also interesting to note that

$$\sum_{r=1}^{m} \mu_{r;m} = m\mu \tag{8.4 – 17a}$$

$$\sum_{r=1}^{m} \sum_{s=1}^{m} \sigma_{rs;m} = m\sigma^2 \tag{8.4 – 17b}$$

where μ, σ^2 are the mean and the variance of the parent distribution.

The results presented until now exhaust in principle the subject of evaluating the parameters of the distributions of order statistics when the parent distribution is known. However the integrals involved in the expressions for the expectation and higher order moments are not always easily evaluated and thus arises the need for techniques of approximation. The most important result concerns the evaluation of the expected value of $c_{r;m}$. In fact, for sufficiently large m, an approximation for $\mathrm{E}\{c_{r;m}\}$ is provided by the value of χ satisfying (David, 1981)

$$F(\chi) = \frac{m-r+1}{m+1} \qquad (8.4-18)$$

In terms of the inverse function of $F(\chi)$, $F^{-1}(\chi)$ (that is $F^{-1}[F(\chi)] = \chi$) one has the asymptotic relation

$$\mathrm{E}\{c_{r;m}\} \simeq F^{-1}\left(\frac{m-r+1}{m+1}\right), \quad \text{as} \quad m \to \infty \qquad (8.4-18a)$$

For small sample size there are several inequalities providing bounds for the expected values of order statistics. These are given in Appendix A8.1.

8.4.3 Distribution Free Confidence Intervals for Quantiles

When one deals with order statistics it is possible to estimate the probability with which a given quantile of the parent distribution lies in the interval defined by any two order statistics of the stochastic process under consideration.

Consider the unique solution of the equation for the quantile of order q $(0 < q < 1)$ of the parent distribution.

$$\chi_q = F^{-1}(q) \equiv \inf\{\chi : F(\chi) > q\} \qquad (8.4-19)$$

(This expression guarantees uniqueness of the solution of $F(\chi_q) = q$.) As it was shown by Thomson in 1936 (see David, 1981), for continuous state random variates, the random interval $(c_{r;m}, c_{s;m})$ covers (includes) χ_q with a probability which depends on r, s, m and q but not on $F(\chi)$, allowing in this way the construction of distribution-free confidence intervals for χ_q:

$$\pi(r,s,m,q) = \sum_{i=m-r+1}^{m-s} \binom{m}{i} q^i (1-q)^{m-i} \qquad (8.4-20)$$

8.4.4 Asymptotic Theory of Extremes for Distributions of Air Quality Data

For large sample sizes ($m \to \infty$) the theory of extreme value statistics provides us with asymptotic estimates for the distributions of the highest order statistics of the stochastic process that generates these samples. (See Gumbel, 1958; Galambos, 1978; David, 1981).

Consider i.i.d. variates $c_r(t_i)$, $i = 1, 2, \ldots, m$. As far as distributions that are of the most interest in the description of aerometric data (the lognormal, the normal, the Weibull and the gamma distributions) are concerned as parent distributions of these variates, the following result holds for the distribution of their highest order statistic as $m \to \infty$:

$$F_{1;m}(\chi) = \text{Prob}\left\{c_{1;m} \le \chi\right\} = \exp\left\{-\exp\left[-\frac{(\chi - b_m)}{a_m}\right]\right\} \qquad (8.4-21)$$

(where $F(\chi)$ is lognormal, normal, Weibull or gamma) or, equivalently,

$$\Lambda(\chi) = \lim_{m\to\infty} \text{Prob}\left\{c_{1;m} \le a_m\chi + b_m\right\} = F_{1;m}\left(c^*_{1;m}\right) =$$

$$= \lim_{m\to\infty} \text{Prob}\left\{c^*_{1;m} \le \chi\right\} = \exp\left[-\exp\left(-\chi\right)\right] \qquad (8.4-22)$$

where

$$c^*_{1;m} = \frac{c_{1;m} - b_m}{a_m}$$

Similarly, for the analogous standardized form of the r-th extreme $c_{r;m}$, one has the following limiting distribution as $m \to \infty$:

$$\Lambda_r = \frac{1}{(m-r)!}\int_{-\lambda(\chi)}^{\infty} \exp(-t)\, t^{m-r}\, dt = \Lambda(\chi)\sum_{j=0}^{m-r}\frac{\lambda^j(\chi)}{j} \qquad (8.4-23)$$

where $\lambda(\chi) = -\ln \Lambda(\chi) = \exp(-\chi)$.

In Gumbel's (1958) terminology, the double exponential distribution $\Lambda(\chi)$ is the "first asymptotic distribution of largest values"; it is one of the three possible forms that $\lim_{m\to\infty} F_{1;m}(\chi)$ may have (if it exists) and corresponds to the so-called exponential type of parent distributions.

The normalizing constants a_m, b_m in (8.4-22) depend on the sample size m and on the form of the parent distribution; they are estimated from quantiles of the parent distribution as follows:

$$b_m = F^{-1}\left(1 - \frac{1}{m}\right) \tag{8.4 – 24}$$

and

$$a_m = F^{-1}\left(1 - \frac{1}{em}\right) - F^{-1}\left(1 - \frac{1}{m}\right) \tag{8.4 – 25}$$

Gumbel (1958) thoroughly discusses various techniques of analysis utilizing the asymptotic form $\Lambda(\chi)$ and stresses particularly on applications. Roberts (1979ab) presents a brief discussion as well as applications, of the asymptotic theory in processing air quality data; part (b) of his work is devoted in the determination of the asymptotic distribution from the appropriate treatment of the data.

Analytic expressions for the coefficients a_m and b_m corresponding to the normal, lognormal and gamma distributions are given respectively by Gumbel (1958), Singpurwalla (1972) and Gurland (1975).

Once the parameters a_m, b_m are determined the expected value of the extreme statistic is given directly by

$$\mathrm{E}\{c_{1;m}\} = \gamma a_m + b_m \tag{8.4 – 26}$$

where $\gamma = 0.577\ldots$ is Euler's number. For lognormally distributed initial samples a_m, b_m are estimated analytically from (Singpurwala, 1972)

$$a_m = \frac{b_m}{\lambda_m}, \quad b_m = \exp\left(\mu + \alpha_m \sigma\right) \tag{8.4 – 27}$$

where μ, σ are the parameters of the parent lognormal distribution $F(\chi)$ and

$$\lambda_m = \frac{\sqrt{2\ln m}}{\sigma} \tag{8.4 – 28}$$

$$\alpha_m = \sqrt{2 \ln m} - \frac{\ln(\ln m) + \ln 4\pi}{2\sqrt{2 \ln m}} \qquad (8.4-29)$$

Extensions of this analysis for non i.i.d. (possibly autocorrelated) variates are discussed in Appendix A8.2.

