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EQUILIBRIUM AND TRANSPORT IN A FULLY IONIZED GAS

by

Wesley Emil Brittin

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TABLE OF CONTENTS

TABLE OF CONTENTS (CONTINUED)

Page

SUMMARY

The physics of fully ionized gases is a topic of great present day interest.[1,2] Although a gas is rarely completely ionized, the effect of neutral particles may in many important cases be neglected,[1,3] so it becomes worthwhile to have a theory of fully ionized gases (plasmas).

The origin of this thesis is due to Professor S. Chapman, who suggested that computations of various equilibrium and transport quantities pertaining to a fully ionized gas be carried out by extending the work of Eddington[4] and of Persico.[5] The groundwork for this problem is discussed in Chapters IV and V. However, basic to the completion of the problem is the solution of a non-linear differential equation (Equation 4.35), which must be solved numerically. The differential equation problem has been programmed for a fast electronic computer at Los Alamos, but various delays have made it impossible to include any numerical results in this thesis.

The long range nature of the forces between charged particles opens to question the validity of the Boltzmann equation approach to transport phenomena in a plasma.[6] Arguments favoring the validity are presented in Chapter IV.

Up to the time of writing this thesis there was no general

theory of transport phenomena in a system of charged particles interacting via the electromagnetic field. A general statistical theory of charged particles and electromagnetic field is presented in Chapters I and II. Chapter I deals with non-equilibrium quantum statistical mechanics in which the Wigner[7] distribution function is utilized. The method of analysis follows that of Kirkwood[8] and his collaborators, but is presented in form suitable for dealing with more general systems than those considered by Kirkwood. Much of the material presented in Chapter I may be found explicitly or implicitly in works of other authors,[9,10] however, the form of the presentation is original and suited to the problem at hand. It is believed that the explicit equations for the basic law of transport are new. Some elementary problems in phase space quantum theory are also given, including a new treatment of the simple harmonic oscillator (Appendix III). The material in Chapter II on the transport phenomena in a system of charged particles is new. Maxwell's equations are shown to be valid for the quantum statistical ensemble averaged fields, and an exact form of the hydromagnetic equations is derived.

Chapter III deals with the fundamental equilibrium properties of a fully ionized gas. The lack of existence of the classicial canonical and microcanonical distributions is discussed, and the need for quantum theory established. The quantum statistical treatment is nearly standard, with emphasis placed upon the grand canonical ensemble. An approximate expression for the exchange energy as a function of temperature is new. The exchange energy is quite small for gases at ordinary densities, but may become important at extreme densities.

The last two Chapters, IV and V, deal with the effective potential problem. The effective potential idea originated with Debye and Hückel,[11] who recognized that a given charge on the average would have near it a preponderance of charge of the opposite sign. The use of an effective potential in kinetic theory of ionized gases is due originally to Rosseland[12] and to Fowler and Guggenheim.[13] The potential equation, as modified by Eddington,[4] is discussed in Chapter IV, and symptotic solutions are found for both small and large distances. The last chapter deals with the problem of numerical evaluation of integrals occuring in the kinetic theory of gases. Chapman's[14] procedure for treating these integrals is generalized to apply to an arbitrary central force potential. An asymptotic theory of scattering is developed and applied to the shielded Coulomb problem. Finally, a method of numerical integration of Stieltjes integrals is developed which has direct application to the kinetic theory integrals.

CHAPTER I

STATISTICAL MECHANICAL THEORY

A. Classical Theory

The basic notion of modern statistical mechanics is that of an ensemble of systems. An ensemble[14] is a hypothetical collection of a large number of dynamical systems, each identical in structure with the actual physical system under consideration. The macroscopic behavior of the system is traditionally identified with the ensemble averaged behavior of the systems comprising a suitable representative ensemble.[15] This averaging technique is quite suitable for equilibrium situations, but must be modified by further "coarse-grained" temporal or phase space averaging in the case of non-equilibrium situations.[8, 15]

The state of the system at a given instant of time is determined by the values q, p,* of the coordinates and momenta. The space of the $q\,p$ variables is the phase space of the system and each point in the phase space corresponds to an instantaneous state of motion of the system. The temporal evolution of the state of motion is described in the phase space by the moving point or trajectory $q(t), p(t)$.

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*q, p represents $q_1 \cdots q_f, p_1 \cdots p_f$ where f is the number of degrees of freedom of the complete dynamical system. The equations of motion are assumed to be in Hamiltonian form, $\dot{p} = -H_q, \dot{q} = H_p$.

The statistical behavior of the dynamical system is described by the distribution function $f(q\,p\,t)$. The distribution function is a probability density in phase space and has the significance that $f\,dq\,dp$ represents the probability that a system, chosen at random from the representative ensemble at time t, will have its coordinates and momenta in the range $q,p\,;\ q+dq, p+dp$ Clearly

$$\int f\,dq\,dp = 1 \qquad 1.1$$

where the integration extends over the complete range of the variables. The Hamiltonian form of the equations of motion implies that the distribution function satisfies Liouville's equation[16]

$$\frac{\partial f}{\partial t} + L f = 0 \qquad 1.2$$

where the operator L is defined by the relation

$$L f = \sum_i \left\{ \frac{\partial H}{\partial p_i}\frac{\partial f}{\partial q_i} - \frac{\partial H}{\partial q_i}\frac{\partial f}{\partial p_i} \right\} \qquad 1.3$$

Equation 1.2 expresses the fact that points representing the ensemble move like points in an incompressible fliud. The ensemble average $\langle g \rangle$ of a function $g(q\,p\,t)$ of the coordinates, momenta, and time is given by the scalar product $\langle f, g \rangle$ of f and g,

$$\langle g \rangle = \langle f, g \rangle \equiv \int f\,g\,dq\,dp, \qquad 1.4$$

in which the range of integration is the entire phase space. The scalar product $\langle f, g \rangle$ is symmetric $\langle f, g \rangle = \langle g, f \rangle$, and has all the usual properties of a symmetric scalar product defined on a real Hilbert space.[17] The rate of change of $\langle g \rangle$ may be expressed by the relation

$$\begin{aligned}\frac{\partial \langle g \rangle}{\partial t} &= \left\langle f, \frac{\partial g}{\partial t} \right\rangle + \left\langle \frac{\partial f}{\partial t}, g \right\rangle \\ &= \left\langle f, \frac{\partial g}{\partial t} \right\rangle - \langle L f, g \rangle \\ &= \left\langle f, \frac{\partial g}{\partial t} \right\rangle - \langle f, L^{+} g \rangle , \qquad 1.5\end{aligned}$$

where L^{+} is the operator which is the adjoint of L[*]. Equation 1.5 may be simplified, since L is skew-symmetric, i.e.,

$$\begin{aligned}L^{+} &= \left\{ \sum_i \left(\frac{\partial H}{\partial p_i} \frac{\partial}{\partial q_i} - \frac{\partial H}{\partial q_i} \frac{\partial}{\partial p_i} \right) \right\}^{+} \\ &= -\sum_i \left(\frac{\partial}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial}{\partial p_i} \frac{\partial H}{\partial q_i} \right) \\ &= -\sum_i \left(\frac{\partial H}{\partial p_i} \frac{\partial}{\partial q_i} + \frac{\partial^2 H}{\partial q_i \partial p_i} - \frac{\partial H}{\partial q_i} \frac{\partial}{\partial p_i} - \frac{\partial^2 H}{\partial p_i \partial q_i} \right) \\ &= -L \qquad 1.6\end{aligned}$$

Therefore, equation 1.5 may be written

$$\frac{\partial \langle g \rangle}{\partial t} = \left\langle f, \frac{\partial g}{\partial t} \right\rangle + \langle f, L g \rangle , \qquad 1.7$$

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[*] It is assumed that the function g is sufficiently well-behaved to ensure the existence of L^{+}.

which expresses the fact that the time derivative of the ensemble average of g is the ensemble average of the quantity $\mathring{g}$ defined by

$$\mathring{g} \equiv \frac{\partial g}{\partial t} + L g . \qquad 1.8$$

Equation 1.7 expresses the basic statistical mechanical law of change, and since observable quantities are associated with ensemble averages, this equation will be associated with the rates of change of observable quantities. The actual macroscopic equations of motion for a complex system are obtained as suitable space-time averages of equations of the type 1.7.[18]

Equation 1.7 may also be used to obtain the equation of motion for the various reduced distribution functions. A reduced distribution function is obtained by integrating f over all save a specified number of coordinates and momenta, and is thus a distribution function in a specified sub phase space. For example, if $\vec{r}_K$, $\vec{p}_K$ are the coordinates and momenta of a specific particle K, a one-particle distribution function $f_K^{(1)}(\vec{r},\vec{p})$ may be defined by the relation[18]

$$f_K^{(1)}(\vec{r},\vec{p}) = \langle f, \delta(\vec{r}-\vec{r}_K)\,\delta(\vec{p}-\vec{p}_K)\rangle \qquad 1.9$$

The equation of motion for $f_K^{(1)}$ is therefore

$$\frac{\partial f_K^{(1)}}{\partial t} = \langle f, L\,\delta(\vec{r}-\vec{r}_K)\,\delta(\vec{p}-\vec{p}_K)\rangle \qquad 1.10$$

Ordinarily the right hand side of equation 1.10 may be expressed in terms of various pair distribution functions. Therefore genuine progress in non-equilibrium statistical mechanics can be made only when reasonable approximation procedures become available for the estimation of pair distribution functions. At the present time there exists no general useful theory.[19] What is needed is an analogue of the Boltzmann equation of kinetic theory which could be applied to the pair distribution functions. Kirkwood has shown,[20] for gases with short range forces, that the time averaged distribution function $\tilde{f}^{(1)} \equiv \frac{1}{\tau}\int_0^{\tau} f^{(1)}(t+s)\,ds$ satisfies the Boltzmann equation. He also has obtained approximations, based upon a generalized Brownian motion concept, for the pair distribution functions. Green,[21] assuming short range forces, obtained a series of approximations for various reduced distribution functions in which multiple collisions are taken into account. His method is essentially an extension of the Ursell-Mayer theory to non-equilibrium theory.

In spite of the fact that there exists at present no general method for evaluating the reduced distribution functions, much information can be obtained from the theory. For example, exact forms for various macroscopic transport phenomena can be obtained.[8,18] Part of this thesis will be devoted to the derivation of the exact laws of transport in a fully ionized gas. Since the quantum theory will be shown, for cases of practical interest, to be formally equivalent to the classical theory, these derivations will be performed after the quantum theory is developed. In this manner one derivation serves in a uniform manner both the classical and quantum theory.

B. Quantum Theory

In the quantum theory a pure state is represented by a wave function* $\psi(q\,t)$ which satisfies Schrödinger's time dependent equation

$$i\hbar\frac{\partial\psi}{\partial t} = \mathcal{H}\psi \qquad 1.11$$

in which $\mathcal{H}$ is the Hamiltonian operator. A mixed state represented by an ensemble of systems, for which a_i is the probability that a system chosen at random from the ensemble be found in a quantum state $\psi_i(q\,t)$, is described by the density matrix

$$\rho(q\,;\,q'\,t) = \sum_i a_i\,\psi_i(q\,t)\,\bar{\psi}_i(q'\,t) \qquad 1.12$$

Observables are represented by operators g , and the expectation

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*For simplicity it is assumed that the quantum mechanical properties of the system can be described by the scalar Schrödinger theory. The analysis in terms of the density matrix is quite general, but the phase space distribution function can be readily defined only if the spin can be neglected in the Hamiltonian; however, for an ionized gas the spin contribution to the Hamiltonian can be neglected.

value of g for the state ψ by the scalar product $\int \bar{\psi} g \psi \, dq$. Thus the ensemble average for the dynamical variable g is expressed by the equation

$$\langle g \rangle = \sum_i a_i \int \bar{\psi}_i \, g \, \psi_i \, dq \qquad 1.13$$

The function $g\psi_i$ may be expressed in terms of the matrix elements $g(q, q')$ of g,

$$g \psi_i(q) = \int \psi_i(q') \, g(q', q) \, dq' \qquad 1.14$$

Therefore

$$\langle g \rangle = \sum_i a_i \iint \bar{\psi}_i(q') \, g(q', q) \, \psi(q) \, dq \, dq'$$

$$= \iint \rho(q \, q') \, g(q', q) \, dq \, dq'$$

or

$$\langle g \rangle = tr\,(\rho g) \,, \qquad 1.15$$

in which $tr\,g$ represents the trace or spur of the matrix g. The density matrix satisfies the equation of motion

$$i\hbar \frac{\partial \rho}{\partial t} = \{ H(q) - H(q') \} \rho \qquad 1.16$$

where $H(q)$ signifies that the operator H is applied to the q variables. Equation 1.16 may also be written in matrix form

$$i\hbar \frac{\partial}{\partial t} \rho(q, q' t) = \int \{ H(q, q'' t) \rho(q'', q' t)$$

$$- \rho(q \, q'' t) \, H(q'', q' t) \} \, dq'' \qquad 1.17$$

or, in terms of the commutator $[\rho, H] = \rho H - H \rho$, as

$$i\hbar \frac{\partial \rho}{\partial t} + [\rho, H] = 0 \qquad 1.18$$

The latter equation is frequently taken to be the quantum analogue of the Liouville equation. However, Wigner[7] has shown that there exists a function $f_w(q\,p\,t)$ which is a closer analogue of the classicial distribution function. The Wigner distribution function is defined by the expression

$$f_w(q\,p\,t) \equiv \int_y e^{2\pi i\, p \cdot y} \rho(q - \pi\hbar y ; q + \pi\hbar y) \qquad 1.19$$

The density matrix is Hermitian, and therefore f_w is a real function, although not necessarily a positive function. If $tr\,\rho = 1$, f_w is normalized to unity, since $\int_{qp} f_w = tr\,\rho = 1$. This distribution function is the closest analogue to the classical distribution function. If the Weyl[22] representation of operators is used, $\langle g \rangle$ is obtained by phase space integration of the product of the classical g and f_w.

$$\langle g \rangle = \langle f_w, g \rangle = \int f_w\, g\, dq\, dp. \qquad 1.20$$

For completeness a proof[23] of relation 1.20 is included here. This proof is based on the ideas of Irving and Zwanzig.[23] The expression 1.15 may be written

$$\langle g \rangle = \int_{q'q''} \delta(q' - q'')\, g(q')\, \rho(q'q'') \qquad 1.21$$

in which $g(q')$ is the quantum mechanical operator representing g, but which acts upon the q' variables of $\rho(q'q'')$. If $g(q\,p)$ is the classical dynamical variable representing g, the Weyl expression for $g(q')$ is given by[23]

$$g(q') = \int_{uvqp} e^{-2\pi i(u\cdot q + v\cdot p)}\, g(q,p)\; e^{2\pi i(u\cdot q' + \frac{\hbar}{i} v\cdot\frac{\partial}{\partial q'})} \qquad 1.22$$

The operator $exp\, 2\pi i(u\cdot q' + \frac{\hbar}{i} v\cdot\frac{\partial}{\partial q'})$ may be split into the product

$$e^{2\pi i(u\cdot q' + \frac{\hbar}{i} v\cdot\frac{\partial}{\partial q'})} = e^{2\pi^2 i\hbar u\cdot v}\, e^{2\pi i u\cdot q'}\, e^{2\pi\hbar\frac{\partial}{\partial q'}} \qquad 1.23$$

This latter expression is reported[23] to be due to McCoy.[24] However, McCoy's paper is not available to the writer, so a one-page proof is given in Appendix I. The use of relation 1.23 in 1.22 leads to the following expression for $g(q')$:

$$g(q') = \int_{uvqp} e^{-2\pi i(u\cdot q + v\cdot p)}\, g(qp)\; e^{2\pi^2 i\hbar u\cdot v}\cdot e^{2\pi i u\cdot q'}\cdot e^{2\pi\hbar v\frac{\partial}{\partial q'}} \qquad 1.24$$

Since $exp(2\pi\hbar v\cdot\frac{\partial}{\partial q'})\rho(q',q'') = \rho(q'+2\pi\hbar v, q'')$, the result of using 1.22 in 1.21 yields the following expression for $\langle g\rangle$:

$$\langle g\rangle = \int_{uvqpq'} e^{-2\pi i(u\cdot q + v\cdot p)}\cdot g(q\,p)\cdot e^{2\pi^2 i\hbar u\cdot v}\, e^{2\pi i u\cdot q'}\, \rho(q'+2\pi\hbar v; q')$$

$$= \int_{uvqpq'} e^{-2\pi i(u\cdot q + v\cdot p)}\, g(q,p)\; e^{2\pi i u\cdot q'}\, \rho(q'+\pi\hbar v; q'-\pi\hbar v) \qquad 1.25$$

However, equation 1.19 may be inverted to give ρ in terms of f_W,

$$\rho(q'+\pi\hbar v; q'-\pi\hbar v) = \int_{p'} e^{2\pi i v\cdot p'} f_W(q; p') \qquad 1.26$$

Therefore, equation 1.25 becomes

$$\langle g\rangle = \int_{uvqpq'p'} e^{2\pi i\{u\cdot(q-q')+v\cdot(p-p')\}} g(q,p) f_W(q'p')$$

$$= \int_{qp} g(q,p)\, f_W(q,p) \,, \qquad 1.27$$

which was to be shown.

The equation of motion for ρ may be used to find that of f_W, with the result that

$$i\hbar \frac{\partial f_W}{\partial t} = \int_y e^{2\pi i p\cdot y}\{\mathcal{H}(u) - \overline{\mathcal{H}}(v)\}\rho(u,v) \qquad 1.28$$

where $u \equiv q - \pi\hbar y$, $v \equiv q + \pi\hbar y$. If ρ in the above expression is replaced by the inverse of equation 1.19, the following equation is obtained:

$$\frac{\partial f_W}{\partial t} + \frac{i}{\hbar}\int_{y.p'} e^{2\pi i p\cdot y}\{\mathcal{H}(u) - \overline{\mathcal{H}}(v)\} f_W\left(\frac{u+v}{2}, p'\right) = 0 \qquad 1.29$$

Equation 1.26 is in a form suitable for the computation of $\dot{f}_W$ for a specific $\mathcal{H}$. However, a matrix form is more suitable for proving general properties of $\dot{f}_W$. The matrix form of 1.26 is expressed by the relation

$$\frac{\partial f_W}{\partial t} = -\frac{i}{\hbar}\int e^{2\pi i p\cdot y}\left[\mathcal{H}(q-\pi\hbar y; q'')\rho(q''; q+\pi\hbar y)\right.$$

$$- \mathcal{H}(q''; q+\pi\hbar y)\rho(q-\pi\hbar y; q'')\Big]$$

$$\frac{\partial f_w}{\partial t} = -\frac{i}{\hbar}\int_{q''yp'} e^{2\pi i p\cdot y}\Big\{\mathcal{H}(q-\pi\hbar y, q'')\cdot e^{i(q''-q-\pi\hbar y)} f_w\Big(\frac{q+q''+\pi\hbar y}{2}, p''\Big) - \mathcal{H}(q''; q+\pi\hbar y)\, e^{-i(q''-q+\pi\hbar y)}\cdot f_w\Big(\frac{q+q''-\pi\hbar y}{2}, p'\Big)\Big\} \qquad 1.30$$

The latter expression may be written in the form

$$\frac{\partial f_w}{\partial t} + \mathcal{L} f_w = 0 \qquad 1.31$$

where

$$\mathcal{L} f_w(qpt) \equiv \int_{q'p'} L(qp; q'p') f_w(q'p'). \qquad 1.32$$

and where the kernel $L(qp; q'p')$ is given by

$$L(qp; q'p') = \frac{i}{\hbar}\int_y e^{-2\pi i y\cdot(p-p')} e^{2i(q'-q)\cdot p'/\hbar}\cdot \mathcal{H}(q-\pi\hbar y; 2q'-q-\pi\hbar) - e^{2\pi i y\cdot(p-p')} e^{-2i(q'-q)\cdot p'/\hbar}\cdot \mathcal{H}(2q'-q-\pi\hbar y; q-\pi\hbar y),$$

or, more symmetrically, by the equation

$$L(qp;q'p') = \frac{i}{\hbar}\int_y e^{-2\pi i y\cdot(p-p')}\, e^{2i(q'\cdot p-q\cdot p')/\hbar}\, \mathcal{H}(q-q'+\pi\hbar y;\, q'-q+\pi\hbar y) - e^{2\pi i y\cdot(p-p')}\, e^{-2i(q'-q)\cdot p'/\hbar}\, \mathcal{H}(q'-q+\pi\hbar y;\, q-q'+\pi\hbar y). \qquad 1.33$$

Because $\mathcal{H}$ is Hermitian, $\mathcal{H}(qq') = \overline{\mathcal{H}}(q'q)$, L is real $L = \overline{L}$ and skew-symmetric

$$L(qp:q'p') = -L(q'p';qp). \qquad 1.34$$

Therefore the quantum mechanical expression for the rate of change of the ensemble average $\langle g\rangle$ may be written in the form

$$\begin{aligned} \frac{\partial}{\partial t}\langle g\rangle &= \left\langle f_w, \frac{\partial g}{\partial t}\right\rangle + \left\langle \frac{\partial f_w}{\partial t}, g\right\rangle \\ &= \left\langle f_w, \frac{\partial g}{\partial t}\right\rangle - \langle \mathcal{L} f_w, g\rangle \\ &= \left\langle f_w, \frac{\partial g}{\partial t}\right\rangle + \langle f_w, \mathcal{L} g\rangle. \end{aligned} \qquad 1.35$$

Equation 1.32 expresses the basic law of change for the quantum mechanical ensemble average $\langle g\rangle$. The rate of change of $\langle g\rangle$ is the ensemble average of the quantity $\overset{\circ}{g}$ defined by

$$\mathring{g} \equiv \frac{\partial g}{\partial t} + \mathcal{L} g \qquad 1.36$$

These last two equations closely resemble the corresponding classical equation 1.7, 1.8. This resemblance becomes formal identity for the class of functions g_c having the property

$$L g_c = \mathcal{L} g_c \qquad 1.37$$

It will be shown that in the case of ionized gases the functions of type g_c form a class large enough to include most dynamical variables of practical interest.

The use of the Wigner distribution function as defined above is limited to systems which can be described by the Schrödinger scalar theory, since, for example, if the density matrix contains spin quantities there is no simple way to define f_w. Further, the existence of non-classical variables complicates matters. If the Hamiltonian of the system does not contain spin-dependent terms, a scalar theory for the density matrix is possible and the Wigner distribution function may be simply defined. This question is considered further in Chapter I, Part D.

