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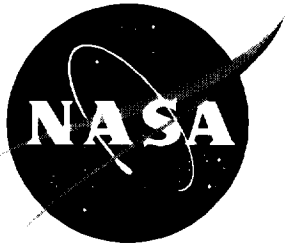
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ON THE VARIOUS FORMS OF THE ENERGY EQUATION FOR A DILUTE, MONATOMIC MIXTURE OF NONREACTING GASES

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Introduction

Choosing the appropriate form of the governing equation set to solve in fluid dynamics is the first step in the solution of a particular problem. In the case of gas mixtures, the governing equations become rather formidable and a complete listing of the equations in their various forms and methods to evaluate the transport coefficients is difficult to find. This paper seeks to compile common as well as less well known results in a single document.

Forms for the various quantities involved in multicomponent hydrodynamics may be derived either phenomenologically^{6, 18, 10} or by methods of kinetic theory^{31, 11}. Ideally, the full limitations of the derivation need to be stated a priori. For this reason, we choose the kinetic theory approach. In addition, kinetic theory allows us to explicitly calculate the relevant transport coefficients. This paper will focus on the issue of complications to the governing equations because of multiple species but will not concern itself with issue of internal degrees of freedom of the molecules leading to relaxation phenomena³⁴ or antisymmetric stress^{27, 24}, exothermic heat release that may cause high-energy “tails” to the distribution function of particle velocities²⁰ and differing temperatures of certain species²³, or the effects of ternary, quaternary, etc. collisions found in dense gases¹⁴ and liquids. Having made those severe restrictions, we also limit discussion to small perturbations from equilibrium where one may safely assume that the first nonequilibrium expression derived from the Chapman-Enskog-Burnett³ method of approximating the solution to the Boltzmann equation is valid. In terms of classical irreversible thermodynamics, “local” equilibrium prevails. This means that although the flow is not in equilibrium, locally, equilibrium thermodynamic variables are still defined. Results using the Chapman-Enskog-Burnett method are not valid for severe spatial gradients and for sufficiently high frequency phenomena. This amounts to no variation in quantities whose characteristic lengths and times are of the order of the mean free path or the time between collisions. Collision times are also presumed to be much smaller than the time between collisions. In cases where more severe phenomena occur, local equilibrium does not exist and unique definitions for the nonequilibrium temperature and entropy are not forthcoming². This is the topic of “Extended Irreversible Thermodynamics^{26, 12}”. Techniques

such as Grad's moment method⁹, which allow for terms such as the heat flux vector, stress tensor, and species flux to become independent variables, are likely to lead to more accurate approximations to the Boltzmann equation in situations far from equilibrium²⁹. Although the governing equations derived by Grad's method are more complicated than those traditionally confronted, they are likely to be essential in describing the finer points of polyatomic and reacting dilute gases³³ as well as rarefied gases³⁵ where the Knudsen number may no longer be considered a small expansion parameter.

It is the goal of this paper to summarize the various relationships between equations describing conservation of energy for a dilute, monatomic, nonreacting gas in local equilibrium. The gas is treated as nonrelativistic, not subject to magnetic or electric fields, or radiative effects.

Energy Equations

Using the first nonequilibrium approximation according to the Chapman-Enskog-Burnett theory in the kinetic theory of gases^{31, 8} (the Navier-Stokes level),

$$q_\alpha = \rho \sum_{i=1}^{ncs} (h_i Y_i \tilde{V}_{i\alpha}) - \lambda_0 \nabla_\alpha T - p \sum_{i=1}^{ncs} D_i^T d_{i\alpha} \quad (1)$$

$$= \rho \sum_{i=1}^{ncs} (h_i Y_i \tilde{V}_{i\alpha}) + q_{\alpha(\text{red})} \quad (2)$$

$$\tilde{V}_{i\alpha} = - \sum_{j=1}^{ncs} D_{ij}^M d_{j\alpha} - D_i^T \nabla_\alpha (\ln T) \quad (3)$$

$$d_{i\alpha} = \nabla_\alpha X_i + (X_i - Y_i) \nabla_\alpha (\ln p) + \frac{\rho Y_i}{p} [f_{i\alpha} - \sum_{j=1}^{ncs} Y_j f_{j\alpha}] \quad (4)$$

$$\sigma_{\beta\alpha} = -p\delta_{\alpha\beta} + \lambda_\mu \theta \delta_{\alpha\beta} + 2\mu \mathbf{D}_{\alpha\beta} \quad (5)$$

where i and j are species indices, α and β are spatial indices, ncs is the number of chemical species, q_α is the heat flux vector, $q_{\alpha(\text{red})}$ is the reduced heat flux vector, $\tilde{V}_{i\alpha}$ is the diffusion velocity, $\sigma_{\beta\alpha}$ is the stress tensor, $d_{i\alpha}$ is the diffusion driving force vector, D_i^T is the thermal diffusion coefficient, D_{ij}^M is the multicomponent diffusion coefficient, λ_0 is the partial thermal conductivity, λ_μ is the second coefficient of viscosity, μ is the shear viscosity, X_i is the mole fraction, Y_i is the mass fraction, h_i is the partial enthalpy per unit mass, p is the pressure, T is the temperature, ρ is the density, $f_{i\alpha}$ is the body force per unit mass, θ is the dilatation, $\delta_{\alpha\beta}$ is the kronicker delta, and $\mathbf{D}_{\alpha\beta}$ is the rate of deformation tensor. Several comments about these terms are in order. There are two different definitions in the literature for the multicomponent diffusion and thermal diffusion coefficients, those of Waldmann³⁰ and those of Curtiss et. al.^{4, 16}. It is essential that readers be aware of which one they are confronting at any given moment. We chose those of Waldmann for their

simplicity^{22, 5} and their straightforward correspondence to coefficients found in linear irreversible thermodynamics^{11, 15}. For the second coefficient of viscosity, Stokes hypothesis holds rigorously and we may use $\mu_B = (\lambda_\mu + \frac{2}{3}\mu) = 0$, where μ_B is the bulk viscosity. Note that the partial thermal conductivity is not the conductivity that is measured in experiments because thermal diffusion effects can not be completely isolated. We also note that all diffusion velocities and diffusion driving force vectors are not independent but are related through

$$\sum_{i=1}^{ncs} Y_i \tilde{V}_{i\alpha} = 0 \quad ; \quad \sum_{i=1}^{ncs} d_{i\alpha} = 0 \quad (6)$$