8.5 EXCEEDANCES OF CRITICAL LEVELS AND RELATED WAITING TIMES

The number of exceedances (episodes), $N_\chi(m)$ of a given, time-averaged, concentration level χ_r in a set of m successive observations (time averages) $x_r(t_i)$, or equivalently, the number $N_x(t)$ of crossings - "from below" - of a given level x by the continuous state-continuous time random function $x(t)$ in the interval $(0, t]$, is itself a random function.(*)

Similarly, the number of averaging periods (or observations) between exceedences of the concentration level χ_r , or, equivalently the time periods between successive crossings of the level x in the continuous case, is another random function called *waiting time*, or *passage time*, or *return period*, of crucial interest in the study of pollution episodes.

Clearly, the probabilistic treatment of such random function (stochastic processes) must be based on the analysis of the general problems on *passages* or *level crossing*, which may be very complicated. (See Cramer and Leadbetter, 1967, for an extensive exposition of the level crossing problem; also Feller, 1968, in the study of random walks and related passage times). However, in the discrete time-series case, and for independent, identically distributed observations, the analysis of this problem becomes much easier. This case is examined in this section; in Appendix A8.3 a general formulation of the problem covering continuous or discrete, stationary or nonstationary time series is presented.

8.5.1 Distribution of Exceedances

In the case of i.i.d. variates each one of the observations is a Bernoulli trial and therefore the probability density function of $N_\chi(m)$ is (in terms of the parent

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(*) In the continuous time case the duration of crossings must also be included in a complete description of the situation.

distribution $F(\chi)$)

$$\phi(N_\chi; m, \chi) = \binom{m}{N_\chi} \left[\overline{F}(\chi)\right]^{N_\chi} \left[F(\chi)\right]^{m-N_\chi} \qquad (8.5-1)$$

From this relation we conclude that the expected number of exceedances $\mathrm{E}\{N_\chi(m)\}$ of the level χ in a sample of m measurements is the following function of m

$$\overline{N}_\chi(m) = \mathrm{E}\{N_\chi(m)\} = \overline{F}(\chi) \qquad (8.5-2)$$

Alternatively, the expected percentage of exceedances of a given concentration level x, observed in any set of the data under consideration is

$$\Pi(\chi) = 100\overline{F}(\chi) \qquad (8.5-3)$$

Notice that we can interpret N_χ, which is a function of the sample size, as a *renewal function* (see for example Karlin-Taylor 1975). This fact means that the well developed theory of renewal processes may be utilized in the modeling of related problems.

Parent Distribution-Free Results

The theory of order statistics provides us with another quite general and distribution-free result concerning the distributions of exceedances. As was first shown by Thomas (1948), the probability that n observations of a random variable X will result in N_r values of X that exceed the r-th highest value of m initial observations (regardless of the magnitude of the r-th highest value and the form of the distribution of X) is

$$\phi(N_r^*; r, m, n) = \frac{\binom{m}{r} r \binom{n}{N_r^*}}{(n+m)\binom{n+m-1}{N_r^*+r-1}} \qquad (8.5-4)$$

where

$$\sum_{N_r^*=0}^{n} \phi(N_r^*; r, m, n) = 1$$

Thus, for example, the probability of at least one exceedance of $c_{r;m}$ is

$$\text{Prob}\{N_r^* \geq 1\} = 1 - \phi(0; r, m, n) = 1 - \frac{m!\,(n+m-r)}{(m-r)!\,(n+m)!} \qquad (8.5-5)$$

For $r = 1$ we obtain

$$\text{Prob}\{N_r^* \geq_1\} = \frac{n}{m+n} \qquad (8.5-6)$$

Hence, if $n = m$ we have $\text{Prob}\{N_1 > 1\} = 0.5$. From (8.5-6) we see that the larger the difference between m and n, the smaller the probability of exceedance of the maximum value. Various other conclusions can be obtained from (8.5-6) when appropriate values of N_r, r, m, n are introduced.

For large m, n, (8.5-6) is approximated by

$$\phi(N_1^*; l, m, n) = \left(\frac{m}{m+n}\right)\left(\frac{n}{m+n}\right)^{N_1^*} \qquad (8.5-7)$$

for $r = 1$.

The expected value and the variance of the number of exceedances over the r-th highest value of the m initial observations are calculated from (8.5-4). Thus

$$\text{E}\{N_r^*\} = \frac{rn}{m+1}, \quad \text{Var}\{N_r^*\} = \frac{rn\,(n+m+l)}{(m+2)\,(m+1)^2} \qquad (8.5-8)$$

A final interesting result is that for large equal m and n the average and variance of the number of concentrations that exceed the r-th highest values of m initial observations in a set of n subsequent ones are approximately

$$\text{E}\{N_r^*\} = r, \quad \text{Var}\{N_r^*\} = 2r$$

(independent of the sample size).

8.5.2 Expected Return Period or Waiting Time

The expected return period is defined as the average number of averaging periods (or observations) between exceedances of a given level χ (*)

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* This level must of course be an average over the fixed averaging time.

The probability that the concentration will exceed χ for the first time at observation n is

$$f_n = \text{Prob}\{C \le \chi\}^{n-1}\,\text{Prob}\{c > \chi\} = \overline{F}(\chi)\,[F(\chi)]^{n-1} \tag{8.5 – 9}$$

By definition

$$\text{E}\{n\} = \sum_{n=1}^{\infty} n f_n \tag{8.5 – 10}$$

Using (8.5-9) in (8.5-10) one obtains

$$\text{E}\{n\} = \sum_{n=1}^{\infty} n[F(\chi)]^{n-1}\,[1 - F(\chi)] \tag{8.5 – 11}$$

Since $F(\chi) < 1$ it follows that

$$\sum_{n=1}^{\infty} n[F(\chi)]^{n-1} = 1 + 2F + 3F^2 + \ldots = \frac{1}{[1_F(\chi)]^2} \tag{8.5 – 12}$$

Combining (8.5-11) and (8.5-12) we obtain

$$\text{E}\{n\} = \frac{1}{1 - F(\chi)} = \frac{1}{\overline{F}(\chi)} \tag{8.5 – 13}$$