C. Phase Space Representation of Quantum Mechanics*

The Wigner distribution function may be employed to give a

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*Some of the results obtained in this section have been obtained previously and in a different manner by Moyal[9] and by Ühlhorn.[10]

complete theory of both quantum statistics and of ordinary quantum mechanics. Further, the transition to the corresponding classical theory is obtained directly by letting $\hbar \rightarrow 0$ in the quantum equations. These assertions will be proved after the operator $\mathcal{L}$ in equation 1.28 is re-expressed in terms of the classical Hamiltonian function $H(q, p)$. The Weyl definition of the Hamiltonian operators $H(u)$, $\overline{H}(v)$ yields the expressions

$$H(u) = \int_{u'v'} \xi(u'v')\, e^{2\pi^2 i\hbar u'\cdot v'} e^{2\pi i u'\cdot u} e^{2\pi\hbar v'\cdot\partial/\partial u} \tag{1.38}$$

$$\overline{H}(v) = \int_{u'v'} \xi(u'v')\, e^{-2\pi^2 i\hbar u'\cdot v'} e^{2\pi i u'\cdot v} e^{-2\pi\hbar v'\cdot\partial/\partial v} \tag{1.39}$$

where ξ is the Fourier transform of H. It follows, therefore, from equation 1.26 that

$$\mathcal{L} f_W = \frac{i}{\hbar} \int_{uvyp'} \xi(u,v)\, e^{2\pi i p\cdot y} e^{2\pi^2 \hbar i u\cdot v}$$

$$e^{2\pi i u\cdot(q - \pi\hbar y)} e^{-2\pi i (y-v)\cdot p'} f_W(q+\pi\hbar v, p')$$

$$+ \text{c.c.}$$

$$= \frac{i}{\hbar} \int_{uv} \xi(uv)\, e^{2\pi i(q\cdot u + p\cdot v)} \cdot f_W(q+\pi\hbar v, p-\pi\hbar u)$$

$$+ \text{c.c.}$$

$$= \frac{i}{\hbar}\, e^{i\frac{\hbar}{2}\left\{\frac{\partial}{\partial q}, \frac{\partial}{\partial p}\right\}} \cdot H f_W + \text{c.c.}^*, \qquad 1.40$$

where the symbol $\left\{\frac{\partial}{\partial q}, \frac{\partial}{\partial p}\right\}$ is defined[9] by the expression

$$\left\{\frac{\partial}{\partial q}, \frac{\partial}{\partial p}\right\} f\, g \equiv \left[\left(\frac{\partial}{\partial q}\frac{\partial}{\partial p'} - \frac{\partial}{\partial p}\frac{\partial}{\partial q'}\right) f(q\,p)\, g(q'p')\right]_{\substack{q=q'\\ p=p'}} \qquad 1.41$$

Therefore $\mathcal{L} f_W$ is expressed symbolically by

$$\mathcal{L} f_W = -\frac{2}{\hbar} \sin \frac{\hbar}{2}\left\{\frac{\partial}{\partial q}, \frac{\partial}{\partial p}\right\} H f_W, \qquad 1.42$$

and the equation of motion 1.28 becomes

$$\frac{\partial f_W}{\partial t} - \frac{2}{\hbar} \sin \frac{\hbar}{2}\left\{\frac{\partial}{\partial q}, \frac{\partial}{\partial p}\right\} H f_W = 0 \qquad 1.43$$

In the limit $\hbar \rightarrow 0$, equation 1.43 becomes

$$\frac{\partial f_W}{\partial t} - \left\{\frac{\partial}{\partial q}, \frac{\partial}{\partial p}\right\} H f_W = 0, \qquad 1.44$$

which is precisely the classical equation of motion 1.2. Equation 1.43 corresponds to the Schrödinger picture, f_W carrying the time dependence. The Heisenberg picture makes use of the time-independent state function $f_W(0)$, the value of f_W at time zero. The

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[*] See Appendix II, p. 126.

solution of equation 1.43, which reduces to $f_W(0)$ at $t = 0$ is expressed by

$$f_W(t) = e^{-\mathcal{L}t} f_W(0) \qquad 1.45$$

(assuming H independent of t) and therefore $\langle g \rangle = \langle f_W(t), g \rangle = \langle e^{-\mathcal{L}t} f_W(0), g \rangle = \langle f_W(0), e^{\mathcal{L}t} g \rangle$ The latter expression serves to introduce the Heisenberg operators

$$g(t) \equiv e^{\mathcal{L}t} g(q, p), \qquad 1.46$$

whose equation of change is

$$\frac{dg}{dt} = \mathcal{L} g, \qquad 1.47$$

or, more generally, if g depends explicitly upon time, the equation of motion

$$\frac{dg}{dt} = \frac{\partial g}{\partial t} + \mathcal{L} g, \qquad 1.48$$

Since

$$\frac{\partial}{\partial t} \langle g(t) \rangle = \left\langle \frac{dg}{dt}, f_W(0) \right\rangle, \qquad 1.49$$

the Heisenberg operator $\frac{dg}{dt}$ corresponds to the Schrödinger operator $\overset{\circ}{g}$ given by equation 1.8.

A stationary state has the property that $\frac{\partial f_W}{\partial t} = 0$, and, hence, according to equation 1.43,

$$\frac{2}{\hbar} \sin \frac{\hbar}{2} \left\{ \frac{\partial}{\partial q}, \frac{\partial}{\partial p} \right\} H f_W = 0. \qquad 1.50$$

Equation 1.50 may also be obtained from the relation

$$\frac{\partial \rho}{\partial t}(qq't) = \{H(q) - \bar{H}(q')\}\rho = 0 \qquad 1.51$$

If the state is pure as well as stationary,[16]

$$H(q)\rho(q,q') = \bar{H}(q')\rho(qq') = E\rho, \qquad 1.52$$

and

$$\int_{q''} \rho(qq'')\rho(q''q') = \rho(q,q') \qquad 1.52a$$

Equation 1.52 may be transformed into the corresponding phase space equation by means of relation 1.19

$$E f_W = E\int_y e^{2\pi i p\cdot y} \rho(q-\pi\hbar y;\, q+\pi\hbar y)$$

$$= \int_y e^{2\pi i p\cdot y} \mathcal{H}(q-\pi\hbar y)\cdot$$

$$\rho(q-\pi\hbar y;\, q+\pi\hbar y) \qquad 1.53$$

The Weyl operator for $\mathcal{H}$ is substituted into the above equation with the result that

$$E f_W = \int_{yuv} e^{2\pi i p\cdot y}\, \xi(u,v)\, e^{2\pi^2 i\hbar u\cdot v}\,.$$

$$e^{2\pi i u\cdot(q-\pi\hbar y)} \rho(q-\pi\hbar y+2\pi\hbar v;\, q+\pi\hbar y) \qquad 1.54$$

where $\xi(uv)$ is the Fourier transform of the classical Hamiltonian $H(qp)$. If ρ in the above equation is replaced by the inverse of equation 1.19, there results

$$E f_w = \int_{yuvp'} e^{2\pi i p\cdot y} \; \xi(u,v) \; e^{2\pi^2 i \hbar u\cdot v}$$

$$e^{2\pi i u\cdot q} \; e^{-2\pi^2 i \hbar u\cdot y} \; e^{-2\pi i p'\cdot(u-v)} f_w(q-\pi\hbar v, p') \qquad 1.55$$

Since

$$\xi(uv) = \int_{q''p''} H(q''p'') \, e^{-2\pi i (uq'' + vp'')}$$

$$E f_w = \int_{yuvp'u''v''} e^{2\pi i p\cdot y} \; e^{-2\pi i u\cdot q''} \; e^{-2\pi i v\cdot p''}$$

$$e^{2\pi i u\cdot q} \; e^{-2\pi^2 i \hbar u\cdot y} \quad e^{-2\pi i p'\cdot(y-v)}$$

$$H(q''p'') \, f_w(q+\pi\hbar v, p') \qquad 1.56$$

The result of integration of the above equation with respect to u is expressed by

$$E f_w = \int_{yvp'q''p''} e^{2\pi i p\cdot y} \; e^{-2\pi i v\cdot p''} \; e^{-2\pi i p'\cdot y}$$

$$e^{2\pi i p'\cdot v} \; \delta(q - \pi\hbar y + \pi\hbar v - q'') H(q''p'') f_w(q+\pi\hbar v, p')$$

$$= \int_{yvp'p''} e^{2\pi i p\cdot y} \; e^{-2\pi i v\cdot p''} \; e^{-2\pi i p'\cdot y} \; e^{2\pi i p'\cdot v}$$

$$H(q-\pi\hbar y+\pi\hbar\nu, p'')\, f_w(q+\pi\hbar\nu, p') \qquad 1.57$$

Therefore, $E f_w = \exp i\frac{\hbar}{2}\{\frac{\partial}{\partial q}, \frac{\partial}{\partial p}\} H f_w$, or since according to equation 1.50, $\sin\frac{\hbar}{2}\{\frac{\partial}{\partial q}, \frac{\partial}{\partial p}\} H f_w = 0$

$$\cos\frac{\hbar}{2}\left\{\frac{\partial}{\partial q}, \frac{\partial}{\partial p}\right\} H f_w = E f_w \; . \qquad 1.58$$

The fact that, for a pure state, ρ is a projection operator may be expressed in terms of f_w. Since $\rho = \rho^2$

$$f_w = \int_y e^{2\pi i p\cdot y} \rho^2(q-\pi\hbar y ; q+\pi\hbar y) \qquad 1.59$$

$$= \int_{y q'} e^{2\pi i p\cdot y} \rho(q-\pi\hbar y ; q')\rho(q' ; q+\pi\hbar y)$$

$$= \int_{y q' p' p''} e^{2\pi i p\cdot y}\, e^{i(q-q'-\pi\hbar y)\cdot p'/\hbar}\, e^{i(q'-q-\pi\hbar y)\cdot p''/\hbar}$$

$$f_w\left(\frac{q+q'-\pi\hbar y}{2}, p'\right) f_w\left(\frac{q+q'+\pi\hbar y}{2}, p''\right) \qquad 1.60$$

Let

$$q+q'-\pi\hbar y = 2(q-\pi\hbar\nu'),\quad q+q'+\pi\hbar y = 2(q+\pi\hbar\nu),$$

or $q' = q+\pi\hbar(\nu-\nu')$, $y = \nu+\nu'$. Then equation 1.60 may be written as the following expression

$$f_w(q, p) = \int_{\nu\nu' p' p''} e^{2\pi i \nu\cdot(p-p')}\, e^{2\pi i \nu'\cdot(p-p'')}$$

$$f_w(q-\pi\hbar\nu'; p')\, f_w(q+\pi\hbar\nu, p''). \qquad 1.61$$

Therefore (see Appendix II),

$$f_W = e^{i\frac{\hbar}{2}\left\{\frac{\partial}{\partial q} \leftarrow \frac{\partial}{\partial p}\right\}} f_W \, f_W \qquad 1.62$$

Equations 1.57 and 1.62 represent the phase space equivalent of the Schrödinger energy eigenvalue problem. Equation 1.62 is the condition that f_W represent a pure state, and equation 1.57 that f_W is an eigenfunction of the energy . Equation 1.62 when integrated over the entire phase space expresses an equivalent[10] condition that the state represented by f_W be pure. This latter condition is expressed by the relation.

$$1 = \int_{qp} f_W$$

$$= \int_{qpq'p'} \delta(q-q')\,\delta(p'-p)$$

$$e^{i\frac{\hbar}{2}\left\{\frac{\partial}{\partial q'}\frac{\partial}{\partial p} - \frac{\partial}{\partial p'}\frac{\partial}{\partial q}\right\}} f_W(q'p')\, f_W(q,p). \qquad 1.63$$

The operator $\left\{\frac{\partial}{\partial q'}\frac{\partial}{\partial p} - \frac{\partial}{\partial p'}\frac{\partial}{\partial q}\right\}$ is Hermitian in the space which is the direct sum of the phase space and itself. Therefore equation 1.63 becomes

$$1 = \int_{qpq'p'} f_W(qp)\, f_W(q'p')\, e^{-i\frac{\hbar}{2}\left(\frac{\partial}{\partial q'}\frac{\partial}{\partial p} - \frac{\partial}{\partial p'}\frac{\partial}{\partial q}\right)} \cdot \delta(q-q')\,\delta(p-p'). \qquad 1.64$$

Since

$$e^{-i\frac{\hbar}{2}\left(\frac{\partial}{\partial q'}\frac{\partial}{\partial p} - \frac{\partial}{\partial p'}\frac{\partial}{\partial q}\right)} \delta(q-q')\,\delta(p-p') =$$

$$\int_{uv} e^{-i\frac{\hbar}{2}\left(\frac{\partial}{\partial q}\cdot\frac{\partial}{\partial p} - \frac{\partial}{\partial p}\cdot\frac{\partial}{\partial q}\right)} e^{2\pi i u\cdot(q-q')} e^{2\pi i v\cdot(p-p')} =$$

$$\int_{uv} e^{-\frac{\hbar}{2}4\pi^2(u\cdot v - v\cdot u)} e^{2\pi i u\cdot(q-q')} e^{2\pi i v\cdot(p-p')} =$$

$$\int_{uv} e^{2\pi i u\cdot(q-q')} e^{2\pi i v\cdot(p-p')} = \delta(q-q')\,\delta(p-p'), \qquad 1.65$$

equation 1.63 reduces to

$$1 = \int_{qp} f_W = \int_{qp} f_W^2 \qquad 1.66$$

As an example of the phase space treatment of quantum mechanics, we consider first the case of a free particle. The Hamiltonian is given by

$$H = \vec{p}^{\,2}/2m \qquad 1.67$$

Therefore,

$$\left\{\frac{\partial}{\partial q}, \frac{\partial}{\partial p}\right\} H f_W = \nabla_r H \cdot \nabla_p f_W - \nabla_p H \cdot \nabla_r f_W$$

$$= -\frac{\vec{p}}{m} \cdot \nabla_r f_W,$$

$$\left\{\frac{\partial}{\partial q}, \frac{\partial}{\partial p}\right\}^2 H f_W = \frac{1}{m} \nabla_r^2 f_W, \qquad 1.68$$

and

$$\left\{\frac{\partial}{\partial q}, \frac{\partial}{\partial p}\right\}^m H f_W = 0 \quad , \quad m > 2 \, . \tag{1.69}$$

The eigenvalue problem in phase space is therefore expressed by the equations

$$-\frac{\vec{p}}{m} \cdot \nabla_r f_W = 0 \tag{1.70}$$

and

$$H f_W - \frac{\hbar^2}{8m} \nabla_r^2 f_W = E f_W \, . \tag{1.70a}$$

Since $\vec{p}$ in equation 1.70 is arbitrary, f_W is independent of $\vec{r}$. This means that f_W does not really exist. However, if the configuration space is made periodic, and if f_W is normalizee in the volume of periodicity, this difficulty disappears. The second equation 1.70a becomes

$$\frac{\vec{p}^{\,2}}{2m} f_W = E f_W \, , \tag{1.71}$$

which has the solution

$$f_W = C \, \delta(\vec{p} - \vec{p}_0) \, , \tag{1.72}$$

$$E = \vec{p}_0^{\,2}/2m \tag{1.73}$$

where $\vec{p}_0$ is arbitrary. The normalization condition is

$$\int f_W \, d\vec{r} \, d\vec{p} = C V = 1 \tag{1.74}$$

or $C = 1/V$. Hence

$$f_W = V^{-1} \, \delta(\vec{p} - \vec{p}_0) \, . \tag{1.75}$$

The use of the definition of f_W in terms of the density matrix serves as a check of equation 1.75. The free particle wave functions in ordinary quantum theory are[26]

$$\psi(\vec{r}) = V^{-1/2}\, e^{i\vec{p}_0\cdot\vec{r}/\hbar} . \qquad 1.76$$

Therefore, according to equation 1.19

$$f_W = \int_{\vec{y}} e^{2\pi i\vec{p}\cdot\vec{y}}\, \psi(\vec{r}-\pi\hbar\vec{y})\, \bar{\psi}(\vec{r}+\pi\hbar\vec{y})$$

$$= V^{-1}\int_{\vec{y}} e^{2\pi i\vec{p}\cdot\vec{y}}\, e^{i\vec{p}_0\cdot(\vec{r}-\pi\hbar\vec{y})-i\vec{p}_0(\vec{r}+\pi\hbar\vec{y})} \qquad 1.77$$

$$= V^{-1}\int_{\vec{y}} e^{2\pi i\vec{y}\cdot(\vec{p}-\vec{p}_0)}$$

$$= V^{-1}\,\delta(\vec{p}-\vec{p}_0) , \qquad 1.78$$

which is in agreement with equation 1.75.

The particle in a box problem would at first sight appear to be a simple problem. However, this is not the case. The problem of the walls cannot be built into the problem as simple boundary conditions on combinations of free particle solutions. A method of solution would be to solve the problem with an analytical potential which is a function of a parameter such that this potential has a limit which is the potential of the box. Such problems cannot be expressed in closed form. The complexity of the box problem is demonstrated by the expression for the result, obtained from the original definition 1.19 of f_W. For a 1-dimensional box of length L,*

$$f_W = C' \int_y e^{2\pi i p y} \sin \frac{\pi n}{L}(x - \pi\hbar y) \sin \frac{\pi n}{L}(x + \pi\hbar y)$$

$$= C \int_{y=0}^{a(x)} \cos 2\pi p y \sin \frac{\pi n}{L}(x - \pi\hbar y) \sin \frac{\pi n}{L}(x + \pi\hbar y) \qquad .79$$

where

$$a(x) = \begin{cases} x \,, & x \leq L/2 \\ x - L/2 \,, & x \geq L/2 \,. \end{cases} \qquad 1.80$$

Therefore

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*The wave function for the nth energy state is[26]

$$\psi(x) = \begin{cases} 0 \,, & x \leq 0 \\ A \sin \pi n x / L \,, & 0 \leq x \leq L \,, \\ 0 \,, & x \geq L \end{cases}$$

$$f_w(x,p) = \left\{ \frac{\sin\left[\left(\frac{p}{\hbar} + \frac{2\pi n}{L}\right) a(x)\right]}{\left(\frac{p}{\hbar} + \frac{2\pi n}{L}\right)} + \frac{\sin\left[\left(\frac{p}{\hbar} - \frac{2\pi n}{L}\right) a(x)\right]}{\left(\frac{p}{\hbar} - \frac{2\pi n}{L}\right)} - 2 \cos\frac{2\pi n x}{L} \, \frac{\sin\left[\frac{p}{\hbar} a(x)\right]}{p/\hbar} \right\}, \qquad 1.81$$

Ühlhorn[10] has shown that for the simple harmonic oscillator f_w may be expressed in terms of Laguerre Polynomials. In Appendix III, pp. 128 , the simple harmonic oscillator is treated using the elegant method of Fock, adapted to phase space.

D. Spin and Statistics

Particles having integral spin obey Bose-Einstein statistics while particles having half odd-integral spin obey Fermi Dirac statistics.[31] The wave functions which represent particles with spin contain spin variables ξ *, in addition to space variables r . The wave functions $\psi(r\ \xi)$ satisfy a Schrödinger equation in which the Hamiltonian operator, in general, depends upon the spin,

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* ξ stands for $\xi_1, \ldots, \xi_N$

$$i\hbar \frac{\partial}{\partial t}\psi(r,\xi t) = \sum_{\xi} H_{\xi\xi'}\psi(r\xi' t) \, . \qquad 1.82$$

The density matrix may now be defined by the relation:

$$\rho(r\xi;\, r'\xi' t) = \sum_{j} a_j\, \psi(r\xi t)\bar{\psi}(r'\xi' t) \qquad 1.83$$

If P is a permutation operator which permutes both space and spin coordinates of indentical particles, the wave functions of appropriate symmetry are characterized by the property

$$P\psi = \lambda_P \psi \quad , \qquad 1.84$$

where $\lambda_P = 1$ for Bose-Einstein systems and $\lambda_P = \sigma_P$, where σ_P is the signature of the permutation P , for Fermi-Dirac systems. The symmetry of the wave functions expressed by equation 1.84 is reflected in that of the density matrix.

$$P\rho = \lambda_P \rho \qquad 1.85$$

Further, if P' is the same permutation applied to the $r'\xi'$ variables,

$$P'\rho = \lambda_P \rho \qquad 1.86$$

However,

$$PP'\rho = \lambda_P^2 \rho = \rho \qquad 1.87$$

It is, therefore, observed that the symmetry properties of the system must be determined by the symmetry of ρ with respect to either the variables $r\xi$ or $r'\xi'$, but not both. A spin-independent density matrix may be defined by the equation

$$\rho(r; r') = \sum_{\xi} \rho(r\xi; r'\xi) \qquad 1.88$$

In general $\rho(r; r')$ does not possess any simple symmetry. The general equation of motion for $\rho(r; r')$ is complicated by the presence of spin terms in the Hamiltonian. However, if the Hamiltonian is diagonal in the spin,

$$H_{\xi\xi'} = \delta_{\xi\xi'} H(r) \, , \qquad 1.89$$

$\rho(r; r')$ satisfies equation 1.16. The Wigner distribution function may be simply defined in this case by relation 1.19. That $\rho(r; r')$ has no simple symmetry may be illustrated by consideration of a system consisting of two identical particles of spin 1/2. Let $\varphi_n^S(\vec{r}_1, \vec{r}_2)$ and $\varphi_n^A(\vec{r}_1, \vec{r}_2)$ be complete sets of symmetric and antisymmetric configuration space wave functions. Then, if the system has a Hamiltonian of the form 1.89, a complete set of admissible states are given in terms of the products[26]

$$\psi_n^S = \varphi_n^S u^A(\xi) \qquad 1.90$$

$$\psi_{nj}^A = \varphi_n^A u_j^S(\xi) \, . \qquad 1.91$$

The super-scripts S, A on the left-hand side of equation 1.91 refer to the spacial symmetry alone. The definition 1.88 gives for $\rho(\vec{r}_1; \vec{r}_2)$ the expression

$$\rho(r;r') = \sum_{n\xi\xi'} a_n \varphi_n^S(r)\bar{\varphi}_n^S u^A(\xi\xi')\bar{u}^A(\xi\xi')$$

$$+ \sum_{mj\xi\xi'} a_{mj} \varphi_m^A(r)\bar{\varphi}_m^A(r') u_j^S(\xi\xi')\bar{u}_j^S(\xi\xi')$$

$$= \sum_n a_n \varphi_n^S(r)\bar{\varphi}_n^S(r')$$

$$+ \sum_{mj} a_{mj}\varphi_m^A(r)\bar{\varphi}_m^A(r') \qquad 1.92$$

where $r : \vec{r}_1, \vec{r}_2$ If φ_n^S, φ_n^A are energy eigenstates, belonging to the same energy E_n a weight of 1 would normally be assigned to each spin state giving the result $a_{mj} = a_m$. It is observed that ρ is the sum of a symmetric and an anti-symmetric part, and hence has no symmetry. (Of course it is symmetric with respect to an interchange of both sets of variables $r, r' \longrightarrow r', r$).

A system consisting of N weakly interacting spin 1/2 particles has for state functions the Slater determinants, which apart from a normalizing factor are given by

$$\psi(r,\xi) = \begin{vmatrix} u_{n_1}(r_1)u_{s_1}(\xi_1) \cdots u_{n_1}(r_N)u_{s_1}(\xi_N) \\ \vdots \qquad\qquad \vdots \\ \\ u_{n_N}(r_1)u_{s_N}(\xi_1) \cdots u_{n_N}(r_N)u_{s_N}(\xi_N) \end{vmatrix} \qquad 1.93$$

where the u_s , $s = \pm 1/2$ are spin 1/2 eigenfunctions. The u_s have the properties

$$\sum_{\xi'} \sigma_{z\,\xi\xi'}\, u_{\pm 1/2}(\xi') = \qquad 1.94$$

where

$$\| \sigma_z \| = \left\| \begin{matrix} 1 & 0 \\ 0 & -1 \end{matrix} \right\| . \qquad 1.95$$

If the spin variables are assigned the values ± 1/2, equations 1.94, 1.95 imply that

$$u_{1/2}(1/2) = u_{-1/2}(-1/2) = 1 \qquad 1.96$$

and

$$u_{+1/2}(-1/2) = u_{-1/2}(1/2) = 0 . \qquad 1.97$$

The assumption that the Hamiltonian is independent of the spin variables leads to the conclusion that the system may be considered to be composed of two distinct kinds of particles[32] corresponding to spin up (u-particles) and spin down (d-particles). Further, the number of each type is a constant of the motion. For a state representing m u-particles and $N-m$ d-particles the wave function 1.93 becomes

$$\Psi = \begin{vmatrix} u_{n_1} u_{1/2}(\xi_1) & \cdots & u_{n_1} u_{1/2}(\xi_N) \\ u_{n_2} u_{1/2}(\xi_1) & \cdots & u_{n_2} u_{1/2}(\xi_N) \\ \vdots & & \vdots \\ u_{n_m} u_{1/2}(\xi_1) & \cdots & u_{n_m} u_{1/2}(\xi_N) \\ u_{n_{m+1}} u_{-1/2}(\xi_1) & \cdots & u_{n_{m+1}} u_{-1/2}(\xi_N) \\ \vdots & & \vdots \\ u_{n_N} u_{-1/2}(\xi_1) & \cdots & u_{n_N} u_{-1/2}(\xi_N) \end{vmatrix} \qquad 1.98$$

The columns of the determinant 1.98 are of the form[32]

$$\begin{pmatrix} u_{n_1} \\ \vdots \\ u_{n_m} \\ 0 \\ \vdots \\ 0 \end{pmatrix} , \quad \xi = 1/2 \qquad 1.99$$

or

$$\begin{pmatrix} 0 \\ \vdots \\ 0 \\ u_{n_{m+1}} \\ \vdots \\ u_{n_N} \end{pmatrix} , \quad \xi = -1/2 , \qquad 1.100$$

Therefore the wave function vanishes unless m of the ξ are plus one half and $N-m$ are minus one half. The value of the wave function in the latter case is[32]

$$\Psi_{m,N-m} = \pm \begin{vmatrix} u_{n_1}(r_{\alpha_1}) & \cdots & u_{n_1}(r_{\alpha_m}) \\ \vdots & & \\ u_{n_m}(r_{\alpha_1}) & \cdots & u_{n_m}(r_{\alpha_m}) \end{vmatrix} \begin{vmatrix} u_{n_{m+1}}(r_{\alpha_{m+1}}) & \cdots & u_{n_{m+1}}(r_{\alpha_N}) \\ \vdots & & \vdots \\ u_{n_N}(r_{\alpha_{m+1}}) & \cdots & u_{n_N}(r_{\alpha_N}) \end{vmatrix} \qquad 1.101$$

where $\alpha_1, \ldots, \alpha_N$ is some permutation of $(1, 2, \ldots\ldots N)$. Equation 1.101 is the configuration space probability amplitude for a specified set of m u-particles and $N-m$ d-particles. It is observed that the m u-particles and $N-m$ d-particles separately satisfy the Pauli exclusion principle. If $r_1, \ldots, r_m$ are assigned to the u-particles and $r_{m+1}, \ldots, r_N$ to the d-particles, the normalized state corresponding to 1.101 is

$$\Psi_{m,N-m} = (m!(N-m)!)^{-1/2}\, \det_m\left(u_{n_i}(r_j)\right) \det_{N-m}\left(u_{n_i}(r_j)\right) \qquad 1.102$$

If P_m is the probability of the system having m spins up, the density matrix consists of terms of the form

$$\sum_m P_m \Psi_{m,N-m}(r)\, \bar{\Psi}_{m,N-m}(r'), \qquad 1.103$$

which again shows that $\rho(r; r')$ has no special symmetry.