By defining the velocity gradient tensor as

$$\mathbf{L}_{\alpha\beta} = \nabla_\beta u_\alpha \quad (7)$$

the rate of deformation tensor and its deviator are given by

$$\mathbf{D}_{\alpha\beta} = \frac{1}{2} (\mathbf{L}_{\alpha\beta} + \mathbf{L}_{\beta\alpha}) \quad ; \quad \overset{\circ}{\mathbf{D}}_{\alpha\beta} = \mathbf{D}_{\alpha\beta} - \frac{1}{3} \theta \delta_{\alpha\beta} \quad (8)$$

where u_α is the barycentric, hydrodynamic, or center-of-mass velocity of the gas. It will also be useful to write out the equations of state (9), species continuity (10), overall continuity (11), and momentum conservation (12) for future reference;

$$P = nkT = \left(\sum_{i=1}^{ncs} n_i \right) kT = \left(\sum_{i=1}^{ncs} \frac{\rho_i}{W_i} \right) R^0 T = \frac{\rho R^0 T}{W} = \rho R T \quad (9)$$

$$\rho \frac{DY_i}{Dt} + \nabla_\alpha \cdot (\rho Y_i \tilde{V}_{i\alpha}) = \dot{\omega}_i \quad (10)$$

$$\frac{D\rho}{Dt} + \rho\theta = 0 \quad (11)$$

$$\rho \frac{Du_\alpha}{Dt} = \nabla_\beta \cdot (\sigma_{\beta\alpha}) + \rho \sum_{i=1}^{ncs} Y_i f_{i\alpha} \quad (12)$$

where the reaction rate, $\dot{\omega}_i$, is presumed to vanish and n and k are the number of atoms per unit volume and Boltzmann's constant. The conservative forms of equations (10) and (12) may be obtained by simply adding zero to both equations in the form of Eq. (11) times Y_i and u_α , respectively. Use of the following relations has been made in order to transform the equation of state; $n = \sum_{i=1}^{ncs} n_i$, $\rho_i = n_i m_i$, $\rho = \sum_{i=1}^{ncs} \rho_i$, where m_i being the mass per atom, $Y_i = \frac{\rho_i}{\rho}$, $X_i = \frac{n_i}{n}$, $R = \frac{R^0}{W}$, $R^0 = k N_a$, $W_i = N_a m_i$, where W_i , W , R^0 , N_a are the atomic weight of species i , the average atomic weight of the mixture, the universal gas constant, and Avogadro's number. Clearly $\sum_{i=1}^{ncs} X_i = \sum_{i=1}^{ncs} Y_i = 1$.

The mole and mass fractions may be related by,

$$X_i = \frac{\frac{Y_i}{W_i}}{\left(\sum_{k=1}^{ncs} \frac{Y_k}{W_k} \right)} \quad , \quad Y_i = \frac{X_i W_i}{\left(\sum_{k=1}^{ncs} X_k W_k \right)} \quad (13)$$

and the average molecular weight, W , is given by

$$W = \frac{1}{\left(\sum_{k=1}^{ncs} \frac{Y_k}{W_k}\right)} = \sum_{k=1}^{ncs} (X_k W_k) \quad (14)$$

These may be related through

$$\frac{W_i}{W} = \frac{Y_i}{X_i} \quad (15)$$

Equations for the heat flux vector and diffusion vector appear in many different, but equivalent forms. Beginning with the expression^{25, 17, 16}

$$\sum_{j=1}^{ncs} \frac{X_i X_j}{D_{ij}^B} [D_{it}^M - D_{jt}^M] = \delta_{it} - Y_i \quad (16)$$

where D_{ij}^B is the binary diffusion coefficient, we may rewrite the diffusion velocity equation (3) as the Stefan-Maxwell equation (17) using $\sum_{i=1}^{ncs} k_i^T = 0$ and $\sum_{i=1}^{ncs} d_{i\alpha} = 0$ as

$$\sum_{j=1}^{ncs} \frac{X_i X_j}{D_{ij}^B} (\tilde{V}_{j\alpha} - \tilde{V}_{i\alpha}) = d_{i\alpha} + k_i^T \nabla_\alpha (\ln T) \quad (17)$$

$$= d_{i\alpha} + \sum_{j=1}^{ncs} X_i X_j \alpha_{ij}^T \nabla_\alpha (\ln T) \quad (18)$$

where the thermal diffusion ratios, k_i^T , and antisymmetrical thermal diffusion factors, α_{ij}^T , are defined by

$$\sum_{j=1}^{ncs} D_{ij}^M k_j^T = D_i^T ; \quad k_i^T = \sum_{j=1}^{ncs} X_i X_j \alpha_{ij}^T \quad (19)$$

or, equivalently, using (16),

$$k_i^T = \sum_{j=1}^{ncs} \frac{X_i X_j}{D_{ij}^B} (D_i^T - D_j^T) ; \quad \alpha_{ij}^T = \frac{D_i^T - D_j^T}{D_{ij}^B} \quad (20)$$