This result can also be derived using renewal process theory: The expected value of the waiting time (expected return period), $\bar{t}$, is related to the renewal function $N_\chi(m)$ through the equation (see, e.g., Karlin and Taylor, 1975)

$$\lim_{m\to\infty} \frac{1}{m}\overline{N}_\chi = \frac{1}{\bar{t}}$$

Hence, from (8.5-2) it follows that

$$\bar{t} = \text{E}\{n\} = \left[\overline{F}(\chi)\right]^{-1}$$

The variance of the number of observations between exceedances of a given level χ is

$$\text{Var}\{n\} = \sum_{n=1}^{\infty} (n - \text{E}\{n\})^2 f_n = \sum_{n=1}^{\infty} \left[1 - \frac{1}{1 - F(\chi)}\right]^2 [F(\chi)]^{n-1}\overline{F}(\chi)$$

$$= (1-F)\sum_{n=1}^{\infty} n^2 F^{n-1} - 2\sum_{n=1}^{\infty} nF^{n-1} + \frac{1}{1-F}\sum_{n=1}^{\infty} F^{n-1} \qquad (8.5-14)$$

Introducing the relations

$$\sum_{n=0}^{\infty} F^n = \frac{1}{1-F}$$

$$\sum_{n=1}^{\infty} nF^{n-1} = \frac{1}{(1-F)^2}$$

$$\sum_{n=1}^{\infty} n(n-1)F^{n-2} = \frac{2}{(1-F)^3}$$

(8.6-14) gives

$$\mathrm{Var}\{n\} = \frac{F}{(1-F)^2} \qquad (8.5-15)$$

8.6. EVALUTION OF ALTERNATIVE FORMS OF AIR QUALITY STANDARDS

In this section it is shown how a distribution can be used in evaluating air quality standards. As an example, the focus will be on the photochemical oxidant air quality standard, although the procedures that will be followed are obviously applicable to any pollutant.

Four possible forms of an oxidant air quality standard are listed in Table 8-3. In the application of these standards, aerometric data are to be used to estimate expected concentrations and their frequency of occurrence. If it is assumed that the data conform to a specific probability distribution then the distribution is fit to actual data and the parameters of the distribution are estimated. As it was already pointed out in Section 8.2, the distribution determined from the set of available data is time invariant and it is assumed that holds for future data also, since the distribution will be used to predict expected future concentration frequencies. That is, one will be able to make statistical inferences about the expected number of occurrences (or frequency) of certain concentration levels. One will not, of course, be able to predict when the events will occur but only how often.

The choice of one form of the standard over another (from a regulator's point of view) can be based on the impact (health effects for example) that each form implies for the concentration distribution as a whole.(*) For example, one form could be stated in such a way that it requires a lower maximum concentration to be attained than a second standard, however the average concentration under the first standard may be higher than for the second standard. Standards may also be expressed in terms of different averaging times. It has also been pointed out (Roberts, 1979ab) that a more logical structure for air quality standards would be in terms of a largest

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(*) See, for example, the discussion of the total suspended particulate matter (TSP) standard by Mage (1980) and the general discussion of Curran and Hunt (1975).

concentration with an acceptable return period. That is, the standard would be specified in terms of accepted return periods within which, for example, the highest and the second highest concentrations would exceed given values. The evaluation of this kind of air quality standard, as well as of the previous ones, is done by using elementary results of the methods which were presented in the previous sections.

The first step in the evaluation of an air quality standard is to select the statistical distribution that supposedly best fits the data. We will assume that the frequency distribution that best fits hourly-averaged oxidant concentration data is the Weibull distribution (EPA, 1978). Since the standards are expressed in terms of expected events during a one year period of one-hour average concentrations we will always use the number of trials m equal to the number of hours in a year, 8760. We would only use $m < 8760$ to evaluate the distribution (determine how well the data fit the assumed distribution) since some of the 8760 hours are usually missing from the data set.

8.6.1 First Alternative

Expected Number of Exceedances of 0.12 ppm Hourly Average
Less Than or Equal to One Per Year

The expected number of exceedances $N_\chi(m)$ of a given concentration level in m measurements is given by (8.5-2)

$$\overline{N}_\chi(m) = m\overline{F}(\chi)$$

In the case of the Weibull distribution,

$$\overline{N}_\chi = m \exp\left[-\left(\frac{\chi}{\sigma}\right)^\lambda\right] \qquad (8.6-1)$$

If we desire the expected exceedance to be once out of m hours, that is, $N_\chi 1 = 1$, the concentration corresponding to that choice is

$$\chi_1 = \sigma(\ln m)^{1/\lambda} \qquad (8.6-2)$$

Table 8-3

Alternative Statistical Forms of the Photochemical Oxidant Standard

No.	Form
1	0.12 ppm hourly average with expected number of exceedences per year less than or equal to one
2	0.12 ppm hourly average not to be exceeded on the average by more than 0.01% of the hours in one year
3	0.12 ppm annual expected maximum hourly average
4	0.12 ppm annual expected second highest hourly average

[a] For most practical purposes forms 1 and 3 can be considered equivalent.

For $m = 8760$, (8.6-2) becomes

$$\chi_1 = \sigma(9.08)^{1/\lambda}$$

8.6.2 Second Alternative

0.12 ppm Hourly Average Not to be Exceeded on the Average

by More than 0.01 Percent of the Hours in One Year

The expected percentage of exceedance of given concentration, x, is given by (8.5-3),

$$\Pi(\chi) = 100\overline{F}(\chi)$$

For the Weibull distribution,

$$\Pi(\chi) = 100 \exp\left[-\frac{\chi}{\sigma}^{\lambda}\right] \tag{8.6 – 3}$$

Eqn. (8.6-3) can be arranged to determine the concentration level that is expected to be exceeded $\Pi(\chi)$ percent of the time,

$$\chi = \sigma\left[\ln\left(\frac{100}{\Pi(\chi)}\right)\right]^{1/\lambda} \tag{8.6 – 4}$$

Therefore, we can calculate the concentraton that is expected to be exceeded 0.01 percent of the hours in one year,

$$\chi_{0.01} = \sigma(9.21)^{1/\lambda} \tag{8.6 – 5}$$

8.6.3 Third Alternative

0.12 ppm Annual Expected Maximum Hourly Average

and 0.12 ppm Annual Expected Second Highest Hourly Average

The "exact" expected value of the *rth* highest concentration is given by (8.4-13),

$$\mu_{r;m} \equiv \mathrm{E}\{c_{r;m}\} = m\binom{m-1}{m-r}\int_{-\infty}^{\infty} \chi[F(\chi)]^{m-r}\left[\overline{F}(\chi)\right]^{r-1} dF(\chi)$$

where $dF(\chi) = p(\chi)d\chi$. For the Weibull distribution

$$\mu_{r;m} = \frac{m!}{(r-1)!\,(m-r)!}\int_0^\infty \left(\frac{\chi}{\sigma}\right)^\lambda \left\{1-\exp\left[-\left(\frac{\chi}{\sigma}\right)^\lambda\right]\right\}^{m-r}\left\{\exp\left[-\left(\frac{\chi}{\sigma}\right)^\lambda\right]\right\}^r d\chi \tag{8.6-6}$$