If the Hamiltonian has no spin dependence, the probability that a specified electron has its spin up is 1/2, therefore the probability P_m that m electrons have their spins up is $P_m = \binom{N}{m}$. P_m has its maximum value for $m \approx \frac{N}{2}$, and if N is large, the distribution P_m is strongly peaked near this value.

The wave function 1.102 for $m = N/2$ has been used[33] in the statistical treatment of the many electron problem.

For spin zero particles $\rho(r; r')$ is symmetric in each set of variables.

Perhaps the most elegant method of handling the problem of spin and statistics is that of second quantization. To each type ν of particle is associated an operator field $\psi_\nu(\vec{r})$. The field satisfies a commutation relation

$$[\psi_\nu(\vec{r}), \psi_\nu^+(\vec{r}')]_\pm = \delta(\vec{r} - \vec{r}') \qquad 1.104$$

the plus sign holding for Fermions and the minus sign for Bosons. The Hamiltonian involves space integrals of products of the ψ_ν, ψ_ν^+. For example, for identical particles interacting via the Coulomb field

$$H = -\frac{\hbar^2}{2m}\int \psi^+ \nabla^2 \psi \, d\vec{r} +$$

$$\frac{e^2}{2}\iint \frac{\psi^+(\vec{r})\,\psi^+(\vec{r}')\,\psi(\vec{r})\,\psi(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}\, d\vec{r}'. \qquad 1.105$$

The Schrödinger equation for the system is

$$i \hbar \frac{\partial}{\partial t} \Psi = H \Psi \qquad 1.106$$

The Ψ are vectors in a Hilbert space S, and expectation values of operators A are given by scalar products

$$\langle A \rangle = (\Psi, A \Psi) \qquad 1.104$$

If Ψ is a vector in S, an operator $\Psi \Psi^+$ is defined by the expression

$$(\Psi \Psi^+) \Phi = (\Psi, \Phi) \Psi \qquad 1.108$$

where Φ is an arbitrary vector in S. It follows from 1.108 that

$$\begin{aligned} (\Psi \Psi^+ H) \Phi &= \Psi \Psi^+ (H \Phi) \\ &= (\Psi, H \Phi) \Psi \\ &= (H \Psi, \Phi) \Psi \\ &= \left[\Psi \, (H \Psi)^+\right] \Phi \end{aligned} \qquad 1.109$$

The density or statistical ρ is defined by

$$\rho = \sum_j a_j \Psi_j \Psi_j^+ \qquad 1.110$$

where a_j is the probability for the state Ψ_j. It follows from equations 1.106, 1.108, 1.109 and 1.110 that

$$i\hbar \frac{\partial \rho}{\partial t} = H\rho - \rho H \qquad 1.111$$

If Ψ_j form a complete orthonormal set of states in S, the trace of an operator A is defined by

$$\mathrm{tr}\, A = \sum_i (\Psi_i, A\Psi_i). \qquad 1.112$$

If A is an operator, the trace of ρA is equal to the ensemble average of A[25], since

$$\begin{aligned} \mathrm{tr}(\rho A) &= \sum (\Psi_i\ A\rho\Psi_i) \\ &= \sum_{ij} (\Psi_i\ ,\ A a_j \Psi_j \Psi_j^+ \Psi_i) \\ &= \sum_{ij} (\Psi_i, A\Psi_j) a_j (\Psi_i, \Psi_j) \\ &= \sum_i a_i (\Psi_i, A\Psi_i) \\ &= \langle A \rangle \qquad 1.113 \end{aligned}$$

The second quantization procedure will be applied to the equilibrium of a binary gas composed of electrons and bare nuclei.

E. Equilibrium

De Boer[15] has given an excellent survey of the methods customarily employed in equilibrium statistical mechanics. Scheidegger and McKay have considered the quantum statistics of free fields.[34] In this section an outline of the equilibrium theory is given in which the statistical operator ρ is employed,[17] contemplating its use in the equilibrium theory of a binary ionized gas.

The density operator for a canonical ensemble is given by

$$\rho = Z^{-1} e^{-\beta H} \qquad 1.114$$

in which

$$Z = tr\, e^{-\beta H} \qquad 1.115$$

and $\beta = 1/kT$. The Helmholtz free energy F is given by[35]

$$F = \beta^{-1} \ln Z \qquad 1.116$$

The energy U is the ensemble average of H

$$U = Z^{-1}\, tr\, H e^{-\beta H}$$

or,

$$U = -\frac{\partial}{\partial \beta} \ln Z \qquad 1.117$$

Since[36] $F = U - TS$, the entropy is expressed by

$$S = \frac{\partial}{\partial T}\left(\beta^{-1} \ln Z\right) \qquad 1.118$$

Also, since

$$dF = -p\,dV - S\,dT$$

$$p = -\frac{\partial F}{\partial V}$$

$$p = \frac{1}{\beta}\frac{\partial}{\partial V} \ln Z \, . \qquad 1.119$$

Equation 1.117 and 1.119 are referred to as the caloric and thermal equations of state respectively.[15]

An illustration of the use of this formalism is furnished by the problem of non-interacting particles of spin s . The treatment is essentially that of Scheidegger and McKay.[34] It is assumed that the spin s is half-odd integer, so the particles obey the Pauli principle. Let $u_{k\sigma}(\vec{r}\;\xi)$ be a complete set of 1-particle energy eigenfunctions. Then the field operator $\psi(\vec{r}\;\xi)$ may be expanded in terms of $u_{k\sigma}$

$$\psi(\vec{r}\xi) = \sum\nolimits_{k\sigma} u_{k\sigma}\, a_{k\sigma} \qquad 1.120$$

where $a_{k\sigma}$ are the destruction operators for particles in the state $u_{k\sigma}$. The exclusion principle requires[37] that $a_{k\sigma}$ satisfy the anticommutation relations

$$[\, a_{k\sigma} \, , \; a_{k'\sigma'}^{+} \,]_{+} = \delta_{kk'}\, \delta_{\sigma\sigma'} \qquad 1.121$$

The Hamiltonian operator is expressed by

$$H = \sum\nolimits_{k\sigma} E_{k\sigma}\, n_{k\sigma} \qquad 1.122$$

where $n_{k\sigma} = a_{k\sigma}^{+}\, a_{k\sigma}$ and $E_{k\sigma}$ are the 1-particle energy eigenvalues. Therefore the canonical ρ is expressed by

$$\rho = Z^{-1} e^{-\beta \sum_{k\sigma} E_{k\sigma} n_{k\sigma}} \qquad 1.123$$

The trace of ρ is easily obtained by using a representation in which the $n_{k\sigma}$ are diagonal (occupation number representation). Equation 1.121 implies that the eigenvalues of $n_{k\sigma}$ are 0 and 1, hence

$$\begin{aligned} Z &= \sum_{N_{k\sigma}=0,1} e^{-\beta \sum_{k\sigma} E_k N_{k\sigma}} \\ &= \prod_{k\sigma} \sum_{N_{k\sigma}} e^{-\beta E_k N_{k\sigma}} \\ &= \prod_{k\sigma} \left(1 + e^{-\beta E_k}\right) \\ &= \prod_k \left(1 + e^{-\beta E_k}\right)^{2s+1}. \end{aligned} \qquad 1.124$$

The free energy is, therefore,

$$F = -\beta^{-1}(2s+1)\sum_k \ln\left(1 + e^{-\beta E_k}\right). \qquad 1.125$$

For particles in a large volume V, the free energy may be evaluated in terms of known functions.[34]

The average number of particles in the state $u_{k\sigma}$ is

$$\begin{aligned} \langle n_{k\sigma} \rangle &= \sum_{N'_{k'\sigma'}} N_{k\sigma}\, e^{-\beta \sum_{k'\sigma'} E_{k'} N'_{k'\sigma'}} \\ &= e^{-\beta E_k} / 1 + e^{-\beta E_k} \end{aligned} \qquad 1.126$$

or

$$\langle n_{k\delta} \rangle = (1 + e^{\beta E_k})^{-1} , \qquad 1.127$$

Equation 1.127 expresses the average number of particles in the state $u_{k\delta}$ as a function of temperature. It represents the number of particles when equilibrium is truly attained. (E_k must include the rest energy of the particle). Ordinarily equilibrium in the above sense is not realized, and it becomes meaningful to speak of equilibrium of a fixed number N of particles. The situation in the latter case may be handled by restricting the statesto those for which $\sum_{k\delta} N_{k\delta} = N$. Such a restriction corresponds to what may be termed a "particle-microcanonical ensemble," as distinguished from the "particle-uniform-ensemble" used to derive 1.127. The restriction $\sum_{k\delta} N_{k\delta} = N$ makes the evaluation of sums very difficult, so a grand ensemble is introduced to facilitate the handling of the computations. In the grand ensemble the average number of particles is specified, and, if this number N is large, the relative fluctuations from N will be small. The grand ensemble is defined by the statistical operator

$$\rho = Z^{-1} e^{-\beta(H - \mu \sum n_{k\delta})} \qquad 1.128$$

where μ is the chemical potential. The number of particles and the chemical potential are "complementary" in the same sense that temperature and energy are complementary. The average number $\langle N \rangle$ of particles is expressed by

$$\langle N \rangle = \beta^{-1} \frac{\partial}{\partial \mu} \ln Z \quad , \qquad 1.129$$

and the average number of particles in the state u_{ks} is found to be

$$\langle n_{ks} \rangle = \left\{ 1 + e^{\beta(E_k - \mu)} \right\}^{-1} . \qquad 1.130$$

The average number $\langle n_k \rangle$ having energy E_k is

$$\langle n_k \rangle = \frac{2s+1}{1 + e^{\beta(E_k - \mu)}} \qquad 1.131$$

Equations 1.130 and 1.131 are the customary expressions for Fermions.

There has been presented in this chapter an account of the properties of the Wigner distribution functions, as well as an account of equilibrium theory. The Wigner distribution function plays an important role in the modern theory of transport phenomena. Ross and Kirkwood,[27] H. S. Green,[28] and A. W. Saenz[29] have considered the transport equation in quantum statistics based upon the Wigner distribution function. In addition, Green[30] has considered quantum corrections to the classical equilibrium statistical mechanics. The Wigner distribution function is particularly useful in that large portions of classical statistical mechanics can be taken over directly into quantum statistics.

CHAPTER II

TRANSPORT PHENOMENA IN A SYSTEM COMPOSED OF CHARGED PARTICLES

A. Hamiltonian Description

The system is assumed to consist of N charged particles interacting via the electromagnetic field. Any external fields present are assumed to have a macroscopic dependence upon time. Let r : $\vec{r}_1, \dots \vec{r}_N$ be the position vectors of the particles, $e_1, \dots, e_N$ their electric charges, and $m_1, \dots, m_N$ their masses. It is assumed that the particles have no further electrical or mechanical structure, that is, any spins, and associated magnetic moments are neglected. The particle motions are treated non-relativistically since a correct relativistic treatment automatically brings into consideration the additional complication of spin.* The electromagnetic field, however, is treated exactly.

The electric field $\vec{E}$ is written as the sum of three terms

$$\vec{E} = \vec{E}^{T} + \vec{E}^{C} + \vec{E}^{E} \qquad 2.1$$

where $\vec{E}^{T}$ is the transverse part of the field due to the charged particles, $\vec{E}^{C}$ the instantaneous Coulomb part, and $\vec{E}^{E}$ the external part. The instantaneous Coulomb part is expressed by the relation

---

*At least for electrons and other half-odd integer spin particles.

$$\vec{E}^{c} = -\nabla_r \sum_k e_k / |\vec{r} - \vec{r}_k| \quad , \qquad 2.2$$

and $\vec{E}^{T}$ is characterized by the expression

$$\nabla \cdot \vec{E}^{T} = 0 \quad . \qquad 2.3$$

The magnetic field $\vec{B}$ is written

$$\vec{B} = \vec{B}^{I} + \vec{B}^{E} \qquad 2.4$$

where $\vec{B}^{I}$ is the field produced by the particles and $\vec{B}^{E}$ is the external field. The system is enclosed in a large volume $V = L^3$ so that the internal electromagnetic field may be described by a denumerable set of coordinates. Inside V Maxwell's equations are valid and may be written

$$\nabla \cdot \vec{B} = 0 \qquad 2.5$$

$$\nabla \cdot \vec{E} = 4\pi \rho_e \qquad 2.6$$

$$\nabla \times \vec{E} = -\frac{1}{c}\frac{\partial}{\partial t}\vec{B} \qquad 2.7$$

$$\nabla \times \vec{B} = \frac{1}{c}\frac{\partial}{\partial t}\vec{E} + \frac{4\pi}{c}\vec{J}_e \qquad 2.8$$

where

$$\rho_e = \sum_k e_k \, \delta(\vec{r} - \vec{r}_k) \quad , \qquad 2.9$$

and

$$\vec{J}_e = \sum_k e_k \vec{u}_k \, \delta(\vec{r} - \vec{r}_k) , \qquad 2.10$$

$\vec{u}_k$ being the velocity of the k th particle. The external fields satisfy the homogeneous Maxwell equations and may be subtracted out of equations 2.5 to 2.8.

Let

$$\vec{J}_e = \vec{J}_e^{\,c} + \vec{J}_e^{\,T} \qquad 2.11$$

where $\nabla \times \vec{J}^{c} = 0$ and $\nabla \cdot \vec{J}^{T} = 0$. Then equations 2.5, 2.6, 2.7, and 2.8 may be written in terms of $\vec{E}^{T}$, $\vec{B}^{I}$ as the following:

$$\nabla \cdot \vec{B}^{I} = 0 \qquad 2.12$$

$$\nabla \cdot \vec{E}^{c} = 4\pi \rho_e \qquad 2.13$$

$$\nabla \times \vec{E}^{T} = -\frac{1}{c}\frac{\partial}{\partial t}\vec{B}^{I} \qquad 2.14$$

$$\nabla \times \vec{B}^{I} = \frac{1}{c}\frac{\partial}{\partial t}\vec{E}^{T} + \frac{4\pi}{c}\vec{J}^{T} \qquad 2.15$$

Following Heitler[38] a set of real vector functions $\vec{A}_\lambda(\vec{r})$ is introduced, complete in V with respect to transverse vector fields, and with the following properties

$$\int_V \vec{A}_\lambda \cdot \vec{A}_\mu = 4\pi c^2 \delta_{\mu\nu} \qquad 2.16$$

$$\nabla^2 \vec{A}_\lambda + k_\lambda^2 \vec{A}_\lambda = 0 \qquad 2.17$$

$$\nabla \cdot \vec{A}_\lambda = 0 \qquad 2.18$$

In the above equations $\delta_{\mu\nu}$ is the Kronecker delta, and $\vec{k}_\lambda = \frac{2\pi \vec{n}_\lambda}{L}$ where $\vec{n}_\lambda$ is a vector having non-negative integral components. k_λ is related to the angular frequency ω_λ by the relation $\omega_\lambda = c\,k_\lambda$, c being the speed of light. The vector potential $\vec{A}^{I}$ is expressed in terms of $\vec{A}_\lambda$ and the field coordinates

q_λ by the relation,[18]

$$\vec{A}^{I} = \sum_\lambda q_\lambda \vec{A}_\lambda \; , \qquad 2.19$$

which yields the following expressions for $\vec{E}^{T}$ and $\vec{B}^{I}$:

$$\vec{E}^{T} = -\frac{1}{c}\sum_\lambda \dot{q}_\lambda \vec{A}_\lambda \; , \qquad 2.20$$

and

$$\vec{B} = \sum_\lambda q_\lambda \nabla \times \vec{A}_\lambda \; . \qquad 2.21$$

The current density $\vec{J}^{T}$ may be expanded in the series

$$J^{T} = \sum_\lambda J_\lambda \vec{A}_\lambda \qquad 2.22$$

where the coefficients $J_\lambda(t)$ are determined by using the orthogonality relations 2.16.

Since

$$\vec{J}_e = \sum_\lambda J_\lambda \vec{A}_\lambda + \vec{J}^{c} \; , \qquad 2.23$$

$$J_\lambda = \frac{1}{4\pi c^2}\int_V (\vec{J}_e - \vec{J}_c)\cdot\vec{A}_\lambda \qquad 2.24$$

The contribution from $\vec{J}c$ is zero, since

$$\int_V \vec{J}^{c}\cdot\vec{A}_\lambda = -\frac{1}{k_\lambda^2}\int_V (\nabla^2\vec{A}_\lambda)\cdot\vec{J}_c$$

$$= -\frac{1}{k_\lambda^2}\int_V \vec{A}_\lambda\cdot\nabla^2\vec{J}_c \qquad 2.25$$

However, $\nabla\times(\nabla\times\vec{J}c) = \nabla\nabla\cdot\vec{J}^{c} - \nabla^2\vec{J}^{c} = 0$ and, therefore

$$\int_V \vec{J}^c \cdot \vec{A}_\lambda = -\frac{1}{k_\lambda^2}\int_V \vec{A}_\lambda \cdot \nabla\nabla\cdot\vec{J}^c$$

$$= \frac{1}{k_\lambda^2}\int_V (\nabla\cdot\vec{A}_\lambda)(\nabla\cdot\vec{J}^c)$$

$$= 0 \; . \qquad 2.26$$

The coefficients $\mathcal{J}_\lambda$ may now be expressed by the relation

$$\mathcal{J}_\lambda = \frac{1}{4\pi c^2}\int_V \vec{J}_e \cdot \vec{A}_\lambda$$

$$= \frac{1}{4\pi c^2}\sum_k \int_V \vec{A}_\lambda \cdot \vec{u}_k \, \delta(\vec{r} - \vec{r}_k)$$

$$= \frac{1}{4\pi c^2}\sum_k \vec{A}_\lambda(\vec{r}_k) \cdot \vec{u}_k \qquad 2.27$$

Since

$$\nabla \times \vec{B}^r = \sum_\lambda q_\lambda \nabla\times(\nabla\times\vec{A}_\lambda)$$

$$= -\sum_\lambda q_\lambda \nabla^2\vec{A}_\lambda$$

$$= \sum_\lambda q_\lambda k_\lambda^2 \vec{A}_\lambda \, , \qquad 2.28$$

a system of equations equivalent to Maxwell's equations is given by the set

$$\ddot{q}_\lambda + \omega_\lambda^2 q_\lambda = \sum_k \frac{e_k}{c} \vec{u}_k \cdot \vec{A}_\lambda(\vec{r}_k) \qquad 2.29$$

The Hamiltonian H for the coupled particle and electromagnetic field system is given by[38]

$$H = \sum_k \frac{1}{2m_k} \left(\vec{P}_k - \frac{e_k}{c}\vec{A}(\vec{r}_k)\right)^2$$

$$+ \mathcal{V}(r) + \frac{1}{2}\sum_\lambda \left(P_\lambda^2 + \omega_\lambda^2 q_\lambda^2\right), \qquad 2.30$$

where

$$\vec{A}(\vec{r}_k) = \vec{A}^{\epsilon}(\vec{r}_k) + \sum_\lambda q_\lambda \vec{A}_\lambda(\vec{r}_k), \qquad 2.31$$

is the vector potential at the position of the k th particle, and

$$\mathcal{V} = \mathcal{V}^{\epsilon} + \frac{1}{2}\sum_{i \neq k} e_i e_k |\vec{r}_i - \vec{r}_k|^{-1} \qquad 2.32$$

is the total potential energy. Hamilton's equations of motion for the system are

$$\dot{\vec{r}}_k \equiv \vec{u}_k = \frac{1}{m_k}\left(\vec{P}_k - \frac{e_k}{c}\vec{A}(\vec{r}_k)\right) \qquad 2.33$$

$$\dot{\vec{P}}_k = \frac{e_k}{c}\vec{u}_k \cdot \left(\vec{A}(\vec{r}_k)\overleftarrow{\nabla}_{r_k}\right) - \nabla_{r_k}\mathcal{V} \qquad 2.34$$

$$\dot{q}_\lambda = P_\lambda \qquad 2.35$$

$$\dot{P}_\lambda = -\omega_\lambda^2 q_\lambda + \sum_k \frac{e_k}{c}\vec{u}_k \cdot \vec{A}_\lambda(\vec{r}_k) \qquad 2.36$$

The symbol $\overleftarrow{\nabla}$ signifies the usual gradient operator acting upon the quantity on the left.

The distribution function f is a function of $r, P, q_\lambda, P_\lambda, t$ and the Liouville operator L defined by the relation 1.3 is given by the expression

$$
\begin{aligned}
Lf = -\left\{\frac{\partial}{\partial q}, \frac{\partial}{\partial p}\right\} H f = \\
\sum_k \vec{u}_k \cdot \nabla_{r_k} f + \sum_\lambda P_\lambda \frac{\partial f}{\partial q_\lambda} + \\
\sum_k \left[\frac{e_k}{c} \vec{u}_k \cdot \vec{A}(\vec{r}_k) - V\right] \overleftarrow{\nabla}_{r_k} \cdot \nabla_{P_k} f + \\
\sum_{\lambda k} \frac{e_k}{c} \vec{u}_k \cdot \vec{A}_\lambda(\vec{r}_k) \frac{\partial f}{\partial P_\lambda} - \\
\sum_\lambda \omega_\lambda^2 q_\lambda \frac{\partial f}{\partial P_\lambda} ,
\end{aligned}
\qquad 2.36a
$$

where it is to be understood that $\overleftarrow{\nabla}$ does not act upon $\vec{u}_k$.

A formal difficulty appears in that the distribution function is a function of infinitely many variables. This difficulty may be circumvented by employing an arbitrarily large cut-off value for the number of field coordinates. However, all results of practical interest will be expressed in terms of reduced distribution functions having small numbers of variables, so the formal difficulty appears only in the basic equations. Until a valid approximation procedure to estimate the various reduced distribution functions is found, this theory is not useful for the computation of numerical values. Nevertheless it is a useful theory for the derivation of the basic macroscopic equations of transfer.