Because there is no explicit mole fraction dependence in the thermal diffusion factors, they are sometimes the preferred term to describe thermal diffusion effects. There are $[ncs(ncs + 1)/2]$ independent multicomponent diffusion coefficients and thermal $(ncs - 1)$ independent thermal diffusion coefficients, as can be seen in the relations

$$\sum_{i=1}^{ncs} Y_i D_{ij}^M = 0 ; \quad \sum_{i=1}^{ncs} Y_i D_i^T = 0 \quad (21)$$

Each of the terms, D_{ij}^M , D_{ij}^B , and $R_{ij} = \frac{X_i X_j}{D_{ij}^B}$ are symmetrical, the last term being referred to as the impedance matrix. In the special case of a

binary mixture, the multicomponent diffusion coefficients are related to the binary diffusion coefficient as

$$D_{12}^B = \frac{X_1 X_2}{Y_1 Y_2} D_{12}^M = \frac{X_1 X_2}{Y_2^2} D_{11}^M = \frac{X_1 X_2}{Y_1^2} D_{22}^M \quad (22)$$

Solving the Stefan-Maxwell equation (17) for $d_{i\alpha}$ and then substituting the result into the original expression for the heat flux vector (1) gives

$$\begin{aligned} q_\alpha = & \left(-\lambda_0 + \frac{p}{T} \sum_{i=1}^{ncs} k_i^T D_i^T \right) \nabla_\alpha T + \rho \sum_{i=1}^{ncs} (h_i Y_i \tilde{V}_{i\alpha}) \\ & - p \sum_{i=1}^{ncs} \sum_{j=1}^{ncs} \left(\frac{X_i X_j D_i^T}{D_{ij}^B} (\tilde{V}_{j\alpha} - \tilde{V}_{i\alpha}) \right) \end{aligned} \quad (23)$$

An experimenter measuring thermal conductivity is likely to measure it when all diffusion velocities vanish at steady state. For this reason the thermal conductivity is defined in terms of the partial thermal conductivity as

$$\lambda = \lambda_0 - \frac{p}{T} \sum_{i=1}^{ncs} k_i^T D_i^T \quad (24)$$

so that in the absence of a diffusion velocity, the coefficient in front of $\nabla_\alpha T$ is the value which is measured. With this we may write four equivalent forms of the heat flux vector (1),

$$q_\alpha = -\lambda \nabla_\alpha T + \sum_{i=1}^{ncs} \left(\frac{5}{2} n_i k T + p k_i^T \right) \tilde{V}_{i\alpha} \quad (25)$$

$$= -\lambda \nabla_\alpha T + \sum_{i=1}^{ncs} \left(\rho h_i Y_i + p k_i^T \right) \tilde{V}_{i\alpha} \quad (26)$$

$$= -\lambda \nabla_\alpha T + p \sum_{i=1}^{ncs} \left(\frac{5}{2} X_i + k_i^T \right) \tilde{V}_{i\alpha} \quad (27)$$

$$= -\lambda \nabla_\alpha T + \rho \sum_{i=1}^{ncs} h_i Y_i \tilde{V}_{i\alpha} - p \sum_{i=1}^{ncs} \sum_{j=1}^{ncs} \left(\frac{X_i X_j D_i^T}{D_{ij}^B} (\tilde{V}_{j\alpha} - \tilde{V}_{i\alpha}) \right) \quad (28)$$

where $\frac{5}{2} k T$ is the enthalpy per atom, or with the use of the equation of state, $\frac{5p}{2n}$, and h_i is the partial enthalpy per unit mass. The relation between the thermal and partial thermal conductivities may also be written in terms of the thermal diffusion coefficients instead of the thermal diffusion ratios as

$$\lambda = \lambda_0 - \frac{p}{T} \sum_{i=1}^{ncs} \sum_{j=1}^{ncs} \frac{X_i X_j D_i^T}{D_{ij}^B} (D_i^T - D_j^T) \quad (29)$$

$$= \lambda_0 - \frac{p}{2T} \sum_{i=1}^{ncs} \sum_{j=1}^{ncs} \frac{X_i X_j}{D_{ij}^B} (D_i^T - D_j^T)^2 \quad (30)$$

The energy equation may be found in the literature in many forms. It may derived as^{6, 18, 10}

TOTAL ENERGY EQUATION (e_0)

$$\rho \frac{De_0}{Dt} = -\nabla_\alpha \cdot q_\alpha + \nabla_\beta \cdot (\sigma_{\beta\alpha} \cdot u_\alpha) + \rho \sum_{i=1}^{ncs} Y_i f_{i\alpha} \cdot (\tilde{V}_{i\alpha} + u_\alpha) \quad (31)$$

Dotting the momentum equation (12) with the center-of-mass velocity, u_α , yields

MECHANICAL ENERGY EQUATION ($\frac{1}{2}u_\alpha u_\alpha$)

$$\rho \frac{D\left(\frac{u_\alpha u_\alpha}{2}\right)}{Dt} = u_\alpha \nabla_\beta \cdot (\sigma_{\beta\alpha}) + \rho \sum_{i=1}^{ncs} Y_i f_{i\alpha} \cdot u_\alpha \quad (32)$$

and upon subtracting (32) from (31), we get

$$\rho \frac{De_0}{Dt} - \rho \frac{D\left(\frac{u_\alpha u_\alpha}{2}\right)}{Dt} = \rho \frac{De}{Dt} \quad (33)$$

or

INTERNAL ENERGY EQUATION (e)

$$\rho \frac{De}{Dt} = -\nabla_\alpha \cdot q_\alpha + \sigma_{\beta\alpha} : \mathbf{L}_{\alpha\beta} + \rho \sum_{i=1}^{ncs} Y_i f_{i\alpha} \cdot \tilde{V}_{i\alpha} \quad (34)$$