We would like to evaluate this equation for $r = 1$ and $r = 2$ corresponding to standards 3 and 4, respectively, in Table 8-3. The results, $\mathrm{E}\{c_{1;m}\}$ and $\mathrm{E}\{c_{2;m}\}$, are the expected highest and second highest hourly concentrations, respectively, in the year, when $m = 8760$. Unfortunately, the integral in (8.6-6) cannot be evaluated easily. Even numerical techniques fail to give consistent results due the singularity at $\chi = 0$. Thus the asymptotic relation for large m, (8.4-18a) must be used in this case

$$\mathrm{E}\{c_{r;m}\} \simeq F^{-1}\left(\frac{m-r+1}{m+1}\right)$$

For the Weibull distribution we have

$$1-\exp\left[-\left(\frac{\mathrm{E}\{c_{r;m}\}}{\sigma}\right)^\lambda\right] = \frac{m-r+1}{m+1} \tag{8.6-7}$$

For $m = 8760$ and $r = 1, 2$ we have to solve respectively the equations

$$1-\exp\left[-\left(\frac{\mathrm{E}\{c_{1;m}\}}{\sigma}\right)^\lambda\right] = \frac{8760}{8761} \tag{8.6-8}$$

$$1-\exp\left[-\left(\frac{\mathrm{E}\{c_{2;m}\}}{\sigma}\right)^\lambda\right] = \frac{8759}{8761} \tag{8.6-9}$$

As an alternative we can also use an empirical result from Larsen (1971), who approximated the probability of occurrence of a concentration greater or equal to the r-th highest concentration as

$$\overline{F}(c_{r;m}) = \frac{r-0.4}{m} \tag{8.6-10}$$

Therefore, the probabilities of a concentration exceeding the maximum and second highest concentrations ($c_{1;m}$ and $c_{2;m}$) are

$$\overline{F}(c_{1;m}) = \frac{0.6}{m} \quad \text{and} \quad \overline{F}(c_{2;m}) = \frac{1.6}{m}$$

We can now determine the expected concentrations using the estimated distribution parameters, λ and σ, and applying (8.2-8),

$$\mathrm{E}\{c_{1;m}\} = \sigma\left[\ln\left(\frac{8760}{0.6}\right)\right]^{1/\Lambda} = \sigma(9.59)^{1/\Lambda}$$

$$\mathrm{E}\{c_{2;m}\} = \sigma\left[\ln\left(\frac{8760}{1.6}\right)\right]^{1/\Lambda} = \sigma(9.59)^{1/\Lambda}$$

for $m = 8760$. Notice that this approach is independent of the assumption for Weibull distributed data.

8.6.4 Example

Evaluation of Alternative Forms
of the Oxidant Air Quality Standard
Using 1971 Pasadena, CA Data

In Section 8.3.4, 1971 hourly-average and maximum daily hourly-average oxidant concentrations at Pasadena, CA were fit to Weibull distributions. We now wish to evaluate each of the forms of the oxidant air quality standard that we have been discussing.(*)

Expected Number of Exceedances
of 12 pphm Hourly-Average Concentration
Less Than or Equal to One per Year

The expected number of exceedances of 12 pphm, based on the Weibull fit of the 1971 Pasadena, CA hourly-average data, is from (8.6-1),

$$\overline{N}_{12} = 8760 \exp\left[-\left(\frac{12}{3.555}\right)^{0.808}\right] = 605.2$$

The hourly-average that is exceeded at most once per year is from (8.6-2),

$$\chi_1 = 3.555(\ln 8.760)^{1/0.808} = 54.51 \text{ pphm}$$

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* For convenience all concentration values in this section are given as pphm rather than as ppm.

which agrees well with the actual measured value of 53 pphm.

If, instead of the complete hourly-average Weibull distribution, we use the distribution of daily maximum hourly-average values, the expected number of exceedances of a daily maximum of 12 pphm is

$$\overline{N}_{12} = 365 \exp\left[-\left(\frac{12}{13.189}\right)^{1.416}\right] = 152.2$$

and the daily maximum 1-hour concentration that is exceeded at most once per year is

$$\chi_1 = 13.189(\ln 365)^{1/1.416} = 46.2 \text{ pphm}$$

It is interesting to note that this value is underpredicted if we use the distribution of daily maxima instead of the distribution based on the complete set of data.

12 pphm Hourly Average Not to be Exceeded on the Average by More Than 0.01 Percent of the Hours in One Year

The expected percentage of exceedances of 12 pphm is

$$\Pi\,(12) = 100 \exp\left[-\left(\frac{12}{3.555}\right)^{0.808}\right] = 6.91\%$$

The concentration that is expected to be exceeded 0.01 percent of the hours in the year is

$$\chi_{0.01} = 3.555\left(\ln \frac{100}{0.01}\right)^{1/0.808} = 55.5 \text{ pphm}$$

This form of the standard cannot be evaluated from the distribution of daily maxima.

12 pphm Annual Expected Maximum Hourly Average and 12 pphm Annual Expected Second Highest Average

The annual expected maximum hourly average is obtained from the solution of (8.4-18) for $\chi = \mathrm{E}\{c_1\}$ and for $r = 1$, $m = 8760$, $\sigma = 3.555$, $\lambda = 0.808$.

We have

$$1 - \exp\left[-\left(\frac{\chi}{3.55}\right)^{0.808}\right]_{\chi=\mathrm{E}\{c_1\}} = \frac{8760}{8761}$$

$$\mathrm{E}\{c_1\} = 54.51 \text{ pphm}$$

(whereas the actual maximum hourly average value was 53 pphm). Similarly, for the annual expected second highest hourly average concentration we have

$$1 - \exp\left[-\left(\frac{\chi}{3.555}\right)^{0.808}\right]_{\chi=\mathrm{E}\{c_2\}} = \frac{8759}{8761}$$

$$\mathrm{E}\{c_2\} = 49.40 \text{ pphm}$$

The comparable calculations from the distribution of daily maxima are

$$1 - \exp\left[-\left(\frac{\chi}{13.189}\right)^{1.416}\right]_{\chi=\mathrm{E}\{c_1\}} = \frac{365}{366}$$

giving

$$\mathrm{E}\{c_1\} = 46.21 \text{ pphm}$$

and

$$1 - \exp\left[-\left(\frac{\chi}{13/189}\right)^{1.416}\right]_{\chi=\mathrm{E}\{c_2\}} = \frac{364}{366}$$

giving

$$\mathrm{E}\{c_2\} = 42.31 \text{ pphm}$$

(The agreement with the measured concentrations is not very good now, but this is to be expected since we use an asymptotic relation for infinite m which now is $m = 365$.) Using the empirical relation (8.6-10) we obtain

$$\mathrm{E}\{c_1\} = 3.555\left[\ln\left(\frac{8760}{0.6}\right)\right]^{1/0.808} = 58.3 \text{ pphm}$$

Note that this value differs by 10 53 pphm. The estimation is, however, based on the empirical formula (8.6-10), the accuracy of which cannot be assessed in this case.