It is convenient to introduce a new distribution function f^* which is a function of $r, u, q_\lambda, P_\lambda, t$ The Jacobian of the transformation $r, P, q_\lambda, P_\lambda \rightarrow r, u, q_\lambda, P_\lambda$ is, using an obvious notation,

$$J = \begin{vmatrix} \frac{\partial \vec{r}_i}{\partial \vec{r}_j}, & \frac{\partial \vec{u}_i}{\partial \vec{r}_j}, & \frac{\partial q_\lambda}{\partial \vec{r}_j} & \frac{\partial P_\lambda}{\partial \vec{r}_j} \\ 0 & \frac{1}{m_i}\frac{\partial \vec{P}_i}{\partial \vec{P}_j} & \cdots & \\ & & & \\ & & & \frac{\partial P_\lambda}{\partial P_{\lambda}} \end{vmatrix}$$

$$= \prod_K 1/m_K \; . \tag{2.37}$$

Therefore, since f is a scalar density in phase space,

$$f^* = \left(\prod_K \frac{1}{m_K} \right) f \;, \tag{2.38}$$

and f^* is normalized to the same value as f,

$$\int f^* dr\, du\, dq_\lambda\, dP_\lambda = \int f\, dr\, dP\, dq_\lambda\, dP_\lambda \tag{2.39}$$

The distribution function f^* satisfies the Liouville equation

$$\frac{\partial f^*}{\partial t} + L^* f^* = 0 . \tag{2.40}$$

Since under the above change of variables

$$\begin{aligned}
&\nabla_{p_k} \longrightarrow \nabla_{p_k} \\
&\nabla_{r_k} \longrightarrow \nabla_{r_k} - \frac{e_k}{c}\left(\nabla_{r_k}\vec{A}(\vec{r}_k)\right)\cdot\nabla_{u_k} \\
&\frac{\partial}{\partial p_\lambda} \longrightarrow \frac{\partial}{\partial p_\lambda} \\
&\frac{\partial}{\partial q_\lambda} \longrightarrow \frac{\partial}{\partial q_\lambda} - \sum_k \frac{e_k}{c}\,\frac{\partial \vec{A}(\vec{r}_k)}{\partial q_\lambda}\cdot\nabla_{u_k} ,
\end{aligned} \tag{2.41}$$

L^* is found to be

$$\begin{aligned}
L^* f^* = {} & \sum_k \vec{u}_k\cdot\nabla_{r_k} f^* + \sum_\lambda p_\lambda \frac{\partial f^*}{\partial q_\lambda} + \\
& \sum_k \frac{1}{m_k}\left\{\vec{X}_k + e\vec{E}(\vec{r}_k) + \frac{e_k}{c}\vec{u}_k\times\vec{B}(\vec{r}_k)\right\}\cdot\nabla_{u_k} f^* \\
& + \sum_\lambda\left\{\sum_k \frac{e_k}{c}\vec{u}_k\cdot\vec{A}_\lambda(\vec{r}_k) - \omega_\lambda^2 q_\lambda\right\}\frac{\partial f^*}{\partial p_\lambda} ,
\end{aligned} \tag{2.42}$$

where $\vec{X}_k$ is the value of the non-electrical external force at the position $\vec{r}_k$. The average value $\langle g\rangle$ of any function $g = g(r, u, q_\lambda, p_\lambda)$ may be expressed as

$$\langle g \rangle = (f^*, g) \qquad 2.43$$

where (f^*, g) is the symmetric scalar product

$$(f^*, g) = \int_{r, u, q_\lambda, p_\lambda} f^* g \qquad 2.44$$

The Liouville operator L^* is skew-symmetric with respect to the scalar product 2.44,

$$(L^* f^*, g) = -(f^*, L^* g). \qquad 2.45$$

Therefore,

$$\begin{aligned} \frac{\partial \langle g \rangle}{\partial t} &= \left(f^*, \frac{\partial g}{\partial t}\right) + \left(\frac{\partial f^*}{\partial t}, g\right) \\ &= \left(f^*, \frac{\partial g}{\partial t}\right) - (L^* f^*, g) \\ &= \left(f^*, \frac{\partial g}{\partial t}\right) + (f^*, L^* g). \end{aligned} \qquad 2.46$$

The relation 2.46 is the basic classical equation of transport. The derivation of expressions for the law of change for specific dynamical variables may be accomplished by the use of equation 2.46. These derivations are postponed until after the corresponding quantal expressions are established, since, for the class of dynamical variables of immediate interest, the quantal and classical expressions are formally the same. The quantal expressions, however, make use of quantal (Wigner) distribution functions f_W, f_W^* which replace f, f^* in equations 1.7, 2.46.

The quantum mechanical Hamiltonian is obtained from the classical Hamiltonian by the replacement

$$\vec{P}_K \rightarrow \frac{\hbar}{i} \nabla_{r_K} \quad ,$$
$$P_\lambda \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial q_\lambda} \quad ; \qquad 2.47$$

therefore the quantum mechanical Hamiltonian is expressed by

$$H = \sum_K \frac{1}{2m_K} \left(\frac{\hbar}{i} \nabla_{r_K} - \frac{e_K}{c} \vec{A}(\vec{r}_K) \right)^2$$

$$+ U(r) + \frac{1}{2} \sum_\lambda \left\{ \left(\frac{\hbar}{i} \frac{\partial}{\partial q_\lambda} \right)^2 + \omega_\lambda^2 q_\lambda^2 \right\} . \qquad 2.48$$

The wave functions $\psi(q, t)$ are functions of the coordinates $q: \vec{r}_1, \ldots, \vec{r}_N, q_\lambda$ and the time. t. The quantum mechanical Liouville operator given by equation 1.42 may be expressed as

$$\mathcal{L} f_W = \frac{2}{\hbar} H \sin \frac{\hbar}{2} \{ \overleftarrow{\nabla}_p \cdot \overrightarrow{\nabla}_q - \overleftarrow{\nabla}_q \cdot \overrightarrow{\nabla}_p \} f_W \, , \qquad 2.49$$

where H is the classical Hamiltonian2. 30. Equation 2. 49 may be written in the form

$$\mathcal{L} f_W = \frac{2}{\hbar} H \{ \sin(\frac{\hbar}{2} \overleftarrow{\nabla}_p \cdot \nabla_q) \cos(\frac{\hbar}{2} \overleftarrow{\nabla}_q \cdot \nabla_p)$$

$$- \cos\left(\frac{\hbar}{2} \overleftarrow{\nabla}_p \cdot \nabla_q\right) \sin\left(\frac{\hbar}{2} \nabla_q \cdot \nabla_p\right) \Big\} f_W \qquad 2.50$$

or using the equation 2. 30, in the form

$$\mathcal{L} f_W = \sum_k \left\{ \frac{\vec{p}_k}{m_k} - \frac{e_k}{c} \vec{A}(\vec{r}_k) \cos\left(\frac{\hbar}{2} \overleftarrow{\nabla}_q \cdot \nabla_p\right) \right\} \cdot \nabla_{r_k} f_W$$

$$+ \sum_\lambda p_\lambda \frac{\partial f_W}{\partial q_\lambda} +$$

$$-\left\{ \sum_k \frac{1}{2m_k} \left(\vec{p}_k - \frac{e_k}{c} \vec{A}(\vec{r}_k)\right)^2 + V(r) + \frac{1}{2} \sum_\lambda \omega_\lambda^2 q_\lambda^2 \right\} \frac{\hbar}{2} \sin\left(\frac{\hbar}{2} \nabla_q \cdot \nabla_p\right) f_W \qquad 2.51$$

In the limit $\hbar \to 0$, equation 2. 51 reduces to the classical equation 2. 36.

A class of dynamical variables sufficiently general for many applications consists of functions g_c of the form

$$g_c = g_0(q) + \sum_a g_a(q) p_a + \sum_k \sum_l a_{kl} \vec{u}_k \vec{u}_l \qquad 2.52$$

where the a_{kl} are independent of q p . For such functions

$$\mathcal{L} g_c = L g_c \qquad 2.53$$

and the classical and quantal equations of transport are formally identical. For such functions it is again convenient to transform from the r p q_λ p_λ variables to the $r, u, q_\lambda, p_\lambda$ variables, with the result

$$\frac{\partial}{\partial t} \langle g_c \rangle = \left(f_W^*, \frac{\partial g_c}{\partial t}\right) + \left(f_W^*, L^* g_c\right), \qquad 2.54$$

which is formally identical with equation 2.46. The remainder of this chapter will deal with the applications of equation 2.46 or its formal equivalent equation 2.54.

B. Maxwell's Equations

The charge density at a point $\vec{r}$ is defined by the relation

$$g_c = \sum_k e_k \, \delta(\vec{r} - \vec{r}_k) \; . \qquad 2.55$$

If the average value (f_w^*, g_c) is designated by ρ_e, then according to equation 2.54,

$$\begin{aligned} \frac{\partial \rho_c}{\partial t} &= \left(f_w^*, \; L^* \sum_k e_k \, \delta(\vec{r} - \vec{r}_k)\right) \\ &= \left(f_w^*, \; \sum_\ell \vec{u}_\ell \cdot \nabla_{\vec{r}_\ell} \sum_k e_k \, \delta(\vec{r} - \vec{r}_k)\right) \\ &= -\nabla \cdot \left(f_w^*, \; \sum_\ell e_\ell \, \delta(\vec{r} - \vec{r}_\ell) \vec{u}_\ell\right) \end{aligned} \qquad 2.56$$

The average value $\vec{J}_e$ of the electric current density is defined by the relation

$$\vec{J}_e = \left(f_w^*, \; \sum_\ell e_\ell \vec{u}_\ell \, \delta(\vec{r} - \vec{r}_\ell)\right). \qquad 2.57$$

Therefore, equation 2.56 may be written

$$\frac{\partial \rho_e}{\partial t} + \nabla \cdot \vec{J}_e = 0 \qquad 2.58$$

Equation 2.58 expresses the law of conservation of charge in terms of the quantum mechanical ensemble averaged charge and current densities. The classical and quantum mechanical expressions are formally the same, the only difference occurring in the distribution functions f^*, f_W^*.

The internal magnetic field intensity is expressed by

$$g_c = \vec{B}^I(\vec{r}) = \sum_\lambda q_\lambda \nabla\times\vec{A}_\lambda(\vec{r}), \tag{2.59}$$

and, therefore,

$$\begin{aligned}\frac{1}{c}\frac{\partial}{\partial t}\langle\vec{B}^I(\vec{r})\rangle &= \frac{1}{c}\left(f_W^*,\ L^*\sum_\lambda q_\lambda\nabla\times\vec{A}_\lambda\right)\\ &= \frac{1}{c}\left(f_W^*,\ \sum_{\lambda'} p_{\lambda'}\frac{\partial}{\partial q_{\lambda'}}\sum_\lambda q_\lambda\nabla\times\vec{A}_\lambda(\vec{r})\right)\\ &= \nabla\times\left(f_W^*,\ \frac{1}{c}\sum_\lambda p_\lambda\vec{A}_\lambda(\vec{r})\right)\end{aligned} \tag{2.60}$$

Since $\vec{E}^T = -\frac{1}{c}\sum_\lambda p_\lambda\vec{A}_\lambda(\vec{r})$, equation 2.60 may be written in the following manner:

$$\frac{1}{c}\frac{\partial}{\partial t}\langle\vec{B}^I\rangle = -\nabla\times\langle\vec{E}^T\rangle \tag{2.61}$$

The average value of the instantaneous Coulomb field is given by the equation

$$\langle\vec{E}^c\rangle = \left(f_W^*,\ \sum_k e_k\frac{\vec{r}-\vec{r}_k}{|\vec{r}-\vec{r}_k|^3}\right) \tag{2.62}$$

and since $\nabla \times \frac{\vec{r}}{r^3} \equiv 0$, it follows that

$$\nabla \times \langle \vec{E}^c \rangle = 0 \qquad 2.63$$

The combination of equations 2.16 and 2.63 and the corresponding equation for the external fields leads to the Maxwell equation

$$\nabla \times \langle \vec{E} \rangle + \frac{1}{c}\frac{\partial}{\partial t}\langle \vec{B} \rangle = 0 \qquad 2.64$$

The internal transverse electric field is given by

$$g_c = -\frac{1}{c}\sum_\lambda P_\lambda \vec{A}_\lambda , \qquad 2.65$$

and, hence

$$\frac{1}{c}\frac{\partial}{\partial t}\langle \vec{E}^r \rangle = -\frac{1}{c^2}\Big(f_w^*,$$

$$\Sigma_{\lambda'}\Big[\Sigma_K \frac{e_K}{c}\vec{u}_K \cdot \vec{A}(\vec{r}_k) - \omega_{\lambda'}^2 q_{\lambda'}\Big]\frac{\partial}{\partial P_{\lambda'}}\sum_\lambda P_\lambda \vec{A}_\lambda(\vec{r}')\Big) =$$

$$-\frac{1}{c^2}\Big(f_w^*, \Sigma_\lambda \Big\{\Sigma_K \frac{e_K}{c}\vec{u}_K \cdot \vec{A}_\lambda(\vec{r}_k) - \omega_\lambda^2 q_\lambda\Big\}\vec{A}_\lambda(\vec{r}')\Big) =$$

$$-\frac{4\pi}{c}\Big(f_w^*, \frac{1}{4\pi c^2}\Sigma_\lambda \Sigma_K e_K \vec{u}_K \cdot \vec{A}_\lambda(\vec{r}_k)\vec{A}_\lambda\Big)$$

$$+\Big(f_w^*, \Sigma_\lambda k_\lambda^2 q_\lambda \vec{A}_\lambda(\vec{r}')\Big). \qquad 2.66$$

The last equation may be simplified by the use of the identities

$\nabla \times (\nabla \times \vec{A}_\lambda) = -\nabla^2 \vec{A}_\lambda = k_\lambda^2 \vec{A}_\lambda$ and $\vec{J}^T = \frac{1}{4\pi c^2} \sum_\lambda \sum_k e_k \vec{u}_k \cdot \vec{A}_\lambda(\vec{r}_k) \vec{A}_\lambda(\vec{r})$. There results

$$\frac{1}{c}\frac{\partial}{\partial t}\langle \vec{E}^T \rangle = -\frac{4\pi}{c}\langle \vec{J}^T \rangle + \nabla \times \langle \vec{B} \rangle \qquad 2.67$$

where $\langle \vec{J}^T \rangle$ represents the ensemble average of the transverse electric current density.

If g_c is the instantaneous Coulomb field $g_c = \sum_k e_k \frac{\vec{r}-\vec{r}_k}{|\vec{r}-\vec{r}_k|^3}$ it follows that

$$\frac{1}{c}\frac{\partial}{\partial t}\langle \vec{E}^c \rangle = \left(f_w^*, \sum_k \frac{e_k}{c} \vec{u}_k \cdot \nabla\nabla \frac{1}{|\vec{r}-\vec{r}_k|} \right) \qquad 2.68$$

Equation 2.68 may be simplified by the application of Fourier analysis.

Let

$$\frac{1}{r} = \int e^{2\pi i \vec{k}\cdot\vec{r}} f(\vec{k})\, d\vec{k} \qquad 2.69$$

Then

$$f(\vec{k}) = \int e^{-2\pi i \vec{k}\cdot\vec{r}} \frac{d\vec{r}}{r} = \frac{1}{\pi k^2}, \qquad 2.70$$

and, therefore,

$$\frac{1}{|\vec{r}-\vec{r}_k|} = \frac{1}{\pi} \int e^{2\pi i \vec{k}\cdot(\vec{r}-\vec{r}_k)} \frac{d\vec{k}}{k^2} \qquad 2.71$$

The gradient of the above expression is

$$\nabla \frac{1}{|\vec{r}-\vec{r}_K|} = 2i \int e^{2\pi i \vec{k}\cdot(\vec{r}-\vec{r}_K)} \frac{\vec{k}\, d\vec{k}}{k^2} \qquad 2.72$$

and $\nabla\nabla \frac{1}{|\vec{r}-\vec{r}_K|}$ is, therefore,

$$-4\pi \int_{\vec{k}} \frac{\vec{k}\,\vec{k}}{k^2}\, e^{2\pi i \vec{k}\cdot(\vec{r}-\vec{r}_K)} \qquad 2.73$$

The right hand side of equation 2.68 may now be written in the form $-\frac{4\pi}{c}(f_w^*, \vec{J}^c)$ where $\vec{J}^c$ is defined by the relation

$$\vec{J}^c \equiv \sum_K e_K \int_{\vec{k}} \vec{u}_K\cdot \frac{\vec{k}\,\vec{k}}{k^2}\, e^{2\pi i \vec{k}\cdot(\vec{r}-\vec{r}_K)} \qquad 2.74$$

Since $\vec{u}_K\cdot\vec{k}\,\vec{k}/k^2$ is the projection of $\vec{u}_K$ upon $\vec{k}$, $\vec{J}^e$ is the longitudinal electric current density. Equation 2.68, therefore, becomes

$$\frac{1}{c}\frac{\partial}{\partial t}\langle \vec{E}^c\rangle = -\frac{4\pi}{c}\langle \vec{J}^c\rangle. \qquad 2.75$$

The total average current density $\vec{J}_e$ is the sum $\langle \vec{J}^r\rangle + \langle \vec{J}^c\rangle$, and, if equations 2.67, 2.75 are combined with the corresponding external field equations there results the second Maxwell equation

$$\nabla\times\langle\vec{B}\rangle = \frac{4\pi}{c}\vec{J}_e + \frac{1}{c}\frac{\partial}{\partial t}\langle\vec{E}\rangle \qquad 2.76$$

Clearly, $\nabla\cdot\langle\vec{B}\rangle = 0$, and

$$\nabla\cdot\langle\vec{E}\rangle = \nabla\cdot\langle\vec{E}^c\rangle =$$

$$\nabla \cdot \left(f_W^*, \sum_k e_k \frac{\vec{r}-\vec{r}_k}{|\vec{r}-\vec{r}_k|^3} \right) =$$

$$\left(f_W^*, \sum_k e_k \nabla \cdot \frac{\vec{r}-\vec{r}_k}{|\vec{r}-\vec{r}_k|^3} \right) =$$

$$\left(f_W^*, \sum_k e_k 4\pi \delta(\vec{r}-\vec{r}_k) \right) =$$

$$4\pi \rho_e , \qquad 2.77$$

which demonstrates that Maxwell's equations are valid for the quantum mechnical ensemble-averaged fields

These equations have the form of the usual equations of the macroscopic electromagnetic field. However, as has been emphasized by Irving and Kirkwood,[18] the true macroscopic fields should not be identified with the ensemble averaged fields, but with suitable space-time averages of the ensemble averaged fields. The equations derived above correspond more precisely to the Maxwell-Lorentz equations. The form of the equations is preserved under space-time averaging, so the usual macroscopic Maxwell equations are valid for a system of charged particles.

C. Hydromagnetic Equations

The mass density of particles of type ν is defined by

$$g_c = m_\nu \sum_{(\nu)} \delta(\vec{r} - \vec{r}_k) , \qquad 2.78$$

where the symbol $\sum_{(\nu)}$ designates summation over all k belonging to type ν The mass current density for particles of type ν is defined by

$$g_c = m_\nu \sum_{(\nu)} \vec{u}_k \, \delta(\vec{r} - \vec{r}_k) . \qquad 2.79$$

Let ρ_{m_ν} be the ensemble average of the mass density 2.78, and $\rho_{m_\nu} \vec{u}_\nu$ that of the current density 2.79. Considerations of the same type as those which led to the laws of conservation of charge lead to the equation of continuity for particles of type ν ,

$$\frac{\partial}{\partial t} \rho_{m_\nu} + \nabla \cdot (\rho_{m_\nu} \vec{u}_\nu) = 0 . \qquad 2.80$$

The exact form of the hydromagnetic equations is obtained by application of the law of change 2.46 to the momentum density $m_\nu \sum_{(\nu)} \vec{u}_k \, \delta(\vec{r} - \vec{r}_k)$ for particles of type ν . The result is expressed by

$$\frac{\partial}{\partial t} (\rho_{m_\nu} \vec{u}_\nu) = (f_W^*, \; m_\nu \sum_{(\nu)} \vec{u}_k \cdot \nabla_{r_k} \delta(\vec{r} - \vec{r}_k)) +$$

$$(f_W^*, \sum_{(\nu)} \{ e_k \vec{E}_k + \frac{e_k}{c} \vec{u}_k \times \vec{B}_k + \vec{X}_k \} \, \delta(\vec{r} - \vec{r}_k)). \qquad 2.81$$

The kinetic stress tensor $\underset{\sim}{\sigma}_\nu$ is defined by

$$\underset{\sim}{\sigma}_\nu(\vec{r}) = -m_\nu\left(f_W^*, \sum_{(\nu)}(\vec{u}_k-\vec{u}_\nu)(\vec{u}_k-\vec{u}_\nu)\delta(\vec{r}-\vec{r}_k)\right), \quad 2.82$$

and the number density n_ν of particles of type ν by

$$n_\nu(\vec{r}) = \left(f_W^*, \sum_{(\nu)}\delta(\vec{r}-\vec{r}_k)\right) = N_\nu f_{W\nu}^{(1)}(\vec{r}) \quad 2.83$$

where N_ν is the total number of particles of type ν. The use of the definitions $\underset{\sim}{\sigma}_\nu$, n_ν in equation 2.81 leads to the following equation for $\frac{\partial}{\partial t}(\rho_{m_\nu}\vec{u}_\nu)$;

$$\frac{\partial}{\partial t}(\rho_{m_\nu}\vec{u}_\nu) = \nabla\cdot\underset{\sim}{\sigma}_\nu - \rho_{m_\nu}\vec{u}_\nu\vec{u}_\nu$$

$$+ n_\nu\vec{X}_\nu + \rho_{e_\nu}\vec{E}^E + \frac{\vec{J}_{e_\nu}}{c}\times\vec{B}^E$$

$$+\left(f_W^*, e_\nu\sum_{(\nu)}\left\{\vec{E}_k^I + \frac{\vec{u}_k}{c}\times\vec{B}^I(\vec{r}_k)\right\}\delta(\vec{r}-\vec{r}_k)\right), \quad 2.84$$

where ρ_{e_ν} is the electric charge density for particles of type ν,

$$\rho_{e_\nu} = e_\nu\left(f_W^*, \sum_{(\nu)}\delta(\vec{r}-\vec{r}_k)\right) = n_\nu e_\nu, \quad 2.85$$

and $\vec{J}_{e_\nu}$ is the electric current density for particles of type ν,

$$\vec{J}_{e_\nu} = n_\nu e_\nu\vec{u}_\nu . \quad 2.86$$

If the mobile operator $\frac{d^\nu}{dt} = \frac{\partial}{\partial t} + \vec{u}_\nu\cdot\nabla$ is introduced, equation 2.84 may be written

$$\rho_{m\nu} \frac{d^{\nu}}{dt} \vec{u}_{\nu} = \nabla \cdot \underset{\sim}{\sigma}_{\nu} + n_{\nu} \vec{X}_{\nu} +$$

$$\rho_{e\nu} \vec{E}^{E} + \frac{\vec{J}_{e\nu}}{c} \times \vec{B}^{E} + \vec{G}_{\nu} \tag{2.87}$$

where $\vec{G}_{\nu}$ is defined by the relation

$$\vec{G}_{\nu} = e_{\nu} \sum_{(\nu)} \left(f_{W}^{*}, \left\{ \vec{E}_{K}^{I} + \frac{\vec{u}_{K}}{c} \times \vec{B}_{K} \right\} \delta(\vec{r} - \vec{r}_{K}) \right) \tag{2.88}$$

$$= N_{\nu} e_{\nu} \Big(f_{W}^{*}, \Big\{ \sum_{\mu} N_{\mu} e_{\mu} (\vec{r} - \vec{r}_{\mu}) / |\vec{r} - \vec{r}_{\mu}|^{3}$$

$$- \frac{1}{c} \sum_{\lambda} P_{\lambda} \vec{A}_{\lambda}(\vec{r}) + \frac{\vec{u}_{\nu}}{c} \times \sum_{\lambda} q_{\lambda} \nabla \times \vec{A}_{\lambda}(\vec{r}) \Big\} \cdot$$

$$\delta(\vec{r} - \vec{r}_{\nu}) \Big) . \tag{2.89}$$

If the fields $\Delta\vec{E}$, $\Delta\vec{B}$ are defined by the relations

$$\vec{E} = \langle \vec{E} \rangle + \Delta \vec{E} \tag{2.90}$$

and

$$\vec{B} = \langle \vec{B} \rangle + \Delta \vec{B} \tag{2.91}$$

equations 2.87 may be written in the form

$$\rho_{m\nu} \frac{d^{\nu}}{dt} \vec{u}_{\nu} = \nabla \cdot \underset{\sim}{\sigma}_{\nu} + n_{\nu} \vec{X}_{\nu} +$$

$$\rho_{e\nu} \langle \vec{E} \rangle + \frac{\vec{J}_{e\nu}}{c} \times \langle \vec{B} \rangle + \vec{P}_{\nu} , \tag{2.92}$$

where P_ν is defined by

$$P_\nu = e_\nu \sum_{(\nu)} \left(f_W^*, \left\{ \Delta \vec{E}_K + \frac{\vec{u}}{c}_K \times \Delta \vec{B}_K \right\} \delta(\vec{r}-\vec{r}_K) \right) \qquad 2.93$$

Equations 2.87 or 2.92 are exact forms of the hydromagnetic equations. The quantum hydromagnetic equations and classical hydromagnetic equations have precisely the same form, only the distribution functions f^*, f_W^* being different. The form 2.92 may be compared with the equations customarily considered exact for a gas.[1] Spitzer's equations have the same form as equations 2.92. However they are not the same, since Spitzer's $\vec{P}_\nu$ represents a momentum transfer due to "collisions", and to the extent that collisions are meaningful for a completely ionized gas the collision term corresponds (ignoring magnetic interactions) to the entire Coulomb term,

$$e_\nu \left(f_W^*, \sum_{(\nu)} \frac{\vec{r}-\vec{r}_K}{|\vec{r}-\vec{r}_K|^3} \delta(\vec{r}-\vec{r}_K) \right), \qquad 2.94$$

of equation 2.88. If there were collisions of a non-electrical type, $\vec{P}_\nu$ of equation 2.93 would contain terms corresponding to them, but in addition has terms corresponding to fluctuations of the electric and magnetic fields from their average values.