With the thermodynamic relation $h = e + \frac{p}{\rho}$, one may obtain

$$\frac{Dh}{Dt} = \frac{De}{Dt} + \frac{1}{\rho} \frac{Dp}{Dt} - \frac{p}{\rho^2} \frac{D\rho}{Dt} \quad (35)$$

and hence, with the aid of the continuity equation (11),

ENTHALPY EQUATION (h)

$$\rho \frac{Dh}{Dt} = -\nabla_\alpha \cdot q_\alpha + \tau_{\beta\alpha} : \mathbf{L}_{\alpha\beta} + \frac{Dp}{Dt} + \rho \sum_{i=1}^{ncs} Y_i f_{i\alpha} \cdot \tilde{V}_{i\alpha} \quad (36)$$

Adding the mechanical energy equation to this gives

$$\rho \frac{Dh_0}{Dt} = \rho \frac{Dh}{Dt} + \rho \frac{D\left(\frac{u_\alpha u_\alpha}{2}\right)}{Dt} \quad (37)$$

or

TOTAL ENTHALPY EQUATION (h_0)

$$\rho \frac{Dh_0}{Dt} = -\nabla_\alpha \cdot q_\alpha + \nabla_\beta \cdot (\tau_{\beta\alpha} \cdot u_\alpha) + \frac{\partial p}{\partial t} + \rho \sum_{i=1}^{ncs} Y_i f_{i\alpha} \cdot (\tilde{V}_{i\alpha} + u_\alpha) \quad (38)$$

The viscous stress tensor, $\tau_{\beta\alpha}$, is given by

$$\tau_{\beta\alpha} = \lambda_\mu \theta \delta_{\alpha\beta} + 2\mu \mathbf{D}_{\alpha\beta} = \mu_B \theta \delta_{\alpha\beta} + 2\mu \mathring{\mathbf{D}}_{\alpha\beta} \quad (39)$$

or

$$\sigma_{\beta\alpha} = -p \delta_{\alpha\beta} + \tau_{\beta\alpha} \quad (40)$$

and with it, we may define the viscous dissipation function, Φ , as

$$\Phi = \tau_{\beta\alpha} : \mathbf{L}_{\alpha\beta} = \lambda_\mu \theta^2 + 2\mu \mathbf{D}_{\alpha\beta} : \mathbf{D}_{\alpha\beta} \quad (41)$$

$$= \mu_B \theta^2 + 2\mu \mathring{\mathbf{D}}_{\alpha\beta} : \mathring{\mathbf{D}}_{\alpha\beta} \quad (42)$$

By considering $h = h(Y_k, T, p)$ and $e = e(Y_k, T, \rho)$ in flows where local equilibrium exists, we may write the total differentials of the enthalpy and internal energy as³²

$$dh = \sum_{k=1}^{ncs} \left(\frac{\partial h}{\partial Y_k} \right)_{T,p} dY_k + \left(\frac{\partial h}{\partial T} \right)_{Y_k,p} dT + \left(\frac{\partial h}{\partial p} \right)_{Y_k,T} dp \quad (43)$$

$$de = \sum_{k=1}^{ncs} \left(\frac{\partial e}{\partial Y_k} \right)_{T,\rho} dY_k + \left(\frac{\partial e}{\partial T} \right)_{Y_k,\rho} dT + \left(\frac{\partial e}{\partial \rho} \right)_{Y_k,T} d\rho \quad (44)$$

These may be simplified using $\left(\frac{\partial h}{\partial T} \right)_{Y_k,p} = C_p$, the isobaric heat capacity, $\left(\frac{\partial e}{\partial T} \right)_{Y_k,\rho} = C_v$, the isochoric heat capacity, $\left(\frac{\partial h}{\partial Y_k} \right)_{T,p} = h_k$, the partial enthalpy per unit mass, $\left(\frac{\partial e}{\partial Y_k} \right)_{T,\rho} = h_k - \frac{\alpha T X_k}{\rho Y_k \kappa}$, where κ is coefficient of isothermal compressibility and α is coefficient of thermal expansion at constant pressure, $\left(\frac{\partial h}{\partial p} \right)_{Y_k,T} = \frac{(1-\alpha T)}{\rho}$, $\left(\frac{\partial e}{\partial \rho} \right)_{Y_k,T} = \frac{1}{\rho^2} \left(p - \frac{\alpha T}{\kappa} \right)$. In addition, $C_p - C_v = \frac{T\alpha^2}{\rho\kappa}$. For a perfect gas, $\alpha = \frac{1}{T}$ and $\kappa = \frac{1}{p}$, reducing equations (43) and (44) to

$$dh = \sum_{i=1}^{ncs} h_i dY_i + C_p dT \quad (45)$$

$$de = \sum_{i=1}^{ncs} \left(h_i - \frac{p X_i}{\rho Y_i} \right) dY_i + C_v dT \quad (46)$$

From equations (45), (46) and (35) we may write

$$\rho \frac{Dh}{Dt} = \rho C_p \frac{DT}{Dt} + \rho \sum_{i=1}^{ncs} \left(h_i \frac{DY_i}{Dt} \right) \quad (47)$$

$$\rho \frac{De}{Dt} = \rho C_v \frac{DT}{Dt} + \rho \sum_{i=1}^{ncs} \left[\left(h_i - \frac{p X_i}{\rho Y_i} \right) \frac{DY_i}{Dt} \right] \quad (48)$$

$$\rho \frac{Dh}{Dt} = \rho \frac{De}{Dt} + \frac{Dp}{Dt} + \rho p \theta \quad (49)$$

which enables use to derive

$$\frac{Dp}{Dt} = -p\theta + \rho \sum_{i=1}^{ncs} \left(\frac{pX_i}{\rho Y_i} \frac{DY_i}{Dt} \right) + \rho R \frac{DT}{Dt} \quad (50)$$