Similarly, for the annual expected second highest hourly average concentration we obtain

$$\mathrm{E}\{c_2\} = 3.555\left[\ln\left(\frac{8760}{1.6}\right)\right]^{1/0.808} = 51.04 \text{ pphm}$$

The comparable values calculated from the distribution of daily maxima are

$$\mathrm{E}\{c_1\} = 13.189\left[\ln\left(\frac{365}{0.6}\right)\right]^{1/1.416} = 49.0 \text{ pphm}$$

and

$$\mathrm{E}\{c_1\} = 13.189\left[\ln\left(\frac{365}{1.6}\right)\right]^{1/1.416} = 43.6 \text{ pphm}$$

Again these two quantities are both underpredicted when based on the distribution of daily maxima relative to the distribution of hourly average values.

8.7 ROLLBACK CALCULATIONS AND STATISTICAL DISTRIBUTIONS

The reduction in emission source strength, $\mathcal{R}$, required to meet an air quality goal c_s is often calculated by the so-called simple rollback equation (de Nevers and Morris, 1975)

$$\mathcal{R} = \frac{\kappa c - c_s}{\kappa c - c_b} \tag{8.7 - 1}$$

where κ is a growth factor for future emission sources (the ratio of future source strength to present strength in the absence of controls), c_b is a typical value for the background concentration, and c_s is the air quality standard. Some of the assumptions implicit in the statement of (8.7-1) (such as unchanged spatial distribution of emission sources, a common growth factor for all sources, unchanged average meteorological conditions, etc.) are discussed in de Nevers and Morris (1975). Many modifications of this formula have also appeared in the literature as a result of efforts to relax some of the above assumptions (Larsen, 1969; Horie and Overton, 1974; de Nevers and Morris, 1975; Chang and Weinstock, 1975; Peterson and Moyers, 1980, etc.).

In the usual manner in which (8.7-1) seems to have been applied, c_s is the air quality standard and c is the present concentration corresponding to c_s. For example, if c_s is a value of the hourly-average concentration not be be exceeded more than once per year, then c would be the highest hourly-average concentration of the present year. Used in the manner just described, (8.7-1) implies that the yearly maximum concentration is linearly proportional to source emissions. That is, it is presumed that a 50% reduction in source strength leads to a 50% reduction in the yearly maximum concentration (neglecting the effect of background concentration).

But is this presumption true? What we would expect, upon some thought, for, say, yearly data that conform to a common distribution with mean E$\{c\}$, is that the *expected* concentration E$\{c\}$ would be proportional to source strength (at least for inert pollutants). In fact, if c in (8.7-1) is interpreted as the yearly maximum concentration, then this equation contains a mixture of deterministic (κ, c_s, c_b) and stochastic and stochastic ($c_{\max}$) variables.(*) To apply (8.7-1) to the expected concentration, E$\{c\}$, satisfies the basic notion of conservation of mass for long-term average concentrations of non-reactive species, that is, the long-term average concentration is directly proportional to the total emissions of the species.

It appears, therefore, that the correct statement of the rollback formula is

$$\mathcal{R} = \frac{\kappa \mathrm{E}\{c\} - \mathrm{E}\{c\}_s}{\kappa \mathrm{E}\{c\} - c_b} \qquad (8.7-2)$$

where E$\{c\}_s$ denotes a yearly *expected concentration of a distribution the extreme statistic of which that corrsponds to c_s is exactly equal to c_s*. However, there are many indeterminate factors involved in the estimation of E$\{c\}_s$ from such a distribution; further, from an air quality regulation point of view, we are really interested in how the extreme statistics of the future distribution (e.g $c_{\max}$) and c_s compare. In order to state this formally we must first replace the observed maximum value of c with the extrene statistic of the distribution of c that corresponds to c_s. For the analysis that follows we replace $c_{\max}$ with $\hat{c}$, which is defined as the concentration level that has probability of exceedance equal to that stated in the definition of the air quality standard c_s, under present conditions. That is, if future emissions were to double, we want to know whether $\hat{c}$ would also double or increase by more or less than that amount. In other words we want to know if the quantiles (and in particular those corresponding to extreme values) of the concentration distribution scale linearly with emission levels as it was assumed for E$\{c\}$. In general such a linear relation does *not* exist. However, in the special case of lognormally distributed concentrations empirical results (Larsen, 1969) can be used to show the approximate validity of a linear relationship.

(*) Actually the background concentration is also a stochastic variable, characterized by a statistical distribution of its own that may even change with time (Larsen, 1969; Horie and Overton, 1974). However, for the purposes of the present analysis it will be assumed that both the value and the variation of the typical background concentration appearing in (8.7-1) are small and that in practice a constant value representing the correct order of magnitude of background concentrations is sufficient for calculations.

Thus, let us know consider a concentration that can be represented by a lognormal distribution (under present as well as future conditions). If a current emission rate changes by a factor κ ($\kappa > 0$) while the source distribution remains the same, if meteorological conditions are unchanged, and if background concentrations are negligible, the expected total quantity of inert pollutants having an impact on a given site over the same time period should also change by the factor κ. The expected concentration level for the future period is therefore given, for a lognormally distributed variable, by

$$\mathrm{E}\{c'\} = \exp\left(\mu' + \frac{\sigma'^2}{2}\right) = \kappa \exp\left(\mu + \frac{\sigma^2}{2}\right) \qquad (8.7-3)$$

where the primed quantitites c', μ', σ' apply to the future period and the unprimed quantitites apply to the present. It has been argued by Larsen (1969) and others that if meteorological conditions remain unchanged, the standard geometric deviation of the lognormal pollutant distributions remains unchanged, that is $\exp \sigma' = \exp \sigma$. Thus, $\exp \mu' = \kappa \exp \mu$, or

$$\mu' = \mu + \ln \kappa \qquad (8.7-4)$$

The probability that future concentration level c' will exceed a level χ is

$$\overline{F}_{c'}(\chi) = 1 - \Phi\left(\frac{\ln \chi - \mu'}{\sigma'}\right) =$$

$$= 1 - \Phi\left(\frac{\ln \chi - \mu - \ln \kappa}{\sigma}\right) = 1 - \Phi\left(\frac{\ln \frac{\chi}{\kappa} - \mu}{\sigma}\right) = \overline{F}_c\left(\frac{\chi}{\kappa}\right) \qquad (8.7-5)$$