The following pair distribution functions are introduced:

$$f^{(2)}_{\mu\nu}(\vec{r}_a, \vec{r}_b) = \left(f_W^*, \delta(\vec{r}_\mu - \vec{r}_a)\delta(\vec{r}_\nu - \vec{r}_b) \right) \qquad 2.95$$

$$f^{(2)}_{\nu\lambda}(\vec{r}_a, P_{\lambda'}) = \left(f_W^*,\ \delta(\vec{r}_\nu - \vec{r}_a)\,\delta(P_{\lambda'} - P_\lambda)\right) \qquad 2.96$$

and

$$f^{(2)}_{\nu\lambda}(\vec{r}, \vec{u}, g_{\lambda'}) = \left(f_W^*, \delta(\vec{r}_\nu - \vec{r}_a)\,\delta(\vec{u}_\nu - \vec{u})\,\delta(g_{\lambda'} - g_\lambda)\right), \qquad 2.97$$

in which $\vec{r}_\mu$ $\vec{u}_\mu$ signify any coordinate and velocity of type μ. The value of $f^{(2)}$ is independent of which coordinate or velocity of given type is chosen since f_W^* is a symmetric function of identical particle coordinates

$$f_W^*(\cdots \vec{r}_\mu \vec{u}_\mu \cdots \vec{r}_{\mu'} \vec{u}_{\mu'} \cdots) = f_W^*(\cdots \vec{r}_{\mu'} \vec{u}_{\mu'} \cdots \vec{r}_\mu \vec{u}_\mu \cdots), \qquad 2.98$$

since the density matrix has the property

$$\rho(\cdots \vec{r}_k \cdots \vec{r}_\ell \cdots ; \cdots \vec{r}_{k'} \cdots \vec{r}_{\ell'} \cdots) =$$

$$\rho(\cdots \vec{r}_\ell \cdots \vec{r}_k \cdots ; \cdots \vec{r}_{\ell'} \cdots \vec{r}_{k'} \cdots), \qquad 2.99$$

If the pair distribution functions 2.95, 2.96 and 2.97 are introduced into the expression 2.88 for $\vec{G}_\nu$ there results

$$\vec{G}_\nu = N_\nu e_\nu \sum_\mu N_\mu e_\mu \int \frac{\vec{r} - \vec{r}_\mu}{|\vec{r} - \vec{r}_\mu|^3} f^{(2)}_{\nu\mu}(\vec{r}, \vec{r}_\mu)\, d\vec{r}_\mu$$

$$- \frac{N_\nu e_\nu}{c} \sum_\lambda \vec{A}_\lambda(\vec{r}) \int P_\lambda\, f^{(2)}_{\nu\lambda}(\vec{r}, P_\lambda)\, dP_\lambda$$

$$- \frac{N_\nu e_\nu}{c} \sum_\lambda (\nabla \times \vec{A}_\lambda(\vec{r})) \times \int \vec{u}\, g_\lambda\, f^{(2)}_{\nu\lambda}(\vec{r}\vec{u}g_\lambda)\, d\vec{u}\, dg_\lambda \qquad 2.100$$

Equations representing the transport of other quantities can be obtained by the methods employed here. The theory is useful for deriving general relationships, like the hydromagnetic equations, but at the present time cannot be used to compute numerical values. The reason for this lack is that, so far, the theory is exact and thus depends upon the exact solutions of the equations of motion for the entire system. These equations are, of course, quite intractable. An approximate procedure is needed to estimate reduced distribution functions. The present status of the theory is analogous to a kinetic theory of gases for which a Boltzmann equation exists, but the form of the collision terms is completely unknown. Possible avenues of approach will be discussed later.

CHAPTER III

EQUILIBRIUM PROPERTIES OF A FULLY IONIZED GAS

A. Classical Theory

The classical Hamiltonian for a system composed of charged particles is expressed by*

$$H = \sum_k \vec{p}_k^{\,2}/2m_k + \frac{1}{2}\sum_{k\neq l}\sum \frac{e_k e_l}{r_{kl}} \quad , \qquad 3.1$$

where $r_{kl} = |\vec{r}_k - \vec{r}_l|$. At equilibrium the canonical distribution function is given by

$$\rho(r,p) = e^{-\beta(H-F)} \quad , \qquad 3.2$$

F being the Helmholtz free energy. The normalization

$$\int_{r,p} \rho = 1 , \qquad 3.3$$

yields for F the expression

$$e^{-\beta F} = \int_{r,p} e^{-\beta H} , \qquad 3.4$$

The presence of charges of opposite sign, $e_a e_b < 0$, in 3.1 leads to the conclusion that the integral in equation 3.4 diverges at least as rapidly as the integral,

$$\lim_{a \to 0} \int_a e^{\frac{1}{r}} r^2 \, dr \quad : \qquad 3.5$$

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*Magnetic interactions are here neglected.

therefore, as is known,[39] the classical canonical distribution function does not exist. The physical interpretation of this mathematical result is that, according to classical statistical mechanics, the equilibrium state is "completely collapsed."

Another way of looking at this situation is to ignore the non-existence of ρ , and "compute" the average value of the potential energy $\mathcal{V}$. The average value of $\mathcal{V}$ is given by the expression

$$\langle \mathcal{V} \rangle = \int_r \mathcal{V} e^{-\beta \mathcal{V}} \Big/ \int_r e^{-\beta \mathcal{V}} \qquad 3.6$$

$$= -\frac{\partial}{\partial \beta} \ln \int_r e^{-\beta \mathcal{V}} . \qquad 3.7$$

However, $\mathcal{V}$ is homogeneous of degree -1,

$$\beta \mathcal{V}(r) = \mathcal{V}(r/\beta) ; \qquad 3.8$$

therefore,

$$\langle \mathcal{V} \rangle = -\frac{\partial}{\partial \beta} \ln \int_r e^{-\mathcal{V}(r/\beta)}$$

$$= -\frac{\partial}{\partial \beta} \ln \int_u e^{-\mathcal{V}(u)} \cdot \beta^{3N}$$

$$= -3NkT. \qquad 3.9$$

According to the Virial theorem, the pressure of the gas is given by

$$PV = NkT + \frac{1}{3}\langle \mathcal{V} \rangle \qquad 3.10$$

Hence,

$$PV = NkT - NkT = 0 \qquad 3.11$$

The "result" that PV is zero is in agreement with the statement that the gas is completely collapsed. Equation 3.9 is independent of the attractive or repulsive nature of the inverse square law of force. If the charges are all of one sign, $PV = 0$ corresponds to the completely expanded state. If walls are introduced in the latter situation, the result 3.9 does not obtain, since the wall potential introduces an inhomogeneity into $\mathcal{V}$.

The presence of arbitrary large negative values of the potential energy is responsible for the divergence of the canonical distribution function. The canonical distribution function permits arbitrarily large negative values for the total energy. On the other hand, the microcanonical distribution function pertains to a fixed value E of the total energy. The possibility that the microcanonical distribution function may exist appears to offer some hope for a classical theory, but it will be shown that in general the microcanonical distribution function also fails to exist.

The microcanonical distribution function is defined by the equation

$$\rho = C \, \delta \, (E - H) \, , \qquad 3.12$$

where δ is the 1-dimensional Dirac delta function, and C is the normalization constant

$$C^{-1} = \int_{rp} \delta \, (E - H(r,p)) \qquad 3.13$$

New coordinates and momenta $\bar{r}, \bar{p}$ are introduced by means of the transformation

$$\begin{aligned} \vec{\bar{r}}_1 &= \vec{r}_1 \\ &\vdots \\ \vec{\bar{r}}_N &= \vec{r}_N \end{aligned} \qquad 3.14$$

$$\begin{aligned} \bar{P}_{1x} &= H \\ \bar{P}_{1y} &= P_{1y} \\ \bar{P}_{1z} &= P_{1z} \\ \vec{\bar{P}}_2 &= \vec{P}_2 \\ &\vdots \\ \vec{\bar{P}}_N &= \vec{P}_N \end{aligned} \qquad 3.14$$

The Jacobian of the transformation 3.14 is expressed by the relation

$$J = \begin{vmatrix} 1 & & & & & & & \\ & 1 & & & & & & \\ & & \ddots & & & & & \\ & & & \frac{\partial H}{\partial P_{1x}} & \frac{\partial H}{\partial P_{1y}} & \cdots & & \\ & & & & 1 & & & \\ & & & & & 1 & & \\ & & & & & & \ddots & \\ & & & & & & & 1 \end{vmatrix} = \frac{\partial H}{\partial P_{1x}} \qquad 3.15$$

and, therefore, equation 3.13 becomes

$$C^{-1} = \int_{r\,H\,p'} \delta(E-H) \Big/ \left| \frac{\partial H}{\partial P_{1x}} \right| \qquad 3.16$$

where $p' : P_{1y}, P_{1z}, P_{2x}, \ldots, P_{Nz}$. The integration with respect to H is carried out, with the result

$$C^{-1} = m_1 \int_{H=E} \frac{dr\,dP'}{|P_{1x}|} \qquad 3.17$$

Let

$$\vec{P}_K = \sqrt{2m_K}\,\vec{p}_K \qquad 3.18$$

and

$$p^2 = \sum_K \vec{p}_K^{\,2} - p_{1x}^2 \, ; \qquad 3.19$$

then equation 3.17 may be written

$$C^{-1} = \frac{1}{2}\left\{\prod_K (2m_K)\right\}^{3/2} \int_{E-V-p^2 \geq 0} \left\{E-V-p^2\right\}^{-1/2} dr\, d^{(n)}p \qquad 3.20$$

where $d^{(n)}p = dp_{1y}\, dp_{1z} \cdots dp_{Nz}$. So far as the integration with respect to $\vec{p}$ is concerned, the integrand is a function of p alone, so the following spherical polar coordinates are introduced into the $n = 3N-1$ dimensional momentum space:

$$\begin{aligned} p_{y_1} &= p \cos\vartheta_1 \\ p_{1z} &= p \sin\vartheta_1 \cos\vartheta_2 \\ &\vdots \\ p_{Ny} &= p \sin\vartheta_1 \sin\vartheta_2 \cdots \sin\vartheta_{n-2} \cos\vartheta_{n-1} \\ p_{Nz} &= p \sin\vartheta_1 \sin\vartheta_2 \cdots \sin\vartheta_{n-2} \sin\vartheta_{n-1} \end{aligned} \qquad 3.21$$

where $0 \leq \vartheta_K \leq \pi$, $K = 1, \ldots, n-2$ and $0 \leq \vartheta_{n-1} \leq 2\pi$. Expressed in terms of the solid angle $d\Omega$, the volume element $d^{(n)}p$ is

$$d^{(n)}p = p^{n-1}\,dp\,d\Omega \qquad 3.22$$

where

$$d\Omega = \sin^{n-2}\vartheta_1 \sin^{n-3}\vartheta_2 \cdots \sin\vartheta_{n-2}\,d\vartheta_1 \cdots d\vartheta_{n-1} \qquad 3.23$$

The total solid angle Ω is

$$\Omega = \int_0^{2\pi} d\vartheta_{n-1} \int_0^{\pi} \sin\vartheta_{n-2}\,d\vartheta_{n-2} \cdots \int_0^{\pi} \sin^{n-2}\vartheta_1\,d\vartheta_1$$

$$= 2\pi^{n/2} / \Gamma(n/2) , \qquad 3.24$$

and, therefore, the integral 3.20 may be written

$$C^{-1} = \frac{\pi^{n/2}}{\Gamma(n/2)} \left\{ \Pi_K (2m_K) \right\}^{3/2} \int dr \int_0^{\sqrt{E-V}} \frac{p^{n-1}\,dp}{\sqrt{E-V-p^2}}$$

$$= \frac{\pi^{n/2}}{\Gamma(n/2)} \left\{ \Pi_K (2m_K) \right\}^{3/2} \frac{\sqrt{\pi}}{2} \frac{\Gamma(n/2)}{\Gamma(n+1/2)} \int_{E-V \geqslant 0} (E-V)^{\frac{n-1}{2}} dr$$

or

$$C^{-1} = \frac{1}{2} \left\{ \Pi_K (2m_K) \right\}^{3/2} \frac{\pi^{\frac{n+1}{2}}}{\Gamma\left(\frac{n+1}{2}\right)} \int_{E-V \geqslant 0} (E-V)^{\frac{n-1}{2}} dr$$

$$= \frac{1}{2} \left\{ \Pi_K (2m_K) \right\}^{3/2} \frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} \int_{E-V \geqslant 0} (E-V)^{\frac{3N}{2}-1} dr , \qquad 3.26$$

The integral over configuration space in expression 3.26 diverges for $\mathcal{N} > Z$ and, hence, the microcanonical distribution function fails to exist. For two particles the microcanonical distribution function exists. However, the average value of the potential energy diverges; for the average potential energy for two particles of opposite charge is given by

$$\langle V \rangle \sim - \int \frac{1}{r_{12}} \left(E + \frac{e^2}{r_{12}} \right) d\vec{r}_1 \, d\vec{r}_2 \bigg/ \int \left(E + \frac{e^2}{r_{12}} \right)^2 d\vec{r}_1 \, d\vec{r}_2 \qquad 3.27$$

$$\sim - \infty \qquad 3.27$$

The origin of the divergence of the classical partition functions lies in the potential energy term of the Hamiltonian. According to quantum theory, the possible energy values of the system are bounded from below, and this classical difficulty disappears. It is, therefore, clear that there exists no valid classical statistical theory of charged particles. Any valid theory must be based upon a quantum theoretical foundation. This conclusion does not mean that classical theory has no application to the problem. For example, the classical virial theorem, under conditions of high temperature, is a valid approximation provided that the average energy is computed using quantum theory.

This section will be completed with a derivation of the equation of state, using the classical virial theorem for a system of charged particles including magnetic interactions up to order $1/c^2$. The force on the k th particle due to electric and magnetic interactions is expressed by

$$\vec{F}_k = \sum_j{}' e_k e_j (\vec{r}_k - \vec{r}_j)/r_{kj}^3 \quad +$$

$$\frac{1}{c^2}\sum_j{}' e_k e_j \vec{u}_k \times [\vec{u}_j \times (\vec{r}_k - \vec{r}_j)]/r_{kj}^3 + \cdots \quad 3.28$$

The virial due to the forces 3.28 is given by

$$\mathcal{V} = \sum_k \vec{F}_k \cdot \vec{r}_k$$

$$= \sum_{jk}{}' e_k e_j \vec{r}_k \cdot (\vec{r}_k - \vec{r}_j)/r_{kj}^3 \quad +$$

$$\frac{1}{c^2} \sum_{jk}{}' \frac{e_k e_j}{r_{kj}^3} \{ (\vec{r}_k \cdot \vec{u}_j)(\vec{u}_k \cdot (\vec{r}_k - \vec{r}_j))$$

$$- \vec{r}_k (\vec{r}_k - \vec{r}_j) \vec{u}_k \cdot \vec{u}_j \}$$

$$= \frac{1}{2} \sum_{jk}{}' e_k e_j / r_{kj} \quad +$$

$$\frac{1}{2c^2}\sum_{jk}{}' \frac{e_k e_j}{r_{kj}^3}\left\{(\vec{r}_{jk}\cdot\vec{u}_k)(\vec{u}_j\cdot\vec{r}_{jk})-r_{jk}^2(\vec{u}_k\cdot\vec{u}_j)\right\}$$

$$\equiv \mathcal{V} + \frac{1}{c^2}\mathcal{W}$$

The equation of state for a system of charged particles is, therefore

$$PV = NkT + \frac{1}{3}\langle \mathcal{V}\rangle + \frac{1}{3c^2}\langle \mathcal{W}\rangle + \cdots \qquad 3.29$$

where

$$\mathcal{W} = \frac{1}{2}\sum_{jk}{}' \frac{e_j e_k}{r_{jk}^3}\left\{\vec{r}_{jk}\cdot\vec{u}_k\,\vec{u}_j\cdot\vec{r}_{jk} - r_{jk}^2\,\vec{u}_j\cdot\vec{u}_k\right\} \qquad 3.30$$

Except at extremely high temperatures (where relativistic effects cannot be neglected) the magnetic contribution $\frac{1}{3c^2V}\langle \mathcal{W}\rangle$ to the pressure is nil, and to a very high degree of accuracy equation 3.29 may be written

$$PV = NkT + \frac{1}{3}\langle \mathcal{V}\rangle \qquad 3.31$$

The correction $\frac{1}{3}\langle \mathcal{V}\rangle$ to the perfect gas law is not large. An estimate of $\langle \mathcal{V}\rangle$ can be obtained by computing the potential energy of a uniformly distributed system of charges. The contribution to $\langle \mathcal{V}\rangle$ from a strictly uniform distribution of charge is, of course, zero for a neutral gas. However, fluctuations will produce a charge density of order of magnitude

$$\Delta\rho \approx \sqrt{N}\, e/V \qquad 3.32$$

and, consequently, a contribution to the energy of magnitude.

$$\langle V \rangle \approx - N e^2/R \tag{3.33}$$

where R is a linear dimension of the container. Therefore,

$$PV \approx NkT\left(1 - \frac{e^2}{RkT}\right) \tag{3.34}$$

For $R = 1$ cm., the correction to PV/NkT is approximately $1.6^{-3}/T$, which is quite small.

That the estimate 3.34 is of the correct order of magnitude for a uniformly distributed system of charged particles may be demonstrated in another way. Consider a binary gas composed of N_e electrons and N_Z nuclei of charge Ze. The electrostatic energy is given by the expression

$$V = \sum_{i<j}^{N_e} \frac{e^2}{r_{ij}} + \sum_{k<l}^{N_Z} \frac{Z^2 e^2}{r_{kl}} - \sum_{i,k} \frac{Z e^2}{r_{ik}} \quad . \tag{3.35}$$

The assumption of uniformity implies that the average of the reciprocal distance between any two particles is the same. Hence,

$$\langle V \rangle = \frac{1}{2}\left\{N_e(N_e-1) + Z^2 N_Z(N_Z-1) - Z N_e N_Z\right\}\left\langle \frac{e^2}{r} \right\rangle \tag{3.36}$$

The condition of electrical neutrality is $N_e = Z N_Z$ so equation 3.36 becomes

$$\langle V \rangle = - \frac{Z+1}{2} N_e e^2 \left\langle \frac{1}{r} \right\rangle . \tag{3.37}$$

For a sphere of radius R,

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{V^2} \iint \frac{d\vec{r}\, d\vec{r}'}{|\vec{r}-\vec{r}'|} = \frac{6}{5R} \qquad 3.38$$

Therefore,

$$\langle V \rangle = -\frac{3}{5}(Z+1)\, e^2/R \qquad 3.39$$

The tendency of negative charges to swarm around positive charges (Debye effect) will produce a contribution to the potential energy. This effect will be considered in some detail in Chapter IV.