With equations (36) and (47), one form of the temperature equation appears as²¹

$$\begin{aligned} \rho C_p \frac{DT}{Dt} &= -\nabla_\alpha \cdot q_\alpha + \tau_{\beta\alpha} : \mathbf{L}_{\alpha\beta} + \frac{Dp}{Dt} \\ &+ \rho \sum_{i=1}^{ncs} \left(h_i \frac{DY_i}{Dt} \right) + \rho \sum_{i=1}^{ncs} Y_i f_{i\alpha} \cdot \tilde{V}_{i\alpha} \end{aligned} \quad (51)$$

By eliminating the material derivative of the pressure from equation (51) with equation (50) we have

TEMPERATURE EQUATION

$$\begin{aligned} \rho C_v \frac{DT}{Dt} &= -\nabla_\alpha \cdot q_\alpha + \sigma_{\beta\alpha} : \mathbf{L}_{\alpha\beta} + \rho \sum_{i=1}^{ncs} Y_i f_{i\alpha} \cdot \tilde{V}_{i\alpha} \\ &+ \rho \sum_{i=1}^{ncs} \left[\left(\frac{pX_i}{\rho Y_i} - h_i \right) \frac{DY_i}{Dt} \right] \end{aligned} \quad (52)$$

Dividing equation (50) by the perfect gas relation $\frac{R}{C_v} = (\gamma - 1)$ results in

$$\rho C_v \frac{DT}{Dt} = \frac{p\theta}{(\gamma - 1)} - \frac{\rho}{(\gamma - 1)} \sum_{i=1}^{ncs} \left(\frac{pX_i}{\rho Y_i} \frac{DY_i}{Dt} \right) + \frac{1}{(\gamma - 1)} \frac{Dp}{Dt} \quad (53)$$

and with this we find

PRESSURE EQUATION

$$\begin{aligned} \frac{1}{(\gamma - 1)} \frac{Dp}{Dt} &= -\frac{\gamma p\theta}{(\gamma - 1)} - \nabla_\alpha \cdot q_\alpha + \tau_{\beta\alpha} : \mathbf{L}_{\alpha\beta} + \rho \sum_{i=1}^{ncs} Y_i f_{i\alpha} \cdot \tilde{V}_{i\alpha} \\ &- \rho \sum_{i=1}^{ncs} \left(h_i \frac{DY_i}{Dt} \right) + \frac{\rho}{(\gamma - 1)} \sum_{i=1}^{ncs} \left(\frac{pX_i}{\rho Y_i} \frac{DY_i}{Dt} \right) \end{aligned} \quad (54)$$

The expression for the time rate of change of entropy per unit mass may be written as

$$\rho \frac{Ds}{Dt} = -\nabla_\alpha \cdot J_\alpha^s + \sigma^s. \quad (55)$$

where J_α^s is the flux of entropy and is written in the context of linear irreversible thermodynamics^{10, 6, 18}, with the use of $\mu_i = h_i - Ts_i$, as

$$\begin{aligned} J_\alpha^s &= \frac{q_\alpha - \rho \sum_{i=1}^{ncs} \mu_i Y_i \tilde{V}_{i\alpha}}{T} \\ &= \rho \sum_{i=1}^{ncs} s_i Y_i \tilde{V}_{i\alpha} + \frac{q_{\alpha(\text{red})}}{T} \end{aligned} \quad (56)$$

where μ_i is the chemical potential per unit mass and s_i is the partial entropy per unit mass. Therefore,

$$J_\alpha^s = \rho \sum_{i=1}^{ncs} s_i Y_i \tilde{V}_{i\alpha} - \frac{\lambda_0}{T} \nabla_\alpha T - \frac{p}{T} \sum_{i=1}^{ncs} D_i^T d_{i\alpha} \quad (57)$$

and

$$\begin{aligned} \nabla_\alpha \cdot J_\alpha^s &= \nabla_\alpha \cdot \left(\rho \sum_{i=1}^{ncs} s_i Y_i \tilde{V}_{i\alpha} \right) + \frac{\lambda_0}{T^2} (\nabla_\alpha T) \cdot (\nabla_\alpha T) - \frac{1}{T} \nabla_\alpha \cdot (\lambda_0 \nabla_\alpha T) \\ &+ \frac{p}{T^2} (\nabla_\alpha T) \cdot \left(\sum_{i=1}^{ncs} D_i^T d_{i\alpha} \right) - \frac{1}{T} \nabla_\alpha \cdot \left(p \sum_{i=1}^{ncs} D_i^T d_{i\alpha} \right) \end{aligned} \quad (58)$$

$$= \nabla_\alpha \cdot \left(\rho \sum_{i=1}^{ncs} s_i Y_i \tilde{V}_{i\alpha} \right) + \nabla_\alpha \cdot \left(\frac{q_{\alpha(\text{red})}}{T} \right) \quad (59)$$