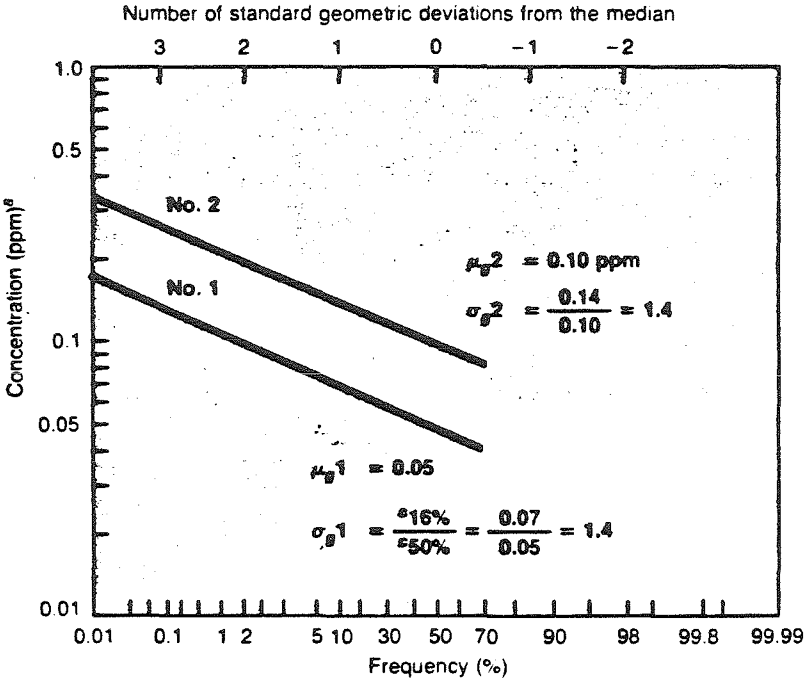
Similarly,

$$\overline{F}_{c'}(\kappa\chi) = \mathrm{Prob}\{c' > \kappa\chi\} = 1 - \Phi\left(\frac{\ln \kappa\chi - \mu'}{\sigma'}\right) =$$

$$= 1 - \Phi\left(\frac{\ln \chi - \mu}{\sigma}\right) = \overline{F}_c(\chi) \qquad (8.7-6)$$

Thus, the probability that the future level $\kappa\chi$ will be exceeded just equals the probability that with current emissions sources the level χ will be exceeded.

FIGURE 5
Two log-normal distributions with the same standard geometric deviation



[a] Quantile values of concentration refer to the complementary distribution function

Figure 8-5

Two Lognormal Distributions

with the Same Standard Geometric Deviation

(Notice that the quantile concentration values refer to the complementary distribution.)

Therefore, with equal σ, all frequency points of the distribution shift according to the factor κ. This results in a parallel translation of the graph of $F(\chi)$ or $\overline{F}(\chi)$. Figure 8-5 shows two lognormal distributions with the same standard geometric deviation but different geometric mean values. The geometric mean concentrations of the two distributions are 0.05 ppm and 0.10 ppm, and the standard geometric deviations are both 1.4. The mean concentrations can be calculated with the aid of (1.3-4) and the results of Section 8.2. We find $\mathrm{E}_1\{c\} = 0.053$ ppm and $\mathrm{E}_2\{c\} = 0.106$ ppm. The variances can likewise be calculated using (1.3-2) to obtain $\mathrm{Var}_1\{c\} = 0.00034\ \mathrm{ppm}^2$ and $\mathrm{Var}_2\{c\} = 0.00134\ \mathrm{ppm}^2$.

Let us suppose that the first distribution represents current conditions and therefore that the current probability of exceeding a concentration of about 0.13 ppm is about 0.0027 – which corresponds to about one day per year if the distribution is of 24-hour averages. If the emission rate were doubled, the new distribution function would be given by the second distribution. The new distribution has a median value twice that of the old one since total loadings due to emissions have doubled. Under the new case, a concentration of 0.13 ppm will be exceeded 22 percent of the time, or about 80 days a year, and the concentration that is exceeded only one day per year rises to 0.26 ppm.

The expected return period and its variance can be calculated from (8.5-13) and (8.5-15) for any given concentration level. For $c = 0.2$ ppm, for example,

$$\mathrm{E}_1\{n\} \to \infty, \quad \mathrm{Var}_1\{n\} \to \infty$$

$$\mathrm{E}_2\{n\} \to 47.3, \quad \mathrm{Var}_1\{n\} \to 2194.0$$

In summary, it was shown that the conventional manner in which the rollback equation (8.7-1) has been used in which the concentrations are extreme values is incorrect. Whereas annual mean concentrations can be expected to scale linearly with emission levels, the extreme values, in general, do not. However, in particular, a lognormally distributed concentration will scale linearly with emission level changes, when it is assumed that the geometric mean scales with the emission level changes, and the standard geometric deviation remains constant. In such a case one can use (8.7-1) modified as

$$\mathcal{R} = \frac{\kappa\hat{c} - c_s}{\kappa\hat{c} - c_b} \qquad (8.7-7)$$

where $\hat{c}$, as defined earlier, is calculated from a lognormal distribution that has been fitted to the whole set of present-year concentration data (averaged over the time period that is stated in the definition of c_s).

8.8 PLUME MODELS AND STATISTICAL DISTRIBUTIONS

In the previous section it was assumed that when emission level changes occur for a pollutant whose statistical distribution is lognormal, the standard geometric deviation remains unchanged and the geometric mean scales with the emission level change. In this section we wish to examine this assumption using a simple plume model.