B. Quantum Theory

The grand ensemble statistical operator for a binary gas is given by the equation

$$\rho = Z^{-1} e^{-\beta(\mathcal{H} - \mu^1 \mathcal{N}^1 - \mu^2 \mathcal{N}^2)} \qquad 3.40$$

In equation 3.40, μ^1, μ^2 represent the chemical potentials of the two constituents, $\mathcal{H}$ is the Hamiltonian operator, and $\mathcal{N}^1, \mathcal{N}^2$ are total number of particle operators. If ψ^1, ψ^2 are the quantized wave fields for the two constituents, the Hamiltonian may be expressed as[37]

$$\mathcal{H} = -\frac{\hbar^2}{2m}\int_{\vec{r}} \psi^{1\dagger}\nabla^2\psi^1 - \frac{\hbar^2}{2M}\int_{\vec{r}} \psi^{2\dagger}\nabla^2\psi^2 +$$

$$\frac{e^2}{2}\iint_{\vec r \vec r'}\left[\psi^1(\vec r)\psi^1(\vec r')\right]^{+}\psi^1(\vec r)\psi^1(\vec r')/|\vec r-\vec r'|$$

$$+\frac{Ze^2}{2}\iint_{\vec r \vec r'}\left[\psi^2(\vec r)\psi^2(\vec r')\right]^{+}\psi^2(\vec r)\psi^2(\vec r')/|\vec r-\vec r'|$$

$$-Ze^2\iint \psi^{2+}(\vec r)\psi^2(\vec r)\psi^{1+}(\vec r')\psi^1(\vec r')/|\vec r-\vec r'| \quad 3.41$$

Let the subscript 1 refer to electrons, and the subscript 2 to nuclei of charge Ze. Then ψ^1, ψ^2 satisfy the commutation relations

$$[\psi^1(\vec r), \psi^{2+}(\vec r')]_+ = \delta(\vec r-\vec r'), \quad 3.42$$

$$[\psi^2(\vec r), \psi^{2+}(\vec r')]_\pm = \delta(\vec r-\vec r') \quad 3.43$$

$$[\psi^1(r), \psi^2(r')]_- = [\psi^1, \psi^{2+}]_- = 0, \quad 3.44$$

where the plus sign in 3. 38 holds for odd A nuclei and the minus sign for even A nuclei. If φ_n^1, φ_n^2 form complete sets of 1-particle wave functions, the wave fields $\psi^k, k=1,2$ may be expressed in terms of destruction operators a_n^k

$$\psi^k = \sum_n \varphi_n^k a_n^k, \quad 3.45$$

$$\psi^{k+} = \sum_n \bar\varphi_n^k a_n^{k+}, \quad 3.46$$

The functions φ_n^k are chosen to be free-particle eigen functions, which satisfy the equation

$$-\frac{\hbar^2}{2m_K}\nabla^2\varphi_n^K = \frac{P_n^2}{2m_K}\varphi_n^K = E_n^K\varphi_n^K \qquad 3.47$$

In terms of a_n^K, a_n^{K+} the Hamiltonian 3.36 is

$$\begin{aligned} H = {} & \sum_{nK} E_n^K n_n^K + \\ & \sum_{ijk\ell K} \bar{\ell}_{ijk\ell}^{K} (a_i^K a_j^K)^+ (a_\ell^K a_k^K) \\ & + \sum_{ijk\ell} \bar{\ell}_{ijk\ell}^{12} a_i^{1+} a_j^1 a_k^{2+} a_\ell^2 , \end{aligned} \qquad 3.48$$

where

$$\bar{\ell}_{ijk\ell}^{1} \equiv \frac{e^2}{2}\iint_{\vec r\vec r'} \frac{\bar{\varphi}_i^1(\vec r)\bar{\varphi}_j^1(\vec r')\varphi_k^1(\vec r)\varphi_\ell^1(\vec r')}{|\vec r-\vec r'|} \qquad 3.49$$

and

$$\bar{\ell}_{ijk\ell}^{2} \equiv \frac{Z^2c^2}{2}\iint_{\vec r\vec r'} \frac{\bar{\varphi}_i^2(\vec r)\bar{\varphi}_j^2(\vec r')\varphi_k^2(\vec r)\varphi_\ell^2(\vec r')}{|\vec r-\vec r'|} \qquad 3.50$$

$$\bar{\ell}_{ijk\ell}^{12} \equiv -Ze^2\iint_{\vec r\vec r'} \frac{\varphi^1(\vec r)\varphi^1(\vec r)\varphi^2(\vec r')\varphi^2(\vec r')}{|\vec r-\vec r'|} \qquad 3.51$$

In equations 3.43 to 3.45 the integration includes summation over spin variables, and each index is actually double $i \rightarrow i\,\sigma_i$ where σ_i is a spin index and i a space index. The wave functions φ_i may be written as a product

$$\varphi_i = \varphi_i(\vec r)\,u_{\sigma_i}(\xi_i), \qquad 3.52$$

where

$$\varphi_i(\vec r) = V^{-1/2} e^{i\vec P_i\cdot\vec r/\hbar}, \qquad 3.53$$

and

$$\vec{P}_i = \frac{2\pi}{L}\hbar\,\vec{n}_i \;, \qquad 3.54$$

Because of the orthogonality of the spin functions, there obtains

$$\bar{\ell}^{\,1}_{ijk\ell} = \delta_{\sigma_i^1 \sigma_h^1}\,\delta_{\sigma_j^1 \sigma_\ell^1}\,\ell^{\,1}_{ijk\ell} \;, \qquad 3.55$$

$$\bar{\ell}^{\,2}_{ijk\ell} = \delta_{\sigma_i^2 \sigma_k^2}\,\delta_{\sigma_j^2 \sigma_\ell^2}\,\ell^{\,2}_{ijk\ell} \;, \qquad 3.56$$

and

$$\bar{\ell}^{\,12}_{ijk\ell} = \delta_{\sigma_i^1 \sigma_j^1}\,\delta_{\sigma_k^2 \sigma_\ell^2}\,\ell^{\,12}_{ijk\ell} \qquad 3.57$$

where

$$\ell^{\,1}_{ijk\ell} \equiv \frac{e^2}{2V^2}\iint \frac{e^{i\{(\vec{P}_k-\vec{P}_i)\cdot\vec{r} + (\vec{P}_\ell-\vec{P}_j)\cdot\vec{r}\,'\}}}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,d\vec{r}\,' \;, \qquad 3.58$$

etc. Equation 3.52 may be integrated by use of the expansion of $\frac{1}{r} = 1/|\vec{r}-\vec{r}\,'|$ in the Fourier series,

$$\frac{1}{r} = \sum_{\vec{k}} f(\vec{k})\,e^{i\vec{k}\cdot\vec{r}} = f_0 + \frac{4\pi}{V}\sum_{\vec{k}}{}' e^{i\vec{k}\cdot\vec{r}}/k^2 \qquad 3.59$$

where $\vec{k} = 2\pi\vec{n}/L$, $f_0 \approx 3/2\left(\frac{3}{4\pi V}\right)^{1/3}$. Thus,

$$\ell^{\,1}_{ijk\ell} = \frac{e^2}{2V^2}\sum_{\vec{k}} f(\vec{k})\cdot$$

$$\iint_{\vec{r}\vec{r}\,'} e^{ik\cdot(\vec{r}-\vec{r}\,')}\,e^{-i\vec{P}_i\cdot\vec{r}/\hbar}\,e^{i\vec{P}_\ell\cdot\vec{r}/\hbar}\,e^{+i\vec{P}_i\cdot\vec{r}\,'/\hbar}\,e^{-i\vec{P}_j\cdot\vec{r}/\hbar}$$

$$= \frac{e^2}{2} \sum_{\vec{k}} f(\vec{k})\, \delta\left(\vec{k} - \frac{(\vec{p}_i - \vec{p}_k)}{\hbar}\right) \delta\left(\vec{k} - \frac{(\vec{p}_l - \vec{p}_j)}{\hbar}\right)$$

$$= \begin{cases} e^2/2 \ \ f\left(\frac{\vec{p}_i - \vec{p}_k}{\hbar}\right), & \vec{p}_i - \vec{p}_k = \vec{p}_l - \vec{p}_j \\ 0 & , \ \vec{p}_i - \vec{p}_k \neq \vec{p}_l - \vec{p}_j \end{cases} \qquad 3.60$$

$$= \begin{cases} e^2/2 \ \ f(0) & , \ \vec{p}_i - \vec{p}_k = \vec{p}_l - \vec{p}_j = 0 \\ 2\pi e^2 \hbar^2 / V\, |\vec{p}_i - \vec{p}_k|^2 & , \ \vec{p}_i - \vec{p}_k = \vec{p}_l - \vec{p}_j \neq 0 \\ 0 & \ \ \ \vec{p}_i - \vec{p}_k \neq \vec{p}_l - \vec{p}_j \end{cases} \qquad 3.61$$

with similar expressions for ℓ^2_{ijkl} and ℓ^{12}_{ijkl}. The Hamiltonian 3.48 may, therefore, be written as

$$\mathcal{H} = \sum_{\vec{k}} \left(E^1_k \, n^1_{k\sigma_k} + E^2_k \, n^2_{k\sigma_k} \right)$$

$$+ \frac{e^2}{2} f(0) \sum_{\vec{p}_i - \vec{p}_k = \vec{p}_l - \vec{p}_j = 0} (a^1_{i\sigma} a^1_{j\sigma'})^{+} (a^1_{k\sigma} a^1_{l\sigma'})$$

$$+ \frac{2\pi e^2 \hbar^2}{V} \sum_{\vec{p}_i - \vec{p}_k = \vec{p}_l - \vec{p}_j \neq 0} \frac{(a^1_{i\sigma} a^1_{j\sigma'})^{+} (a^1_{k\sigma} a^1_{l\sigma'})}{|\vec{p}_i - \vec{p}_k|^2} \qquad 3.62$$

$$+ \cdots,$$

The statistical operator 3.40 with the Hamiltonian 3.62 serves as a basis for a rigorous theory of the thermodynamics of plasmas. Once the partition function Z is found, all thermodynamic properties become known. The partition function is the trace of $e^{-\beta \mathcal{H}} \cdot e^{\beta(\mu^1 \mathcal{N}^1 + \mu^2 \mathcal{N}^2)}$, or

$$Z = \sum_{n_i^1 n_i^2} \left(\Psi_{(n_i^1 n_i^2)}, e^{-\beta(\mathcal{H} - \mu^1 \mathcal{N}^1 - \mu^2 \mathcal{N}^2)} \Psi_{(n_i^1 n_i^2)} \right), \qquad 3.63$$

The evaluation of expression 3.63 is quite difficult and has not been done.

The pressure is expressed by equation 1.119,

$$P = -\frac{1}{\beta Z}\frac{\partial}{\partial V} \operatorname{tr} e^{-\beta(\mathcal{H}-\mu^1 \mathcal{N}^1-\mu^2 \mathcal{N}^2)} \quad 3.64$$

or by

$$PV = -\frac{1}{\beta Z}\frac{\partial}{\partial \ln V} \operatorname{tr} e^{-\beta(\mathcal{H}-\mu^1 \mathcal{N}^1-\mu^2 \mathcal{N}^2)}. \quad 3.65$$

Equation 3.65 may be transformed into the quantum mechanical virial expression[15]

$$PV = \frac{2}{3}\operatorname{tr}(\rho K) + \frac{1}{3}\operatorname{tr}(\rho \mathcal{V}) \quad 3.66$$

where K is the kinetic energy operator and $\mathcal{V}$ the potential energy operator. At high temperatures $\frac{2}{3}\operatorname{tr}(\rho K) \cong NkT$ where N is the average total number of particles. An estimate of $\langle \mathcal{V} \rangle = \operatorname{tr}(\rho \mathcal{V})$ is obtained by first computing $\langle \mathcal{V} \rangle$ for a state $\Psi(n_i^1, n_j^2)$ and then summing over all states using the number densities n_i^1, n_j^2 given by equation 1.125:

$$\langle n_i^1 \rangle = 1 / 1 + e^{\beta(E_i^1-\mu^1)} \quad 3.67$$

$$\langle n_j^2 \rangle = 1 / 1 + e^{\beta(E_j^2-\mu^2)} \quad 3.68$$

(It has been assumed that both types of particles obey Fermi statistics). The average value of $\mathcal{V}$ for the state $\Psi_{(n_i^1, n_j^2)}$ is found to be

$$\langle \mathcal{V} \rangle = \frac{1}{2} f_0 \left\{ e \sum_i n_i^1 - Z e \sum_j n_j^2 \right\}^2$$

$$- \frac{1}{2} \frac{e^2}{V} \sum_{ij}{}' \frac{4\pi\hbar^2}{|\vec{p}_i - \vec{p}_j|^2} n_i^1 n_j^1$$

$$- \frac{1}{2} \frac{Z^2 e^2}{V} \sum_{ij}{}' \frac{4\pi\hbar^2}{|\vec{p}_i - \vec{p}_j|^2} n_i^2 n_j^2 \; . \qquad 3.69$$

Equation 3.69 must be averaged over the various states (occupation numbers) using 3.67 and 3.68 for the average occupation numbers, and $\langle n_i^2 \rangle \approx \langle n_i \rangle^2 + \langle n_i \rangle$.[41] The result is

$$\langle \mathcal{V} \rangle = \frac{1}{2} (Z+1) e^2 N_e f(0)$$

$$- \frac{1}{2} \sum_{ij}{}' \frac{4\pi\hbar^2}{V|\vec{p}_i - \vec{p}_j|^2} \frac{2}{\left(1+e^{\beta(E_i^1-\mu^1)}\right)\left(1+e^{\beta(E_j^1-\mu^1)}\right)}$$

$$- \frac{1}{2} Z^2 e^2 \sum_{ij}{}' \frac{4\pi\hbar^2}{V|\vec{p}_i - \vec{p}_j|^2} \frac{2s^2+1}{\left(1+e^{\beta(E_i^2-\mu^2)}\right)\left(1+e^{\beta(E_j^2-\mu^2)}\right)} \; . \qquad 3.70$$

The first term in $\langle \mathcal{V} \rangle$ of equation 3.70 corresponds to fluctuations, and has the same value as that given by equation 3.39. The next two terms are exchange terms. Correlation terms have been neglected in this crude approximation, but will be considered in Chapter IV. The sums in 3.70 may be approximated by integrals,

Define

$$I = \sum_{ij}{}' \frac{4\pi\hbar^2}{V|\vec{P}_i-\vec{P}_j|^2} \frac{1}{1+e^{\beta(E_i-\mu)}} \frac{1}{1+e^{\beta(E_j-\mu)}} \qquad 3.71$$

$$\cong \frac{V}{\pi(2\pi\hbar)^4} \iint \frac{d\vec{P}_1\, d\vec{P}_2}{|\vec{P}_1-\vec{P}_2|^2\left(1+e^{\beta(\frac{P_1^2}{2m}-\mu)}\right)\left(1+e^{\beta(\frac{P_2^2}{2m}-\mu)}\right)} . \qquad 3.72$$

If θ is the angle between $\vec{P}_1$ and $\vec{P}_2$, the above expression may be expressed as

$$I(m,\mu,\beta) = \frac{8\pi V}{(2\pi\hbar)^4} \int_0^\infty\int_0^\infty\int_0^\pi \frac{P_1^2 dP_1\, P_2^2 dP_2 \sin\theta\, d\theta}{P_1^2+P_2^2-2P_1P_2\cos\theta} ,$$

$$\frac{1}{\left(1+e^{\beta(P_1^2/2m-\mu)}\right)} \frac{1}{\left(1+e^{\beta(P_2^2/2m-\mu)}\right)}$$

$$= \frac{4\pi V}{(2\pi\hbar)^4} \int_0^\infty\int_0^\infty \frac{P_1 dP_1\, P_2 dP_2 \ln\left(\frac{P_1+P_2}{P_1-P_2}\right)^2}{\left(1+e^{\beta(P_1^2/2m-\mu)}\right)\left(1+e^{\beta(P_2^2/2m-\mu)}\right)} , \qquad 3.73$$

The value of the exchange terms in equation 3.70 may be expressed in terms of the integrals $I(m\mu\beta)$ with the result that

$$\langle V \rangle = \frac{1}{2} f(0)\,(Z+1)\, N_e\, e^2$$

$$- \frac{2\pi V}{(2\pi\hbar)^4} e^2 \left\{ 2\, I(m,\mu;\beta) + (2\sigma^2+1) I(M,\mu^2,\beta) \right\} . \qquad 3.74$$

For $T=0$ (ground state) the integrals I become

$$I(m,\mu^0) = \int_0^{P_0}\int_0^{P_0} \frac{4\pi V}{(2\pi\hbar)^4} P_1\,dP_1\,P_2\,dP_2 \ln\left(\frac{P_1+P_2}{P_1-P_2}\right)^2$$

$$= \frac{4\pi V}{(2\pi\hbar)^4}\int_0^{P_0} P_1\,dP_1\left\{(P_0^2-P_1^2)\ln\frac{P_0+P_1}{P_0-P_1}+2P_0P_1\right\}$$

$$= \frac{4\pi V}{(2\pi\hbar)^4}P_0^4\,, \quad P_0^2 \equiv 2m\mu^0 \qquad 3.75$$

which gives for the exchange energy of the electrons,

$$\langle V_{exch}\rangle = -\frac{4\pi e^2}{h^4} V P_0^4 \,. \qquad 3.76$$

The above result agrees with that given by Gombas.[33] For other values of temperature the integrals 3.73 are not elementary, and have not been evaluated. The exchange energy is extremely small for a completely ionized non-dense gas, but is quite large for electrons bound in an atom, and may be important for extremely dense gases.

This chapter is concluded with a derivation of an expression for the quantum mechanical phase space distribution function for a system of spinless particles in thermodynamic equilibrium. The density matrix $\rho(q;q')$ is given by the expression

$$\rho(q;q') = \frac{1}{Z}\sum_n e^{-\beta E_n}\varphi_n(q)\bar{\varphi}_n(q'), \qquad 3.77$$

and, therefore, the Wigner ditribution function is given by

$$f_W = \frac{1}{Z}\sum_n e^{-\beta E_n} f_n \qquad 3.78$$

where f_n are the phase space eigen functions. However, according to equation 1.58

$$H_W f_W \equiv \cos\frac{\hbar}{2}\left\{\frac{\partial}{\partial q}\cdot\frac{\partial}{\partial p}\right\} H f_W \qquad 3.79$$

and, since H_W is a linear operator,

$$e^{-\beta E_n} f_n = e^{-\beta H_W} f_n \qquad 3.80$$

The operator $e^{-\beta H_W}$ is independent of n. Thus,

$$f_W = \frac{1}{Z} e^{-\beta H_W} \sum_n f_n \, . \qquad 3.81$$

Let

$$g \equiv \sum_n f_n \qquad 3.82$$

and

$$F = \sum_n a_n f_n \qquad 3.83$$

be an arbitrary integrable function. The f_n are orthonormal,

$$\langle f_n, f_m \rangle = \delta_{nm} \qquad 3.84$$

and

$$\langle f_n, f_n \rangle = \langle 1, f_n \rangle = 1 \qquad 3.85$$

Therefore,

$$\langle g, F\rangle = \langle \textstyle\sum_n f_n, F\rangle = \sum_n a_n \qquad 3.86$$

However,

$$\langle 1, F\rangle = \langle 1, \textstyle\sum_n a_n f_n\rangle = \sum_n a_n \qquad 3.87$$

and therefore

$$\langle 1-g, F\rangle = \int_{qp} (1-g)F \equiv 0 \qquad 3.88$$

which yields the result

$$g = \textstyle\sum_n f_n = 1 \,. \qquad 3.89$$

The equilibrium canonical distribution function 3.81 may now be written

$$f_W^{\text{canon.}} = Z^{-1}\, e^{-\beta H_W} \cdot 1 \qquad 3.90$$

In the limit $\hbar \to 0$ the canonical Wigner distribution function goes over into the classical canonical distribution function 3.2. It is to be noted that only even powers of $\hbar$ are contained in the canonical f_W. Wigner noted this fact, but did not express f_W in a closed form.

CHAPTER IV

THE EFFECTIVE POTENTIAL

A. Introduction

The difficulties with a long range potential such as the Coulomb potential are well-known. For example, in the kinetic theory of gases, certain integrals required for the computation of transport phenomena diverge.[42,43] The reason for this divergence resides in the kinetic theory assumption that the motion of a molecule consists of an essentially free part interrupted by occasional collisions which produce sudden changes in the velocity. The change in the 1-particle molecular distribution function is described by a Liouville type equation with an extra term accounting for the relatively infrequent collisions. The collision term is then expressed in terms of the 1-particle distribution functions and parameters describing a binary encounter.[43] The Coulomb potential, however, is such that at any time a particle is acted upon by all of the other particles in the system, and, although distant particles exert small forces, the cumulative effect may be appreciable. Of course close encounters producing large changes of velocity also play an important role. There are thus two aspects of the situation, which have been clearly recognized by Gascorowicz, Neumann and Riddell,[44] the "Poisson" aspect, corresponding to a discrete set of relatively rare large scale events (collisions), and the "stochastic" aspect corresponding to a nearly continuous set of individually small scale but collectively appreciable events. Chapman much earlier[43, 45] noted the difficulty and handled it by means of a cut-off at the mean-molecular distance. Arguments supporting the cut-off procedure are given by Chapman and Cowling,[43] and by Cowling.[46] These arguments may be summed up by the assertion[46] that although the electrostatic forces are large with respect to other (e.g., external field) forces, they are not strong enough to produce large effects except at distances small compared with the mean distance between pairs of molecules. The motion is then amenable to treatment using the Boltzmann equation, in which the close encounters are treated as binary, and the distant encounters as contributing to the body force terms in the Boltzmann equation. This method appears to be correct in principle but there is some question as to the value of the cut-off[1] and to the method to be used to account for the long range contributions. Spitzer and his collaborators[47, 48] have attempted to treat the long range interactions as a diffusion process in velocity space. In this treatment the collision term in the Boltzmann equation is split into two parts, the first a binary collision term with a cut-off and the second a Fokker-Planck type term to account for the diffusion or Brownian motion in velocity space. Spitzer's treatment suffers cut-off problems also, but the results agree roughly with those of Chapman and Cowling.

There appear to be three main approaches to the problem of long range interactions. The first approach may be termed stochastic, and treats the long range part of the interaction statistically. Gasiorowicz, Neumann, and Riddell have given a clear account of this method,[44] in which the behavior of a plasma is described due solely to the Markovian motion of single particles, and in which the effect of close encounters is neglected completely. The second approach, initiated by Bohm and Pines[49, 50] makes use of "collective" coordinates which depict ordered motions of the entire system (Plasma oscillations). The behavior of the charges is analyzed in terms of their density fluctuations. These fluctuations are split into two components, one corresponding to organized motion and the other to random thermal motions. It is shown that for phenomena involving distances greater than the Debye length $\sim (kT/8\pi n e^2)^{1/2}$, the system behaves collectively. For phenomena involving distances less than the Debye length, the motion of the system may be treated on a binary collision basis. The third approach may be termed the effective interaction theory, and was initiated in its simplest form by Debye and Hückel.[11] The remainder of this chapter will be devoted to an approximate treatment of the effective potential.

The above discussion shows that the effect of the long-range interaction is quite naturally divided into two parts, one representing the effect produced by individual close particles and the other representing a collective effect produced by the combined effects of distant particles. Both of these effects may be taken into account by the use of an effective two body potential, which, in general, will be velocity dependent.

Following along lines of the Debye-Hückel theory of strong electrolytes, Rosseland[12] and Fowler and Guggenheim[13] estimated the electrostatic correction to the perfect gas law. Eddington[4] pointed out that the Debye-Hückel approach, although correct in principle, was actually incorrect. Eddington also indicated lines along which improvement can be made. According to the Debye-Hückel theory, the average charge density ρ_e around a nucleus due to nuclei of charge Ze and electrons of charge $-e$ is given by the expression

$$\rho_e = n_Z^0 Ze \left\{ e^{-Ze\psi/kT} - e^{e\psi/kT} \right\} \qquad 4.1$$

where n_z^o is the average number density of nuclei, and ψ is the average or effective potential. Close to the nucleus the boundary condition $\psi \sim Ze/r$ obtains and the charge density behaves as

$$\rho_e \sim - n_z^o \, Z e \; e^{Ze^2/kTr} . \qquad 4.2$$

The charge density 4.2 approaches minus infinity in an exponential manner, which shows that the total amount of charge $4\pi \int_0^{\varepsilon} \rho \, r^2 dr$ in an arbitrary ε neighborhood of the nucleus is also infinite. This divergence of the charge density in the Debye-Hückel theory is quite analogous to the "collapsed" state situation for the classical canonical distribution. Eddington showed that the difficulty can be removed. The error in the theory is due to the fact that arbitrarily large negative energies of an electron are allowed, whereas for a completely ionized gas, the total energy must be positive. Eddington[4] made a very rough correction to the theory in order "to remove its most glaring defects."

Persico[5] applied Eddington's method to the kinetic theory of ionized gases, by using the approximate statistical potential as an effective two-particle interaction. Persico's results agree in order of magnitude with those obtained by Chapman,[51] using the cut-off at mean molecular distance. The present approach to the problem was suggested by S. Chapman, and consists in extending the work of Eddington and Persico by computing more accurately the effective potential around nuclei and electrons in a fully ionized gas. This done, the equation of state may be obtained by use of the virial theorem. The effective potential can also be used to estimate the transport properties of the gas. In the latter problem, the effective potential is used to evaluate certain kinetic theory integrals, the values of which determine the various transport coefficients.

B. The Effective Potential

Consider a binary gas consisting of nuclei of charge Ze and electrons of charge $-e$. At equilibrium the number of free (non-bound) electrons per unit volume is approximately given by the Fermi-Dirac distribution law[52]

$$n_e = \frac{8\pi}{h^3} \int_{H \geq 0} p^2 dp \,/\, 1 + e^{\beta(H-\mu)} \qquad 4.3$$

where $H = p^2/2m - e\psi$ and ψ is the effective potential, $\psi \geq 0$. Recently Kirkwood and Plock[53] developed a similar theory of plasmas in which n_e was taken to be

$$n_e = \frac{8\pi}{h^3} \int_0^\infty p^2 dp \,/\, 1 + e^{\beta(H-\mu)} \qquad 4.4$$

However, it is clear that Eddington's argument applies to the problem at hand, and equation 4.3 is a more nearly correct expression for nearly free electrons. Of course, expressions 4.3 and 4.4 differ by very little except where ψ is large. Therefore, the expressions for ψ differ only in the immediate neighborhood of the nucleus. However, this difference will be of significance in the estimates of thermodynamic properties of the gas. If $\psi = 0$

$$n_e^o = \frac{8\pi}{h^3} \int_0^\infty p^2 dp \Big/ 1 + e^{\beta\left(\frac{p^2}{2m} - \mu\right)} ; \qquad 4.5$$

this serves to determine the chemical potential μ as a function of temperature and density. The order of magnitude of $e^{-\beta\mu}$ may be estimated from that of the quantity[45]

$$\alpha = n_e^o \left(2\pi \hbar^2 \beta / m \right)^{3/2} , \qquad 4.6$$

If $\alpha << 1$, $exp(-\beta\mu) >> 1$ and since $H \geq 0$, equation 4.3 may be written in the classical form

$$n_e = \frac{8\pi}{h^3} \int_{H \geq 0}^\infty e^{-\beta(H-\mu)} p^2 dp . \qquad 4.7$$

It is to be noted that the Kirkwood-Plock expression 4.4, does not possess this feature. The condition $\alpha << 1$ may be expressed as

$$n_e^o / T^{3/2} << 10^{16} , \qquad 4.8$$

which is assumed valid in a subsequent work.