Equations (58) and (59) represent the reversible change of entropy. The irreversible component of the change in entropy is derived by noting that the entropy generation is of the bilinear form

$$\begin{aligned} \sigma^s &= \sum JX \\ &= \sum LXX \end{aligned} \quad (60)$$

where $J = LX$, X , and L are the respective thermodynamic fluxes, thermodynamic forces, and Onsager coefficients. Summation is considered over all forces and fluxes of the same tensorial order. The four thermodynamic forces are the diffusion force ($\mathbf{X}_{i\alpha}^{(d)}$), the thermal force ($\mathbf{X}_\alpha^{(t)}$), and the scalar ($\mathbf{X}^{(v0)}$) and tensor viscous forces ($\mathbf{X}_{\alpha\beta}^{(v2)}$) given by⁷

$$\mathbf{X}_{i\alpha}^{(d)} = -\frac{p}{\rho T Y_i} d_{i\alpha} \quad (61)$$

$$\mathbf{X}_\alpha^{(t)} = -\frac{1}{T^2} \nabla_\alpha T \quad (62)$$

$$\mathbf{X}^{(v0)} = -\frac{1}{T} \theta \quad (63)$$

$$\mathbf{X}_{\alpha\beta}^{(v2)} = -\frac{1}{T} \overset{\circ}{\mathbf{D}}_{\alpha\beta} \quad (64)$$

Similarly, the six Onsager coefficients are given by

$$\mathbf{L}_{ij}^{(d,d)} = \frac{1}{p} \rho^2 T Y_i Y_j D_{ij}^M \quad (65)$$

$$\mathbf{L}_i^{(t,d)} = \mathbf{L}_i^{(d,t)} = \rho T Y_i D_i^T \quad (66)$$

$$\mathbf{L}^{(t,t)} = \lambda_0 T^2 \quad (67)$$

$$\mathbf{L}^{(v0,v0)} = \mu_B T \quad (68)$$

$$\mathbf{L}^{(v2,v2)} = 2\mu T \quad (69)$$

and hence

$$\mathbf{J}_{i\alpha}^{(d)} = \sum_{j=1}^{ncs} \mathbf{L}_{ij}^{(d,d)} \mathbf{X}_{j\alpha}^d + \mathbf{L}_i^{(t,d)} \mathbf{X}_\alpha^t = \rho Y_i \tilde{V}_{i\alpha} \quad (70)$$

$$\mathbf{J}_\alpha^{(t)} = \mathbf{L}^{(t,t)} \mathbf{X}_\alpha^t + \sum_{i=1}^{ncs} \mathbf{L}_i^{(d,t)} \mathbf{X}_{i\alpha}^d = q_{\alpha(\text{red})} \quad (71)$$

$$\mathbf{J}^{(v0)} = \mathbf{L}^{(v0,v0)} \mathbf{X}^{v0} = -\mu_B \theta \quad (72)$$

$$\mathbf{J}_{\alpha\beta}^{(v2)} = \mathbf{L}^{(v2,v2)} \mathbf{X}_{\alpha\beta}^{v2} = -2\mu \overset{\circ}{\mathbf{D}}_{\alpha\beta} \quad (73)$$

where

$$\mathbf{J}^{(v0)} \delta_{\alpha\beta} + \mathbf{J}_{\alpha\beta}^{(v2)} = -\tau_{\beta\alpha} \quad (74)$$

The irreversible generation of entropy, σ^s , is then given by

$$\begin{aligned} \sigma^s &= \sum_{i=1}^{ncs} \sum_{j=1}^{ncs} \mathbf{L}_{ij}^{(d,d)} \mathbf{X}_{i\alpha}^{(d)} \cdot \mathbf{X}_{j\alpha}^{(d)} + \sum_{i=1}^{ncs} \mathbf{L}_i^{(t,d)} \mathbf{X}_\alpha^{(t)} \cdot \mathbf{X}_{i\alpha}^{(d)} + \sum_{i=1}^{ncs} \mathbf{L}_i^{(d,t)} \mathbf{X}_{i\alpha}^{(d)} \cdot \mathbf{X}_\alpha^{(t)} \\ &+ \mathbf{L}^{(t,t)} \mathbf{X}_\alpha^{(t)} \cdot \mathbf{X}_\alpha^{(t)} + \mathbf{L}^{(v0,v0)} \mathbf{X}^{(v0)} \cdot \mathbf{X}^{(v0)} + \mathbf{L}^{(v2,v2)} \mathbf{X}_{\alpha\beta}^{(v2)} : \mathbf{X}_{\alpha\beta}^{(v2)} \end{aligned} \quad (75)$$

$$= \sum_{i=1}^{ncs} \mathbf{J}_{i\alpha}^{(d)} \cdot \mathbf{X}_{i\alpha}^{(d)} + \mathbf{J}_\alpha^{(t)} \cdot \mathbf{X}_\alpha^{(t)} + \mathbf{J}^{(v0)} \cdot \mathbf{X}^{(v0)} + \mathbf{J}_{\alpha\beta}^{(v2)} : \mathbf{X}_{\alpha\beta}^{(v2)} \quad (76)$$

or

$$\begin{aligned} \sigma^s &= \frac{\lambda_0}{T^2} (\nabla_\alpha T) \cdot (\nabla_\alpha T) + \frac{1}{T} \left[\mu_B \theta^2 + 2\mu (\overset{\circ}{\mathbf{D}}_{\alpha\beta} : \overset{\circ}{\mathbf{D}}_{\alpha\beta}) \right] \\ &+ \frac{p}{T} \sum_{i=1}^{ncs} \sum_{j=1}^{ncs} \left[(d_{i\alpha} \cdot d_{j\alpha}) D_{ij}^M \right] + \frac{2p}{T} (\nabla_\alpha \ln T) \cdot \left(\sum_{i=1}^{ncs} D_i^T d_{i\alpha} \right) \end{aligned} \quad (77)$$

$$= \frac{1}{T} \left[-\frac{1}{T} (\nabla_\alpha T) \cdot (q_{\alpha(\text{red})}) + \tau_{\beta\alpha} : \mathbf{L}_{\alpha\beta} - p \sum_{i=1}^{ncs} (\tilde{V}_{i\alpha} \cdot d_{i\alpha}) \right] \quad (78)$$