The statistical distribution of pollutant concentrations over a region is a result of the day-to-day fluctuations in meteorological conditions (since emission levels are more or less constant from day to day). The lognormal (or any other of the distributions in Table 8-1) behavior has been demonstrated by Bencala and Seinfeld (1976) to be a possible result of similar distributions for wind speed variations.(*)

To assess the relationship between emission level changes and changes in the statistical distribution of a pollutant's concentration let us consider the following idealized situation. Consider a city occupying the square region in the (x, y) plane $[0, L] \times [0, L]$ in the (x, y) plane. Assume that over the city exists a spatially continuous ground-level area source of strength $S_a(x, y) = Q_a s(x, y)$, where Q_a is a source strength scaling parameter and $s(x, y)$ is the source spatial distribution. Thus, if emission level changes occur, they affect only Q_a and not $s(x, y)$.

If the steady state form of the Gaussian plume equation can be assumed to apply, the predicted concentration at location (x, y) is given by

$$\bar{c}(x, y) = \int_0^L \int_0^L \frac{Q_a s(\alpha, \beta)}{\bar{u} \pi \sigma_x (x - \alpha) \sigma_y (x - \alpha)} \exp\left[-\frac{(y - \beta)^2}{2\sigma_y^2 (x - \alpha)}\right] d\alpha d\beta \qquad (8.8 - 1)$$

(*) In fact it is the bivariate normal distribution that is usually used for the statistical description of the two orthogonal components (the third considered negligible) of the wind speed. In this case the wind speed itself, independent of direction, must have a chi-square distribution with two degrees of freedom, also called the Rayleigh distribution, which is very similar in appearance to a lognormal but it is a different distribution.

It is now *assumed* that the wind speed $\overline{u}$ is lognormally distributed over the time period of interest, e.g. one year,

$$p_{\overline{u}}(\overline{u}) = \frac{1}{\overline{u}\sigma_{\overline{u}}\sqrt{2\pi}} \exp\left[-\frac{(\ln \overline{u} - \mu_{\overline{u}})^2}{2\sigma_{\overline{u}}^2}\right] \qquad (8.8-2)$$

For simplicity, the mean wind direction is taken as always oriented in the direction of the positive x-axis.

One can now calculate the statistical variation of $\overline{c}(x,y)$ given that for $\overline{u}$ in (8.8-2). In doing so, one must assume that the time scale associated with wind speed changes (e.g. several hours) is much longer than that over which a steady state concentration is achieved. In that case, the Gaussian plume equation in (8.8-1) can be assumed to apply, a presumption that underlies the use of most multiple source urban plume models (Calder, 1977).

Equation (8.8-1) can be expressed as

$$\overline{c}(x,y) = \frac{g(x,y)}{\overline{u}} \qquad (8.8-3)$$

The pdf's of the random variables $\overline{u}$ and $\overline{c}$ are related by

$$p_{\overline{c}}(\overline{c}; x, y) = \frac{p_{\overline{u}}(\overline{u})}{|\frac{dc}{d\overline{u}}|} \qquad (8.8-4)$$

Since $|dc/d\overline{u}| = g(x,y)/\overline{u}^2$, (8.8-2)-(8.8-4) yield

$$p_{\overline{c}}(\overline{c}; x, y) = \frac{1}{\overline{c}\sigma_{\overline{u}}\sqrt{2\pi}} \exp\left\{-\frac{[\ln \overline{c} - (\ln g - \mu_{\overline{u}})]^2}{2\sigma_{\overline{u}}^2}\right\} \qquad (8.8-5)$$

Thus, it follows that the concentration is itself lognormally distributed with $\sigma_{\overline{c}} = \sigma_{\overline{u}}$ and

$$\mu_{\overline{c}} = \ln g - \mu_{\overline{u}}$$

Now let us consider the effect of a change in emission level. If the source strength changes from Q_a to κQ_a, $g(x,y)$ changes to $\kappa g(x,y)$ and the new concentration distribution is given by

$$p_{\overline{c}}\left(\overline{c};x,y\right) = \frac{1}{\overline{c}\sigma_{\overline{u}}\sqrt{2\pi}}\exp\left\{-\frac{\left[\ln\overline{c}-\left(\ln\kappa g-\mu_{\overline{u}}\right)\right]^2}{2\sigma_{\overline{u}}^2}\right\} \tag{8.8 – 6}$$

That is, the concentration variation after the emission level change is also lognormal with parameters

$$\sigma_{\overline{c}} = \sigma_{\overline{u}} \quad \text{and} \mu_{\overline{c}} = \ln g + \ln\kappa - \mu_{\overline{u}}$$

Typically it is supposed that the relevant air quality standard is based on a value not to be exceeded more than P percent of the time. According to the above distribution c_P is given by

$$1 - \Phi\left(\frac{\ln c_P - \mu_{\overline{c}}}{\sigma_{\overline{c}}}\right) = \frac{P}{100} \tag{8.8 – 7}$$

With the aid of tables (8.8-7) can be written as

$$\frac{\ln c_P - \mu_{\overline{c}}}{\sigma_{\overline{c}}} \tag{8.8 – 8}$$

Before a emission level change

$$\left(c_P\right)_{\text{old}} = \exp\left(\nu_P\sigma_{\overline{c}} + \left(\mu_{\overline{c}}\right)_{\text{old}}\right) \tag{8.8 – 9}$$

whereas after the change

$$\left(c_P\right)_{\text{new}} = \exp\left(\nu_P\sigma_{\overline{c}} + \left(\mu_{\overline{c}}\right)_{\text{new}}\right) \tag{8.8 – 10}$$

Defining

$$\eta = \frac{\left(c_P\right)_{\text{new}}}{\left(c_P\right)_{\text{old}}} \tag{8.8 – 11}$$

it follows that

$$\eta = \kappa \tag{8.8 – 12}$$

This result is expected and confirms that with equal $\sigma_{\overline{c}}$'s, all frequency points on the distribution shift according to the factor κ.

Now suppose that the air quality standard is expressed in the form that the concentration not exceed a level c_s more than 0.01 percent of the time, and current air quality is such that c_s is exceeded P percent of the time. We seek to determine the fractional reduction in emissions κ needed to meet the standard. Thus, we have

$$1 - \Phi\left(\frac{\ln c_s - \mu_{\overline{c}}^{(1)}}{\sigma_{\overline{c}}}\right) = \frac{p}{100} \qquad (8.8-13)$$

$$1 - \Phi\left(\frac{\ln c_s - \mu_{\overline{c}}^{(2)}}{\sigma_{\overline{c}}}\right) = 0.0001 \qquad (8.8-14)$$

where

$$\mu_{\overline{c}}^{(1)} = \ln g - \mu_{\overline{u}} \qquad (8.8-15)$$

$$\mu_{\overline{c}}^{(2)} = \ln g + \ln \kappa - \mu_{\overline{u}} \qquad (8.8-16)$$

From (8.8-13) and (8.8-14) it follows that

$$\ln c_s + \mu_{\overline{u}} - \ln g = \nu^{(1)} \sigma_{\overline{u}}$$

$$\ln c_s + \mu_{\overline{u}} - \ln g - \ln \kappa = \nu^{(2)} \sigma_{\overline{u}}$$

which may be solved for κ to give

$$\kappa = \exp\left[\left(\nu^{(1)} - \nu^{(2)}\right) \sigma_{\overline{u}}\right] \qquad (8.8-15)$$

For example, if

$$P = 1.0$$

and $\sigma_{\overline{u}} = 1.0$, $\nu^{(1)} = 2.32635$ and $\nu^{(2)} = 3.71902$, so that $\kappa = 0.2484$. Thus, to reduce the percent of exceedences of the level c_s from 1% to 0.01%, for a situation in which the standard deviation of the wind speed fluctuations is $\sigma_{\overline{u}} = 1.0$, an approximate 75% reduction in emissions is required.