The integral of 4.7 may be evaluated simply, the result being[42]

$$n_e = n_e^{\circ} \left\{ \frac{2}{\sqrt{\pi}} \chi + e^{\chi^2} \operatorname{erfc} \chi \right\} \tag{4.9}$$

where $\chi^2 = e\psi/kT$ and

$$\operatorname{erfc} \chi = 1 - \frac{2}{\sqrt{\pi}} \int_0^{\chi} e^{-y^2} dy \, . \tag{4.10}$$

The number of nuclei per unit volume, in a region where $\psi \geqslant 0$ is expressed by

$$n_z = n_z^{\circ} \, e^{-z\chi^2} \tag{4.11}$$

Where $\psi = 0$ the total charge density is assumed to be zero, hence

$$n_e^{\circ} = z \, n_z^{\circ} \, , \tag{4.12}$$

and, therefore, the total charge density at any point where $\psi \geqslant 0$ is given by the expression

$$\rho = - z e n_z^{\circ} \left\{ \frac{2}{\sqrt{\pi}} \chi + e^{\chi^2} \operatorname{erfc} \chi - e^{-z\chi^2} \right\} . \tag{4.13}$$

The effective potential satisfies Poisson's equation, hence

$$\nabla^2 \psi_z = 4\pi z e n_z^{\circ} \left\{ \frac{2}{\sqrt{\pi}} \chi_z + e^{\chi_z^2} \operatorname{erfc} \chi_z - e^{-z\chi_z^2} \right\} \tag{4.14}$$

Close to a nucleus $\psi_z \sim \frac{ze}{r}$ so equation 4.14 has for boundary conditions

$$\psi_z \rightarrow ze/r \, , \quad r \rightarrow 0 \, , \tag{4.15}$$

$$r\psi_z \rightarrow 0 \quad , \quad r \rightarrow \infty \; . \qquad 4.16$$

Similar considerations lead to the equation for ψ_e, the potential in the vicinity of an electron. The result is expressed by

$$\nabla^2 \psi_e = -4\pi e n_e^0 \left\{ \frac{2}{\sqrt{\pi}} \chi_e + e^{-\chi_e^2} \,\mathrm{erfc}\, \chi_e - e^{\chi_e^2/2} \right\} , \qquad 4.17$$

where $\chi_e^2 = -Ze\psi_e/kT$ and

$$\psi_e \rightarrow -e/r \quad , \quad r \rightarrow 0 \; , \qquad 4.18$$

$$r\psi_e \rightarrow 0 \quad , \quad r \rightarrow \infty \; . \qquad 4.19$$

The substitution

$$\psi_z = \frac{A_z}{r_z} \frac{\varphi_z}{\rho} \qquad 4.20$$

where $r_z = (kT/4\pi z e^2 n_z^0)^{1/2}$ and $A_z = \frac{kT}{e} r_z$ leads to the following equation for φ_z :

$$\frac{d^2\varphi_z}{d\rho^2} = \rho \left\{ \frac{2}{\sqrt{\pi}} \sqrt{\frac{\varphi_z}{\rho}} + e^{\frac{\varphi_z}{\rho}} \sqrt{\frac{\varphi_z}{\rho}} - e^{-\frac{z\varphi_z}{\rho}} \right\} \qquad 4.21$$

The boundary conditions 4.15, 4.16 become

$$\varphi_z \rightarrow \varphi_z(0) = \frac{ze^2}{kTr_z} = \sqrt{4\pi n_z^0} \left(\frac{Ze^2}{kT}\right)^{3/2} , \; \rho \rightarrow 0 \qquad 4.22$$

$$\varphi_z \rightarrow 0 \quad , \quad \rho \rightarrow \infty \; . \qquad 4.23$$

In a similar fashion, the substitution

$$\psi_e = -\frac{A_e}{r_e} \frac{\varphi_e}{\rho} \; , \qquad 4.24$$

where $r_e = (kT/4\pi Z^2 e^2 n^\circ_Z)^{1/2}$ and $A_e = \frac{kT}{Ze} r_e$, leads to the following equation for φ_e :

$$\frac{d^2\varphi_e}{d\rho^2} = \rho\left\{\frac{2}{\sqrt{\pi}}\sqrt{\frac{\varphi_e}{\rho}} + e^{\frac{\varphi_e}{\rho}}\sqrt{\frac{\varphi_e}{\rho}} - e^{-\frac{\varphi_e}{Z\rho}}\right\} \qquad 4.25$$

The boundary conditions on φ_e are

$$\varphi_e \rightarrow \varphi_e(0) = \sqrt{4\pi Z n^\circ_Z}\left(\frac{Ze^2}{kT}\right)^{3/2}, \quad \rho \rightarrow 0 \qquad 4.26$$

$$\varphi_e \rightarrow 0 \quad , \quad \rho \rightarrow \infty \quad . \qquad 4.27$$

Equations 4.21, 4.25 are the same except for the replacement These equations must be solved by numerical methods, and to date have not been solved.

The solutions of the potential problem may be used to estimate the average potential energy per unit volume. The average energy of interaction between a nucleus and its statistical charge cloud is

$$V_Z = Ze\,\psi^\circ_Z \qquad 4.28$$

where

$$\psi^\circ_Z \equiv \lim_{r\rightarrow 0}\left\{\psi_Z(r) - \frac{Ze^2}{r}\right\} \qquad 4.29$$

$$= \frac{A_Z}{r_Z}\varphi_Z'(0) = \frac{kT}{e}\varphi_Z'(0) \qquad 4.30$$

Therefore,

$$V_Z = Z\,kT\,\varphi_Z'(0) \quad . \qquad 4.31$$

Similarly, the average energy of interaction of an electron with its charge cloud is

$$V_e = \frac{kT}{Z}\varphi_e'(0) \qquad 4.32$$

It is to be noted that both V_Z and V_e are negative. The total average potential energy per unit volume is, therefore,

$$\langle V \rangle = \frac{1}{2} n_Z^0 V_Z + \frac{1}{2} n_e^0 V_e$$

or

$$\langle V \rangle = \frac{1}{2} n_Z^0 kT \left\{ Z \varphi_Z'(0) + \varphi_e'(0) \right\} \qquad 4.33$$

Equation 4.33 may also be obtained from the rigorous expression for $\langle V \rangle$ in terms of pair distribution functions, provided the correlation function is suitabley related to ρ_e, ρ_Z. The virial theorem yields the equation of state

$$p = n_Z^0 (Z+1) kT + \frac{1}{6} n_Z^0 kT \left(Z\varphi_Z'(0) + \varphi_e'(0) \right)$$

or

$$p = n^0 kT \left\{ 1 + \frac{1}{6(Z+1)} \left(Z\varphi_Z'(0) + \varphi_e'(0) \right) \right. \qquad 4.34$$

C. Asymptotic Solutions

The basic potential equations, as was mentioned previously, must be solved by numerical methods. The equations, however, may be solved asymptotically for large and small values of ρ . The asymptotic solutions will be of value when the numerical solutions are obtained, since they will serve as analytic representations of the potentials at large and small distances.

The basic equations may be written in the form

$$\varphi'' = \rho \left\{ \frac{2}{\sqrt{\pi}} \chi + e^{\chi^2} \operatorname{erfc} \chi - e^{-\lambda \chi^2} \right\}, \quad 4.35$$

where $\chi = \sqrt{\varphi/\rho}$ and $\lambda = z \, ; \varphi = \varphi_z$ and $\lambda = \frac{1}{z} \, ; \varphi = \varphi_e$. Near the origin φ/ρ is large. Therefore,[47]

$$\varphi'' \sim \rho \left\{ \frac{2}{\sqrt{\pi}} \chi + \frac{1}{\sqrt{\pi}\chi} \left(1 - \frac{1}{2\chi^2} + \frac{3}{4\chi^4} + \cdots \right) \right\},$$

$$\varphi'' \sim \frac{\rho}{\sqrt{\pi}} \left\{ 2\sqrt{\frac{\varphi}{\rho}} + \sqrt{\frac{\rho}{\varphi}} - \frac{1}{2} \left(\frac{\rho}{\varphi} \right)^{3/2} + \frac{3}{4} \left(\frac{\rho}{\varphi} \right)^{2} \cdots \right\} \quad 4.36$$

The potential φ is not an analytic function of ρ , since the origin is a winding point. However, $\varphi^{1/2}$ is analytic in $\rho^{1/2}$,

$$\varphi^{1/2} = \sum_{n=0}^{\infty} a_n \rho^{n/2} \, , \quad 4.37$$

$$\varphi = \sum_n b_n \rho^{n/2} \, , \quad 4.38$$

$$\varphi^{3/2} = \sum_n c_n \rho^{n/2} \, , \quad 4.39$$

and

$$\varphi^2 = \sum_n d_n \rho^{n/2} , \qquad 4.40$$

where

$$b_n = \sum_{k=0}^{n} a_k a_{n-k} \qquad 4.41$$

$$c_n = \sum_{k=0}^{n} a_k b_{n-k} \qquad 4.42$$

and

$$d_n = \sum_{k=0}^{n} b_k b_{n-k} . \qquad 4.43$$

Retaining the first three terms on the right hand side of 4.36 results in the expression

$$\chi^3 \varphi'' \doteq \frac{\rho}{\sqrt{\pi}} \left(2 \chi^4 + \chi^2 - \tfrac{1}{2}\right) \qquad 4.44$$

or

$$\varphi^{3/2} \varphi'' = \frac{\rho^{5/2}}{\sqrt{\pi}} \left(2 \frac{\varphi^2}{\rho^2} + \frac{\varphi}{\rho} - \frac{1}{2}\right) \qquad 4.45$$

However,

$$\varphi'' = \sum_{n=0}^{\infty} b_n \frac{n(n-2)}{4} \rho^{\frac{n-4}{2}} = \frac{1}{4\rho^2} \sum_n n(n-2) b_n \rho^{n/2} \qquad 4.46$$

Hence

$$\varphi^{3/2} \varphi'' = \frac{1}{4\rho^2} \sum_{n=0}^{\infty} f_n \rho^{n/2} \qquad 4.47$$

where

$$f_n = \sum_{l=0}^{n} l(l-2)\, b_l\, c_{n-l} \quad . \qquad 4.48$$

The potential 4.38 will satisfy equation 4.45 if the coefficients satisfy the identity

$$\sum_{n=0}^{\infty} f_n \rho^{n/2} = \frac{4}{\sqrt{\pi}} \rho^{5/2} \Big\{ 2\sum_{n=0}^{\infty} d_n \rho^{n/2}$$

$$+ \rho \sum_n b_n \rho^{n/2} - \frac{1}{2}\rho^2 \Big\} \qquad 4.49$$

Since 4.49 is an identity the coefficients of $\rho^{n/2}$ must be the same on each side of the equation. Therefore,

$$f_0 = f_1 = f_2 = f_3 = f_4 = 0$$

$$f_5 = \frac{8}{\sqrt{\pi}} d_0$$

$$f_6 = \frac{8}{\sqrt{\pi}} d_1$$

$$f_7 = \frac{8}{\sqrt{\pi}} d_2 + \frac{4}{\sqrt{\pi}} b_0 \qquad 4.50$$

$$f_8 = \frac{8}{\sqrt{\pi}} d_3 + \frac{4}{\sqrt{\pi}} b_1$$

$$f_9 = \frac{8}{\sqrt{\pi}} d_4 + \frac{4}{\sqrt{\pi}} b_2 - \frac{2}{\sqrt{\pi}}$$

and

$$f_n = \frac{4}{\sqrt{\pi}}\left(2\, d_{n-5} + b_{n-7}\right), \; n \geq 10 \qquad 4.51$$

Using the above recursion relations, there obtains

$$\varphi \sim \varphi_0 + b_2 \rho + \frac{8}{15\sqrt{\pi}} \varphi_0^{1/2} \rho^{5/2} + \frac{4}{35\sqrt{\pi}} \varphi_0^{1/2} (1-b_2) \rho^{7/2} + \cdots \qquad 4.52$$

with $b_2 = \varphi'(0)$. Equation 4.52 is the asymptotic solution for small ρ. For large values of ρ, χ is small, and the differential equation 4.35 may be conveniently written in the form

$$\varphi'' = \sum_{n=0}^{\infty} \rho \, \chi^{2n}/n! + \frac{2\rho}{\sqrt{\pi}} \chi$$

$$- \frac{2\rho}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{2 \cdot 4 \cdots 2n}{1 \cdot 3 \cdot 5 \cdots 2n+1} \frac{\chi^{2n+1}}{n!} - \rho \sum_{n=0}^{\infty} (-\lambda)^n \frac{\chi^{2n}}{n!} \qquad 4.53$$

$$\sim \beta^2 \varphi + C_3 \frac{\varphi^{3/2}}{\rho^{1/2}} + C_4 \frac{\varphi^2}{\rho} + C_5 \frac{\varphi^{5/2}}{\rho^{3/2}} + \cdots \qquad 4.54$$

where $\beta^2 = 1 + \lambda$, $C_3 = -4/3\sqrt{\pi}$, $C_4 = 1 - \lambda^2/2$ and $C_5 = -8/15\sqrt{\pi}$. The asymptotic solution is found by applying a technique similar to the procedure of Chapman and Enskog. Write

$$\varphi'' - \beta^2 \varphi = \lambda C_3 \frac{\varphi^{3/2}}{\rho^{1/2}} + \lambda^2 C_4 \frac{\varphi^2}{\rho} + \lambda^3 C_5 \frac{\varphi^{5/2}}{\rho^{3/2}} + \cdots \qquad 4.54a$$

where λ is a parameter whose power measures the order of magnitude of a term. After the analysis is completed λ will be set equal to unity. Let

$$\varphi^{1/2} = \sum_{n=0}^{\infty} f_n(\rho) \lambda^n \qquad 4.55$$

$$\varphi = \sum_n g_n \lambda^n \quad , \quad g_n = \sum_{k=0}^{n} f_k \, f_{n-k} \qquad 4.56$$

$$\varphi^{3/2} = \sum_n h_n \lambda^n \quad , \quad h_n = \sum_k g_k \, f_{n-k} \quad , \qquad 4.57$$

$$\varphi^2 = \sum_n l_n \lambda^n \quad , \quad l_n = \sum_k g_k \, g_{n-k} \quad , \qquad 4.58$$

and

$$\varphi^{5/2} = \sum_n p_n \lambda^n \quad , \quad p_n = \sum_k l_n \, f_{n-k} \quad . \qquad 4.59$$

Then, equation 4.54 may be written

$$g_n'' - \beta^2 g_n = G_{n-1} \qquad 4.60$$

where*

$$G_{n-1} = c_3 \frac{h_{n-1}}{\rho^{1/2}} + c_4 \frac{l_{n-2}}{\rho} + c_5 \frac{p_{n-3}}{\rho^{3/2}} + \dots \qquad 4.61$$

Write

$$g_n = g_0 W_n \qquad 4.62$$

Then it follows that

$$W_n = \int \frac{d\rho}{g_0^2} \int g_0 G_{n-1} \, d\rho \quad , \qquad 4.63$$

---

* h_{-k}, l_{-k}, p_{-k}, $\cdots$, etc., are all zero, and, therefore, $G_{-k} = 0$, $k > 0$.

$$q_0 = C\, e^{-\beta\rho} , \tag{4.64}$$

The asymptotic solution for large ρ is therefore

$$\varphi \sim q_0 + q_1 + q_2 + \cdots \tag{4.65}$$

or

$$\varphi \sim q_0 \left(1 + w_1 + w_2 + \cdots \right) \tag{4.66}$$

Each term is completely determined by preceding terms. The zeroth term $C\, e^{-\beta\rho} = C\, e^{-r/r_D}$ where r_D is the Debye radius, is frequently taken to be the complete approximate solution. The integrals 4.63 may be evaluated asymptotically. Let

$$e_{mn} = e^{-m\beta\rho/2} \Big/ \rho^{n/2} \tag{4.67}$$

and

$$E_{mn} = \int e_{mn}\, d\rho \ . \tag{4.68}$$

The integral 4.68 has for its asymptotic expression

$$E_{mn} \sim -\frac{2}{m\beta} \sum_{k=0}^{\infty} \frac{(-1)^k\, \Gamma_{nk}\, e_{m,n+2k}}{(m\beta)^k} , \tag{4.69}$$

where

$$\Gamma_{n0} = 1 \quad , \tag{4.70}$$

$$\Gamma_{nk} = n(n+2)(n+4)\cdots(n+2k-2) , \tag{4.71}$$

Define

$$W_{m'n';mn} = \int e_{m'n'} E_{mn} \, d\rho . \qquad 4.72$$

Then, using the above results, equation 4.72 may be integrated asymptotically to yield the asymptotic expansion

$$W_{m'n';mn} \sim \frac{4}{m(m+m')\beta^2} \sum_{r=0}^{\infty} (-1)^r \frac{D_r}{\beta^r} e_{m+m';n+n'+2r} \qquad 4.73$$

where

$$D_r \equiv \sum_{k=0}^{r} \frac{\Gamma_{nk} \Gamma_{n+n'+2k;r-k}}{m^k (m+m')^{r-k}} , \qquad 4.74$$

In terms of the above definitions

$$q_0 = C \; e_{20} \qquad 4.75$$

$$q_0^2 = C^2 \; e_{40} \qquad 4.76$$

and

$$G_1 = C_3 \; C^{3/2} \; e_{31} \qquad 4.77$$

Therefore,

$$W_1 = C^{1/2} C_3 \int d\rho \; e_{-40} \int e_{51} \, d\rho \qquad 4.78$$

$$= C^{1/2} C_3 \int d\rho \; e_{-40} E_{51} \qquad 4.79$$

or

$$W_1 = C^{1/2} C_3 \; W_{-40;51} \qquad 4.80$$

Therefore,

$$W_1 \sim C_3 C^{1/2} \frac{4}{5\beta^2} \sum_{r=0}^{\infty} (-1)^r \frac{D_r}{\beta^r} e_{1,1+2r} \qquad 4.81$$

But, for this case,

$$D_r = \sum_{k=0}^{r} \frac{\Gamma_{1k} \Gamma_{2k+1;r-k}}{5^k} \qquad 4.82$$

and, hence,

$$W_1 \sim C_3 C^{1/2} \frac{4}{5\beta^2} \frac{e^{-\beta\rho/2}}{\rho^{1/2}} \left\{ 1 - \frac{6}{5\beta\rho} + \frac{93}{25(\beta\rho)^2} - \frac{468}{25(\beta\rho)^3} + \cdots \right\}. \qquad 4.83$$

Expressions for higher approximations may be obtained in a similar fashion. For example,

$$W_2 \sim \frac{C}{3\beta^2} \left(C_3 + \frac{6}{5} \frac{C_3^2}{\beta^2} \right) \frac{e^{-\beta\rho}}{\rho} + \cdots \qquad 4.84$$

The resulting asymptotic approximation for φ is therefore expressed by

$$\varphi \sim C e^{-\beta\rho} \left\{ 1 + \frac{4}{5\beta^2} C_3 \sqrt{\frac{C e^{-\beta\rho}}{\rho}} \left(1 - \frac{6}{5\beta\rho} + \frac{93}{25(\beta\rho)^2} - \frac{468}{25(\beta\rho)^3} + \cdots \right) + \right.$$
$$\frac{1}{3\beta^2} (C \qquad 4.85$$

Aside from being an analytic representation of φ for large ρ the above result may be used to start a numerical integration of the potential equation. To each value of C there is one solution, but which solution it is cannot be foreseen until φ is integrated back to $\rho = 0$.

The constants C and $\varphi'(0)$ in equations 4.85, 4.52 are both determined by the value of φ_0 ; however, the determination cannot be made until the entire solution φ is known.

CHAPTER V

KINETIC THEORY INTEGRALS

A. Introduction

In this chapter some of the results of Chapman[55] on certain integrals occurring in the kinetic theory of gases are generalized. In the notation of Chapman and Cowling,[43] the integrals to be evaluated are defined as follows;

$$\phi_{12}^{(\ell)} = \int_0^\infty (1 - \cos^\ell \chi)\, g\, b\, db \qquad 5.1$$

and

$$\Omega_{12}^{(\ell)}(r) = \sqrt{\pi} \int_0^\infty e^{-u^2} u^{2r+2} \phi_{12}^{(\ell)}\, du \qquad 5.2$$

in which g is the magnitude of the relative velocity before collision, b is the impact parameter, χ is the angle of scattering, $u^2 = E/2kT$, and E is energy of relative motion, $E = \frac{1}{2} m_0 M_1 M_2 g^2$ Maxwell treated the case of inverse 5th power forces[55,56] while Chapman treated the general inverse ν-power forces.[55] The general central force law is treated in this chapter. The potential of interaction is taken to be an arbitrary function of r, the distance between molecules, and may be attractive or repulsive.