Because the second law of thermodynamics requires that entropy must increase until it is maximized at equilibrium, it is important to verify that $\sigma_s \geq 0$. By manipulating the Stefan-Maxwell equation (17), using (20), and the definition of the impedance matrix, we may write the diffusion driving force vector as

$$d_{i\alpha} = \sum_{j=1}^{ncs} [R_{ij} (\tilde{V}_{j\alpha} - \tilde{V}_{i\alpha})] - \sum_{j=1}^{ncs} [R_{ij} (D_i^T - D_j^T)] \nabla_\alpha (\ln T) \quad (79)$$

and taking the reduced form of the heat flux vector (28), we have

$$q_{\alpha(\text{red})} = -\lambda \nabla_\alpha T - p \sum_{i=1}^{ncs} \sum_{j=1}^{ncs} \left[D_i^T R_{ij} (\tilde{V}_{j\alpha} - \tilde{V}_{i\alpha}) \right] \quad (80)$$

Upon substitution of (79) and (80) into (78), all occurrences of the thermal diffusion coefficients cancel, leaving

$$\begin{aligned} \sigma^s &= \frac{\lambda}{T^2} (\nabla_\alpha T) \cdot (\nabla_\alpha T) + \frac{2\mu}{T} (\overset{\circ}{\mathbf{D}}_{\alpha\beta} : \overset{\circ}{\mathbf{D}}_{\alpha\beta}) \\ &- \frac{p}{T} \sum_{i=1}^{ncs} \sum_{j=1}^{ncs} \left[R_{ij} (\tilde{V}_{j\alpha} - \tilde{V}_{i\alpha}) \tilde{V}_{i\alpha} \right] \end{aligned} \quad (81)$$

where the vanishing bulk viscosity has been dropped, and may be rewritten as

$$\begin{aligned}\sigma^s &= \frac{\lambda}{T^2}(\nabla_\alpha T) \cdot (\nabla_\alpha T) + \frac{2\mu}{T}(\mathring{\mathbf{D}}_{\alpha\beta} : \mathring{\mathbf{D}}_{\alpha\beta}) \\ &+ \frac{p}{2T} \sum_{i=1}^{ncs} \sum_{j=1}^{ncs} \left[\frac{X_i X_j}{D_{ij}^B} (\tilde{V}_{j\alpha} - \tilde{V}_{i\alpha})^2 \right]\end{aligned}\quad (82)$$

It is now clear that entropy production is never negative because λ, μ and $D_{ij}^B \geq 0$ and all other terms occur in quadratic form (thermal diffusion coefficients may be positive or negative).

Putting the irreversible entropy generation (77) and the entropy flux (58) into (55) yields

ENTROPY EQUATION

$$\begin{aligned}\rho T \frac{Ds}{Dt} &+ T \nabla_\alpha \cdot \left(\rho \sum_{i=1}^{ncs} s_i Y_i \tilde{V}_{i\alpha} \right) = -\frac{2}{3} \mu \theta^2 + 2\mu (\mathbf{D}_{\alpha\beta} : \mathbf{D}_{\alpha\beta}) \\ &+ \nabla_\alpha \cdot (\lambda_0 \nabla_\alpha T) + \nabla_\alpha \cdot \left(p \sum_{i=1}^{ncs} D_i^T d_{i\alpha} \right) \\ &+ p (\nabla_\alpha \ln T) \cdot \left(\sum_{i=1}^{ncs} D_i^T d_{i\alpha} \right) + p \sum_{i=1}^{ncs} \sum_{j=1}^{ncs} \left[(d_{i\alpha} \cdot d_{j\alpha}) D_{ij}^M \right]\end{aligned}\quad (83)$$

$$= \tau_{\beta\alpha} : \mathbf{L}_{\alpha\beta} - \nabla_\alpha \cdot q_{\alpha(\text{red})} - p \sum_{i=1}^{ncs} (\tilde{V}_{i\alpha} \cdot d_{i\alpha}) \quad (84)$$

or

$$\begin{aligned}\rho T \frac{Ds}{Dt} &+ T \nabla_\alpha \cdot \left(\rho \sum_{i=1}^{ncs} s_i Y_i \tilde{V}_{i\alpha} \right) \\ &= p\theta + \rho \frac{De}{Dt} + \sum_{i=1}^{ncs} \left[(\rho Y_i f_{i\alpha} - p d_{i\alpha}) \cdot \tilde{V}_{i\alpha} \right] + \nabla_\alpha \cdot \left(\rho \sum_{i=1}^{ncs} h_i Y_i \tilde{V}_{i\alpha} \right)\end{aligned}\quad (85)$$