8.9 CONCLUSIONS

Prediction of the degree of compliance with air quality standards resulting from control strategy implementation generally requires knowledge of the statistical behavior of air pollutant concentrations. This knowledge can usually be incorporated in sets of statistical distributions of concentrations and utilized appropriately thereafter. In this perspective a variety of similar distributions have been proposed to fit aerometric data. The object of this chapter has been to present a treatment on the general features, the methods of determination and the uses of such distributions when dealing with air quality data. Further, the properties of certain random variables crucial in characterizing aerometric data, such as extreme concentrations, exceedances of critical levels and waiting times between exceedances, were studied and level crossing theory. Using this analysis one can show, for example, how different forms of air quality standards can be evaluated and how rollback calculations can be properly carried out when extreme values are involved.

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APPENDIX A8.1

General Inequalities for the Means of Extreme Values

In the most general case of dependent, non-identically distributed, random variables $c_\tau(t_i)$, distribution-free bounds for individual expected values of the order statistics can be obtained as a consequence of a theorem due to Arnold and Groeneveld (1979) which leads to

$$\frac{1}{m-r+1}\sum_{i=1}^{m-r+1}\mu_{i;m} \leq \mu_{m-r+1;m} \leq \frac{1}{r}\sum_{i=m-r+1}^{m} \tag{A8.1-1}$$

where $\mathrm{E}\{c_\tau(t_i)\} = \mu_i$ and $\mathrm{Var}\{c_\tau(t_i)\} = \sigma_i^2$.

In the case $\mu_i = \mu$ and $\sigma_i = \sigma$ for all i (identically distributed variables) one has

$$\mu - \sigma\left(\frac{r-1}{m-r+1}\right)^{\frac{1}{2}} \leq \mu_{m-r+1;m} \leq \mu + \sigma\left(\frac{m-r}{r}\right)^{\frac{1}{2}} \tag{A8.1-2}$$

For $1 \leq s < r \leq m$ it follows that

$$\mu_{s;m} - \mu_{r;m} \leq \sigma\left[\frac{m(m-s+1+r)}{r(m-s+1)}\right]^{\frac{1}{2}} \tag{A8.1-3}$$

For *independent* variates we obtain the following (sharper) bounds in the case of the highest and the lowest order variate:

$$\mathrm{E}\{c_{1;m}\} \leq \mu + \frac{(m-1)\sigma}{(2m-1)^{1/2}} \tag{A8.1-4}$$

$$\mathrm{E}\{c_{m;m}\} \geq \mu - \frac{(m-1)\sigma}{(2m-1)^{1/2}} \tag{A8.1-4}$$

One must note, however, that these bounds are not usually sharp enough (so as to serve as approximate estimates of the expected values) especially in the case of skew distributions like the ones corresponding to concentrations of air pollutants.

References for Appendix A8.1

Arnold, B.C. and Groenenveld, R.A. (1979) "Bounds on Expectations of Linear Systematic Statistics Based on Dependent Samples," *Ann. Statis.*, *7*, 220-223.

APPENDIX A8.2

Extensions of the Asymptotic Theory of Extremes to Non-I.I.D. Variates

Berman (1969) showed that the results of asymtotic extreme value theory for i.i.d. variates also apply to stationary, autocorrelated, Gaussian processes, provided that $\sum_{i=1}^{\infty} r_i^2 < \infty$, where r_i is the correlation coefficient of the first and $(1+i)$st observations. Of course sequences of air pollutant concentrations are not Gaussian, but if they can be transformed into stationary Gaussian processes satisfying Berman's condition (which is often the case; see Horowitz and Barakat, 1979; Box and Jenkins, 1976), the above results hold for them even if they are autocorrelated.

Horowitz and Barakat (1979) further extended the application of the asymptotic theory to non-stationary time series data resulting from a process that satisfies Berman's condition and has the form:

$$\ln c_\tau(t_i) = f_\tau(t_i) + e_\tau(t_i)$$

where $f_\tau(t_i)$ is a deterministic process and $e_\tau(t_i)$ is normally distributed, possibly autocorrelated, with $\mathrm{E}\{e_\tau(t_i)\} = 0$ for all i. The limiting distribution $\Lambda(\chi)$ (Section 8.4) holds for this case and the norming constants are now determined from

$$a_m = \frac{b_m}{\lambda_m}, \quad b_m = \exp\left(f_m^* + \alpha_m \sigma\right)$$

where $\mathrm{E}\{e^2(t_i)\} = \sigma^2$ for all t_i

$$\lambda_m = \frac{\sqrt{2\ln m}}{\sigma}$$

$$\alpha_m = \sqrt{2\ln m} - \frac{\ln(\ln m) + 4\ln\pi}{2\sqrt{2\ln m}}$$

and

$$f_m^* = \frac{\sigma}{\sqrt{2\ln m}} \ln\left[\frac{1}{m}\sum_{i=1}^{m} \exp\left(\sqrt{2\ln m}\,\frac{f_\tau(t_i)}{\sigma}\right)\right]$$

If $f(t) = \mu$ (constant) this reduces to the result of Singpurwalla (Section 8.4.4).

References
for Appendix A8.2

Berman, S.M. (1964) "Limit Theorems for the Maximum Term in Stationary Sequences," *Ann. Math. Statis.*, *35*, 502-516.

Box, G.E.P. and Jenkins, G.M. (1976) *Time Series Analysis: Forecasting and Control*, Revised Edition, Holden Day, San Francisco.

Horowitz, J. and Barakat, S. (1979) "Statistical Analysis of the Maximum Concentration of Air Pollutants: Effects of Autocorrelation and Non-Stationarity," *Atmospheric Environment*, *13*, 811-818.