Each of the four fundamental transport coefficients appearing the equations $(\mu, \lambda_0, D_{ij}^M, D_i^T)$ may calculated to any desired accuracy, and in particular those occurring in (16). Formally, the transport coefficients are calculated by evaluating the following matrix expressions

$$\eta(\xi + 1) = - \frac{\begin{vmatrix} H^{00} & H^{01} & H^{02} & H^{03} & \dots & H^{0\xi} & X^T \\ H^{10} & H^{11} & H^{12} & H^{13} & \dots & H^{1\xi} & 0 \\ H^{20} & H^{21} & H^{22} & H^{23} & \dots & H^{2\xi} & 0 \\ H^{30} & H^{31} & H^{32} & H^{33} & \dots & H^{3\xi} & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ H^{\xi 0} & H^{\xi 1} & H^{\xi 2} & H^{\xi 3} & \dots & H^{\xi \xi} & 0 \\ X & 0 & 0 & 0 & \dots & 0 & 0 \end{vmatrix}}{\begin{vmatrix} H^{00} & H^{01} & H^{02} & H^{03} & \dots & H^{0\xi} \\ H^{10} & H^{11} & H^{12} & H^{13} & \dots & H^{1\xi} \\ H^{20} & H^{21} & H^{22} & H^{23} & \dots & H^{2\xi} \\ H^{30} & H^{31} & H^{32} & H^{33} & \dots & H^{3\xi} \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ H^{\xi 0} & H^{\xi 1} & H^{\xi 2} & H^{\xi 3} & \dots & H^{\xi \xi} \end{vmatrix}}$$

$$\lambda_0(\xi) = - \frac{\begin{vmatrix} L^{00} & L^{01} & L^{02} & L^{03} & \dots & L^{0\xi} & 0 \\ L^{10} & L^{11} & L^{12} & L^{13} & \dots & L^{1\xi} & X^T \\ L^{20} & L^{21} & L^{22} & L^{23} & \dots & L^{2\xi} & 0 \\ L^{30} & L^{31} & L^{32} & L^{33} & \dots & L^{3\xi} & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ L^{\xi 0} & L^{\xi 1} & L^{\xi 2} & L^{\xi 3} & \dots & L^{\xi \xi} & 0 \\ 0 & X & 0 & 0 & \dots & 0 & 0 \end{vmatrix}}{\begin{vmatrix} L^{00} & L^{01} & L^{02} & L^{03} & \dots & L^{0\xi} \\ L^{10} & L^{11} & L^{12} & L^{13} & \dots & L^{1\xi} \\ L^{20} & L^{21} & L^{22} & L^{23} & \dots & L^{2\xi} \\ L^{30} & L^{31} & L^{32} & L^{33} & \dots & L^{3\xi} \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ L^{\xi 0} & L^{\xi 1} & L^{\xi 2} & L^{\xi 3} & \dots & L^{\xi \xi} \end{vmatrix}}$$

$$D_i^T(\xi) = - \frac{2T}{5P} \frac{\begin{vmatrix} L^{00} & L^{01} & L^{02} & L^{03} & \dots & L^{0\xi} & 0 \\ L^{10} & L^{11} & L^{12} & L^{13} & \dots & L^{1\xi} & X^T \\ L^{20} & L^{21} & L^{22} & L^{23} & \dots & L^{2\xi} & 0 \\ L^{30} & L^{31} & L^{32} & L^{33} & \dots & L^{3\xi} & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ L^{\xi 0} & L^{\xi 1} & L^{\xi 2} & L^{\xi 3} & \dots & L^{\xi \xi} & 0 \\ \delta_i & 0 & 0 & 0 & \dots & 0 & 0 \end{vmatrix}}{\begin{vmatrix} L^{00} & L^{01} & L^{02} & L^{03} & \dots & L^{0\xi} \\ L^{10} & L^{11} & L^{02} & L^{13} & \dots & L^{1\xi} \\ L^{20} & L^{21} & L^{22} & L^{23} & \dots & L^{2\xi} \\ L^{30} & L^{31} & L^{32} & L^{33} & \dots & L^{3\xi} \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ L^{\xi 0} & L^{\xi 1} & L^{\xi 2} & L^{\xi 3} & \dots & L^{\xi \xi} \end{vmatrix}}$$

$$D_{ij}^M(\xi) = -\frac{4T}{25P} \begin{array}{c|cccccc} L^{00} & L^{01} & L^{02} & L^{03} & \dots & L^{0\xi} & \Delta_j^T \\ L^{10} & L^{11} & L^{12} & L^{13} & \dots & L^{1\xi} & 0 \\ L^{20} & L^{21} & L^{22} & L^{23} & \dots & L^{2\xi} & 0 \\ L^{30} & L^{31} & L^{32} & L^{33} & \dots & L^{3\xi} & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ L^{\xi 0} & L^{\xi 1} & L^{\xi 2} & L^{\xi 3} & \dots & L^{\xi \xi} & 0 \\ \delta_i & 0 & 0 & 0 & \dots & 0 & 0 \end{array} \begin{array}{c} L^{00} & L^{01} & L^{02} & L^{03} & \dots & L^{0\xi} \\ L^{10} & L^{11} & L^{12} & L^{13} & \dots & L^{1\xi} \\ L^{20} & L^{21} & L^{22} & L^{23} & \dots & L^{2\xi} \\ L^{30} & L^{31} & L^{32} & L^{33} & \dots & L^{3\xi} \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ L^{\xi 0} & L^{\xi 1} & L^{\xi 2} & L^{\xi 3} & \dots & L^{\xi \xi} \end{array}$$

Formal expressions for the $(ncs \times ncs)$ matrices H^{pq} ($p, q \leq 2$) and L^{pq} ($p, q \leq 3$) are given in the literature^{1, 19, 13}. The variable ξ denotes the order of the approximation and the vectors X , δ_i , and Δ_i are given by $X = \{X_1, X_2, \dots, X_{ncs}\}$, $\delta_i = \{\delta_{i1}, \delta_{i2}, \dots, \delta_{i\ ncs}\}$, $\Delta_i = \{(\delta_{i1} - Y_1), (\delta_{i2} - Y_1), \dots, (\delta_{i\ ncs} - Y_{ncs})\}$. The superscript T denotes transpose. Note that the first approximation to both the partial thermal conductivity and thermal diffusion coefficients vanish identically.

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