The angle χ of scattering may be expressed[57] by the relation, modulo π;

$$\chi(b,E) = \begin{cases} 2\vartheta_0 - \pi & \vartheta_0 \geq \pi \\ \pi - 2\vartheta_0 & \vartheta_0 \leq \pi \end{cases}, \qquad 5.3$$

where ϑ_0 is defined by the integral

$$\vartheta_0 = \int_0^{v_0} \frac{dv}{\sqrt{1 - \frac{1}{E} V\left(\frac{b}{v}\right) - v^2}} \qquad 5.4$$

where v_0 is the zero of the denominator:

$$1 - \frac{1}{E} V\left(\frac{b}{v_0}\right) - v_0^2 = 0 \,. \qquad 5.5$$

The value ϑ_0 gives the value $\cos\chi$ through the relation

$$\cos\chi = -\cos 2\vartheta_0 \,. \qquad 5.6$$

The integral 5.4 for ϑ_0 is not in a form suitable for numerical integration, because of the singularity in the neighborhood of v_0. This singularity can be removed by a standard procedure.[58] The expression $\frac{1}{E} V\left(\frac{b}{v_0}\right) + v_0^2$ is substituted for 1 in the radicand of the integral 5.4, yielding the expression

$$\vartheta_0 = \int_0^{v_0} \frac{dv}{\sqrt{v_0^2 - v^2 + \frac{1}{E}\left\{V\left(\frac{b}{v_0}\right) - V\left(\frac{b}{v}\right)\right\}}} \,, \qquad 5.7$$

The singularity in the above relation is observed to be of the form

$$\int_0^{v_0} dv \Big/ \sqrt{v_0 - v} \qquad 5.8$$

which can be removed by the substitution

$$z \sim \int_0^{v_0} dv / \sqrt{v_0 - v} \qquad 5.9$$

Let

$$z^2 = v_0 + v \quad , \qquad 5.10$$

which transforms the integrals 5.7 into the form

$$\vartheta_0 = 2 \int_0^{v_0^{1/2}} \frac{dz}{\sqrt{2v_0 - z^2 + \frac{1}{E}\left\{\frac{V(\frac{b}{v_0}) - V(\frac{b}{v})}{z^2}\right\}}} \qquad 5.11$$

If $y = z/v_0^{1/2}$ and $x = b/v_0$, the integral 5.11 becomes

$$\vartheta_0 = 2 \int_0^1 \frac{dy}{\sqrt{2 - y^2 + \frac{1}{E - V(x)}\left\{\frac{V(x) - V(\frac{x}{1-y^2})}{y^2}\right\}}} \qquad 5.12$$

The integrand in the integral 5.12 is non singular, or, rather, has a removable singularity at $y = 0$, since $\lim_{y \to 0} \left\{\frac{V(x) - V(\frac{x}{1-y^2})}{y^2}\right\}$ $= \lim_{y \to 0} \frac{-V'(x)\, y^2 x + \cdots}{y^2} = -xV'(x)$ The expression 5.12 for ϑ_0 expresses ϑ_0 as a function of x and E , where x satisfies the equation

$$1 - \frac{V(x)}{E} - \frac{b^2}{x^2} = 0 \quad , \qquad 5.13$$

The solution of equation 5.13 for x as a function of b and E involves, in general, the solution of a transcendental equation. On the other hand, b is simply expressed as a function of x and E, and is given by

$$b^2 = x^2 \left\{ 1 - \frac{1}{E} V(x) \right\} \tag{5.14}$$

As b ranges from 0 to ∞ ranges from x_0 to ∞, where

$$x_0 = \begin{cases} 0 & \text{for attractive potentials} \\ V^{-1}(E) & \text{for repulsive potentials} \end{cases} \tag{5.15}$$

It has been assumed for attractive potentials that

$$\lim_{x \to 0} x^2 V(x) = 0 , \tag{5.16}$$

which rules out, for example, attractive inverse cube-law forces. The kinetic theory integrals 5.1 involve integration over the complete range of the impact parameter b. However, because of the above-mentioned difficulty of expressing χ as a function of b, it is convenient to change the variable of integration in 5.1 from b to x. The result of this change of variable in equation 5.1 is expressed by the following equation

$$\phi_{12}^{(\ell)} = \frac{g}{2} \int_{x_0}^{\infty} \left\{ 1 - \cos^{\ell} \chi(x, E) \right\} d\left\{ x^2 \left[1 - \frac{V(x)}{E} \right] \right\}, \tag{5.17}$$

Equation 5.17 has two features which require further discussion. Firstly, the range of integration is infinite, and secondly the expression is in the form of a Stieltjes integral $\int f\,dg$, where f, g are only known numerically. The first difficulty may be resolved by a change of variable; or if the asymptotic form of $V(x)$ is known analytically, an asymptotic expression for $\chi(\mathcal{I}, E)$ may be found. Then expression 5.17 may be integrated numerically up to a suitably large value $\mathcal{X} = L$, and then analytically from L to ∞ . The second difficulty is resolved by the use of a generalized method of numerical integration. Of course, the integral $\int f\,dg$ may be written

$$\int f\,dg = \int f\,g'\,dx \quad , \qquad 5.18$$

and g' may be computed numerically, after which $f\,g'$ may be integrated using standard techniques. However, it is simpler to develop ab initio a theory of numerical integration of Stieltjes integrals. The remainder of this chapter will be devoted to the asymptotic form of χ , and to the theory of numerical Stieltjes integration.

B. Asymptotic Theory of Scattering

Let $\vec{P}_0, \vec{P}_f$ be the initial and final relative momenta of the scattering system. Then $P_0 = P_f$, and χ is the angle between $\vec{P}_0, \vec{P}_f$. The change in momentum is given by the impulse equation

$$\Delta\vec{P} = \vec{P}_f - \vec{P}_0 = \int \vec{F}\,dt \qquad 5.19$$

and, therefore,

$$\cos\chi = \vec{P}_0 \cdot \vec{P}_f / P_0^2 = (\vec{P}_0 + \Delta\vec{P}) \cdot \vec{P}_0 / P_0^2$$

$$= 1 + \frac{\vec{P}_0}{P_0^2} \cdot \int \vec{F}\, dt \, . \qquad 5.20$$

Let φ be the angle between $-\vec{P}_0$ and $\vec{r}$. Then the law of conservation of angular momentum is expressed by

$$b P_0 = m_0 M_1 M_2 r^2 \frac{d\varphi}{dt} \, . \qquad 5.21$$

If φ replaces t as integration variable in equation 5.20, there results

$$\cos\chi = 1 \mp \frac{1}{2bE} \int_0^{2\vartheta_0} r^2 F(r) \cos\varphi \, d\varphi \, . \qquad 5.22$$

Equation 5.22 may be cast into a more symmetrical form upon letting $\varphi = \vartheta_0 - \psi$. Thus, after some rearrangement,

$$\sin\frac{\chi}{2} = \frac{1}{2bE} \int_0^{\vartheta_0} r^2 F(r) \cos\psi \, d\psi \qquad 5.23$$

Equation 5.23 is in agreement with the expression derived by Gordon.[52] For the Coulomb law[52]

$$r^2 F(r) = C \qquad 5.24$$

and equation 5.23 becomes[59]

$$\sin\frac{\chi}{2} = \frac{C}{2bE} \sin\vartheta_0 = \frac{C}{2bE} \cos\frac{\chi}{2}$$

or

$$\cot \frac{\chi}{2} = 2bE/C \qquad 5.25$$

which is the well-known result. For other laws of force, knowledge of the orbit, $r = r(\psi)$, is requisite to the evaluation of the integral in 5.23. However, since asymptotic values are sought, the orbit may be taken in first approximation to be a straight line. The approximations $b \approx x$ and $\vartheta_0 \approx \frac{\pi}{2}$ then lead to the following expression for χ :

$$\sin \frac{\chi}{2} \approx \frac{x}{2E} \int_x^{\infty} \frac{F(r)\,dr}{\sqrt{r^2 - x^2}} \qquad 5.26$$

The singularity in the above integrand is removed by the substitution

$$x y^2 = r - x \qquad 5.27$$

whence,

$$\sin \frac{\chi}{2} \approx \frac{x}{E} \int_0^{\infty} \frac{F\{x(1+y^2)\}\,dy}{\sqrt{2+y^2}} \qquad 5.28$$

Expression 5.28 may be expected to yield the leading term in the asymptotic expression for χ .

A more accurate expression, in which the deviation of the orbit from a straight line is taken into account, may be found starting from equation 5.12. Define $G(y)$ by means of the expression

$$G(y) = \frac{1}{E - V(x)} \frac{\{V(x) - V(\frac{x}{1-y^2})\}}{y^2(2-y^2)} \qquad 5.29$$

then equation 5.12 may be expanded into the infinite series

$$\vartheta_0(x,E) = 2\sum_{n=0}^{\infty} \binom{-1/2}{n} \int_0^1 \frac{G^n(y)\,dy}{\sqrt{2-y^2}} \text{ , } \quad 5.30$$

Equation 5.30 is exact, and expresses ϑ_0 in powers of $V(x)$.

Since $|\chi| = |2\vartheta_0 - \pi|$

$$|\chi| = 4\left|\sum_{n=1}^{\infty} \binom{-1/2}{n} \int_0^1 \frac{G^n\,dy}{(2-y^2)^{1/2}}\right| \quad 5.31$$

The asymptotic value of χ , correct to the first power of $V(x)$ is given by the first term in the expression 5.31. Hence, apart from sign,

$$\chi \approx \frac{2}{E-V(x)} \int_0^1 \frac{V(x) - V\left(\frac{x}{1-y^2}\right)}{y^2(2-y^2)^{3/2}}\,dy \quad 5.32$$

Expression 5.32 may be transformed into a form suitable for asymptotic integration by means of the transformation $y = z(1+z^2)^{-1/2}$. There results

$$\chi \approx \frac{2^{-1/2}}{E-V(x)} \int_0^\infty dz \frac{1+z^2}{\left(1+\frac{z^2}{2}\right)^{3/2}} \frac{V(x)-V[x(1+z^2)]}{z^2} \quad 5.33$$

For charged particles

$$V \sim c' e^{-\kappa r}/r \quad 5.34$$

where κ is the reciprocal Debye distance. Hence equation 5.33 becomes

$$\chi \sim 2^{-1/2} \frac{e^{-\lambda}}{\lambda} \frac{c}{E-V(x)} \, J \qquad 5.35$$

where $C = K\,C'$, $\lambda = K x$ and

$$J = \int_0^\infty \frac{1+z^2}{(1+\frac{z^2}{2})^{3/2}} \, \frac{1+z^2-e^{-\lambda z^2}}{z^2} \, dz \, , \qquad 5.36$$

After some simplification J may be expressed as the sum

$$J = J_0 + J_1 \qquad 5.37$$

where

$$J_0 = \int_0^\infty \frac{1-e^{-\lambda z^2}}{z^2} \, dz \qquad 5.38$$

and

$$J_1 = \int_0^\infty \frac{1-(1+\frac{z^2}{2})^{-3/2}}{z^2} \, dz \qquad 5.39$$

The integral J_0 is simply evaluated, by forming the derivative

$$\frac{dJ_0}{d\lambda} = \int_0^\infty e^{-\lambda z^2} dz = \frac{\sqrt{\pi}}{2} \lambda^{-1/2} . \qquad 5.40$$

Therefore,

$$J_0 = \sqrt{\pi \lambda} + C \qquad 5.41$$

but since $J_0(0) = 0$, $C = 0$ and

$$J_0 = \sqrt{\pi \lambda} \, . \qquad 5.42$$

The integral J_1 is more complicated. However, for $0 \leq z^2 < 2$,

$$\frac{1-(1+\frac{z^2}{2})^{-3/2}}{z^2} = -\sum_{m=0}^{\infty} \binom{-3/2}{m+1} \frac{z^{2m}}{4^{m+1}} \, . \qquad 5.43$$

Therefore, by Watson's lemma,[60] the asymptotic expression for J_1 is given by

$$J_1 \approx -\sum_{m=0}^{\infty} \binom{-3/2}{m+1} \frac{1}{4^{m+1}} \int_0^{\infty} z^{2m} e^{-\lambda z^2} dz$$

$$\approx -\sum_{m=0}^{\infty} \binom{-3/2}{m+1} \frac{1}{4^{m+1}} \frac{1 \cdot 3 \cdot 5 \cdots (2m-1)}{\lambda^m} \sqrt{\frac{\pi}{\lambda}} \qquad 5.44$$

and χ is asymptotically given by the expression

$$\chi \sim \frac{1}{E - V(x)} C e^{-\kappa x} \sqrt{\frac{\pi}{2\kappa x}} \left\{ 1 + \frac{3}{8\kappa x} + \cdots \right\}, \qquad 5.45$$

If χ is estimated by using equation 5.23, the result is

$$\chi \sim \frac{1}{E} C e^{-\kappa x} \sqrt{\frac{\pi}{2\kappa x}} \left\{ 1 + \frac{1}{8\kappa x} + \cdots \right\}. \qquad 5.46$$

It is observed that the leading terms of expressions 5.45 and 5.46 are in agreement. If L is sufficiently large that 5.45 is a good approximation for $x \geqslant L$, the contribution to $\phi_{12}^{(\ell)}$ from $x \geqslant L$ can be estimated; and is given by

$$\frac{1}{2} g \int_L^{\infty} \left\{ 1 - \cos^{\ell} \chi \right\} d \left\{ x^2 \left[1 - \frac{V(x)}{E} \right] \right\} \cong$$

$$\frac{C^2}{E^2} g \ell \int_L^{\infty} e^{-2\kappa x} \frac{\pi}{2\kappa x} x \, dx =$$

$$\frac{\pi g \ell C^2 e^{-2\kappa L}}{(2\kappa x)^2 E^2} = \pi g \ell \left(\frac{C e^{-\kappa L}}{2\kappa E} \right)^2. \qquad 5.47$$

C. Numerical Evaluation of Stieltjes Integrals

Consider the integral

$$I = \int_a^b f(x)\, dg(x) \qquad 5.48$$

where f and g are known functions of x. The interval is split into a number of sub-intervals, a typical one of which is the interval $[x_0, x_0 + nh]$. Then I is equal to a sum of terms of which

$$I_n = \int_{x_0}^{x_0+nh} f(x)\, dg(x) \qquad 5.49$$

is typical. The functions f, g are approximated on $[x_0, x_0+nh]$ by Newton's interpolation formula[61]

$$f(x_0 + uh) \cong \sum_{l=0}^{n} \varphi_l(u)\, \Delta^l f_0 \qquad 5.50$$

where

$$\varphi_l(u) = \binom{u}{l} = \frac{u(u-1)\cdots(u-l+1)}{l!} \qquad 5.51$$

and

$$\Delta^l f_0 = \sum_{r=0}^{l} (-1)^{l-r} \binom{l}{r} f_r \qquad 5.52$$

with

$$f_r = f(x_0 + rh) \qquad 5.53$$

Similarly,

$$g(x_0 + uh) \cong \sum_{l=0}^{n} \varphi_l(u)\, \Delta^l g_0 \qquad 5.54$$

The integral I_n, therefore, may be approximated by the expression

$$I_n \cong \int_0^n \sum_l \sum_k \varphi_l(u)\,\varphi_k'(u)\,du\,\Delta^l f_0\,\Delta^k g_0 , \qquad 5.55$$

or, by the expression

$$I_n \cong \sum_l \sum_k J_{lk}\,\Delta^l f_0\,\Delta^k g_0 \qquad 5.56$$

where

$$J_{lk} \equiv \int_0^n \varphi_l(u)\,\varphi_k'(u)\,du . \qquad 5.57$$

The integrals J_{lk} may be evaluated by use of the generating function

$$(1+x)^u = \sum_l \varphi_l(u)\,x^l . \qquad 5.58$$

If the above expression is differentiated with respect to u, there results:

$$\ln(1+y)\,(1+y)^u = \sum_k \varphi_k'(u)\cdot y^k \qquad 5.59$$

The product of 5.58 and 5.59 is integrated from $u=0$ to $u=n$ with the result

$$\ln(1+y)\,\frac{e^{n\{\ln(1+x)(1+y)\}}-1}{\ln(1+x)(1+y)} = \sum_l \sum_k J_{lk}\,x^l y^k . \qquad 5.60$$

The left-hand side of equation 5.60 may be expanded into the power series

$$\ln(1+y)\sum_{m=1}^{\infty}\frac{n^m}{m!}\left\{\ln(1+x)(1+y)\right\}^{m-1} = \sum_l \sum_k J_{lk}\,x^l y^k \qquad 5.61$$

and J_{lk} is the coefficient of $x^l y^k$ in the left-hand side of equation 5.61.

For $n=2$, one finds

$$(J_{K\ell}) = \begin{pmatrix} 0 & 2 & 1 \\ 0 & 2 & 5/3 \\ 0 & 1/3 & 1/2 \end{pmatrix}, \; K,\ell = 0, 1, 2. \qquad 5.62$$

The substitution $\Delta^0 f_0 = f_0$, $\Delta^1 f_0 = f_1 - f_0$, $\Delta^2 f_0 = f_2 - 2f_1 + f_0$, $\Delta^0 g_0 = g_0$, etc., into equation 5.56 yields the generalized Simpson's rule formula

$$\int_{x_0}^{x_0+2h} f(x)\,dg(x) \cong \{-3f_0 g_0 + 4f_0 g_1 - f_0 g_2$$

$$-4f_1 g_0 + 4f_1 g_2 + f_2 g_0 - 4f_2 g_1 + 3f_2 g_2\}/6 \qquad 5.63$$

The evaluation of $\int_a^b f(x)\,dg(x)$ is achieved by splitting the interval $[a,b]$ into an even number N of intervals $[x_0, x_1]$ $[x_1, x_2]$, $\cdots$ $[x_{N-2}, x_{N-1}]$, $[x_{N-1}, x_N]$, applying the result 5.63 to each of the sub-intervals $[x_0, x_1, x_2]$, $[x_2, x_3, x_4]$, $\cdots$ $\cdots [x_{N-2}, x_{N-1}, x_N]$ and finally summing the $N/2$ contributions. The result is expressed by the formula

$$\int_{a=x_0}^{b=x_N} f(x)\,dg(x) \cong \frac{1}{6}\{-3f_0 g_0 +$$

$$4(f_0 g_1 + f_1 g_2 + \cdots + f_{N-1} g_N) - 4(g_0 f_1 + g_1 f_2 + \cdots g_{N-1} f_N)$$

$$-(f_0 g_2 + f_2 g_4 + \cdots + f_{N-2} g_N) + (g_0 f_2 + g_2 f_4 + \cdots + g_{N-2} f_N)$$

$$+ 3 f_N g_N\} \qquad 5.64$$

The above formula is quite simple to handle, and has a form independent of the parameterization of the functions f and g. That is, the formula 5.64 is invariant under the transformation $x \rightarrow y = y(x)$ Higher approximations may be obtained in a similar fashion, but they are very complicated.

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APPENDIX I

McCOY'S THEOREM

Theorem: $f \equiv e^{i(\mu q+\lambda p)} = e^{i\frac{\hbar}{2}\mu\lambda}\, e^{i\mu q}\, e^{i\lambda p},$

where μ, λ are scalars and $[q,p]_- = qp - pq = i\hbar$

Proof:

$$\frac{\partial}{\partial\lambda}(\mu q+\lambda p)^n =$$

$$\frac{\partial}{\partial\lambda}(\mu q+\lambda p)(\mu q+\lambda p)\cdots(n)\cdots(\mu q+\lambda p)=$$

$$\left[\frac{\partial}{\partial\lambda}(\mu q+\lambda p)\right](\mu q+\lambda p)^{n-1}+$$

$$(\mu q+\lambda p)\left[\frac{\partial}{\partial\lambda}(\mu q+\lambda p)\right](\mu q+\lambda p)^{n-2}+$$

$$\cdots(\mu q+\lambda p)^{n-1}\frac{\partial}{\partial\lambda}(\mu q+\lambda p)=$$

$$P(\mu q+\lambda p)^{n-1}+(\mu q+\lambda p)P(\mu q+\lambda p)^{n-2}+\cdots(\mu q+\lambda p)^{n-1}p$$

But,

$$[p,[\mu q+\lambda p]^m]_- = \mu m\frac{\hbar}{i}(\mu q+\lambda p)^{m-1}.$$

Hence

$$\frac{\partial}{\partial\lambda}(\mu q+\lambda p)^n = n(\mu q+\lambda p)^{n-1}p+\frac{n(n-1)}{2}\frac{\mu\hbar}{i}(\mu q+\lambda p)^{n-2}$$

and, therefore

$$\frac{1}{i}\frac{\partial f}{\partial\lambda} = fp+\frac{\mu\hbar}{2}f$$

The latter equation may be integrated, with the result

$$f = g\, e^{i(\lambda p + \frac{\hbar}{2}\mu\lambda)}$$

where g is independent of λ. Then $\lambda = 0 \Rightarrow f = g = e^{i\mu q}$ and therefore,

$$f = e^{i\frac{\hbar}{2}\mu\lambda}\, e^{i\mu q}\, e^{i\lambda p}.$$

APPENDIX II

THE OPERATOR $exp\left\{ i\lambda\left\{ \frac{\partial}{\partial q}, \frac{\partial}{\partial p} \right\} \right\}$

The result of application of the operator $e^{i\lambda\left\{\frac{\partial}{\partial q},\frac{\partial}{\partial p}\right\}}$ to the function $g(q\,p)\,f(q,p)$ is evaluated simply by using Fourier analysis. If ξ, η are the Fourier transforms of g, f,

$$e^{i\lambda\left\{\frac{\partial}{\partial q},\frac{\partial}{\partial p}\right\}} g f = \int_{u v u' v'} \xi(u v)\, \eta(u' v')\, e^{i\lambda\left\{\frac{\partial}{\partial q},\frac{\partial}{\partial p}\right\}} e^{2\pi i(u\cdot q+v\cdot p)}\, e^{2\pi i(u'\cdot q+v'\cdot p)} =$$

$$\int_{u v u' v'} \xi(u v)\, \eta(u' v')\, e^{-4\pi^2 i\lambda(u\cdot v'-v\cdot u')} e^{2\pi i(u\cdot q+v\cdot p)}\, e^{2\pi i(u'\cdot q+v'\cdot p)}$$

$$= \int_{\substack{u v u' v' \\ q' p' q'' p''}} g(q' p') f(q'' p'')\, e^{-2\pi i(u\cdot q'+v\cdot p')}\, e^{-2\pi i(u'\cdot q''+v'\cdot p'')} e^{-4\pi^2 i\lambda(u\cdot v'-v\cdot u')}\, e^{2\pi i(u\cdot q+v\cdot p)}\, e^{2\pi i(u'\cdot q+v'\cdot p)}$$

$$= \int_{\substack{v v' \\ q' q'' p' p''}} g(q' p') f(q'' p'')\, e^{2\pi i v\cdot(p-p')}\, e^{2\pi i v'\cdot(p-p'')} \cdot \delta(q-q'-2\pi\lambda v') \cdot \delta(q-q''-2\pi\lambda v)$$

$$= \int_{v v' p' p''} e^{2\pi i v\cdot(p-p')}\, e^{2\pi i v'\cdot(p-p'')}\, g(q-2\pi\lambda v', p')\, f(q+2\pi\lambda v, p'')$$

An equivalent form is obtained from the second line above by integrating with respect to u', v',

$$e^{i\lambda\left\{\frac{\partial}{\partial q},\frac{\partial}{\partial p}\right\}} g f =$$

$$\int_{uv} e^{2\pi i(u\cdot q+v\cdot p)}\,\xi(u,v)\, f\,(q+2\pi\lambda v;\, p-2\pi\lambda u).$$

APPENDIX III

PHASE SPACE TREATMENT OF THE SIMPLE HARMONIC OSCILLATOR

The phase space wave function must satisfy the equations

$$\sin \frac{\hbar}{2}\left\{\frac{\partial}{\partial q},\frac{\partial}{\partial p}\right\} H f = 0 \quad , \qquad \text{III 1}$$

$$\cos \frac{\hbar}{2}\left\{\frac{\partial}{\partial q},\frac{\partial}{\partial p}\right\} H f = E f \quad , \qquad \text{III 2}$$

where

$$H = p^2/2m + m\omega^2 q^2/2 \qquad \text{III 3}$$

The use of expression III 3 in III 1 and III 2 leads to the equations

$$m\omega^2 q \frac{\partial}{\partial p} f - \frac{p}{m}\frac{\partial}{\partial q} f = 0 \, , \qquad \text{III 4}$$

and

$$E f =$$

$$(p^2/2m + m\omega^2 q^2/2) f - \frac{\hbar^2}{8}\left(m\omega^2 \frac{\partial^2 f}{\partial p^2} + \frac{1}{m}\frac{\partial^2 f}{\partial q^2}\right). \qquad \text{III 5}$$

Let the operators a, b be defined as follows:

$$a = \frac{1}{\sqrt{m\omega\hbar}}\, p + \frac{1}{2}\sqrt{m\omega\hbar}\, \frac{\partial}{\partial p} \qquad \text{III 6}$$

$$b = \sqrt{\frac{m\omega}{\hbar}}\, q + \frac{1}{2}\sqrt{\frac{\hbar}{m\omega}}\, \frac{\partial}{\partial q} \qquad \text{III 7}$$

It then follows that

$$[a, a^+]_- = [b, b^+]_- = 1, \qquad \text{III 8}$$

and

$$[a, b] = [a^+, b] = [a, b^+] = [a^+, b^+] = 0, \qquad \text{III 9}$$

In terms of the operations a, b equations III 4 and III 5 become

$$a b^+ f = a^+ b f \qquad \text{III 10}$$

$$\frac{\hbar\omega}{2}\left\{ a^+ a + b^+ b + 1 \right\} f = E f \qquad \text{III 11}$$

Equation III 11 may be simply solved using the method of Fock. The solutions of equation III 11 are expressed in terms of two integers n_1, n_2, and are given by

$$E_{n_1 n_2} = \frac{\hbar\omega}{2}\left(n_1 + n_2 + 1 \right) \qquad \text{III 12}$$

$$f_{n_1 n_2} = \frac{1}{\sqrt{n_1!\, n_2!}} (a^+)^{n_1} (b^+)^{n_2} f_{00} \qquad \text{III 13}$$

where

$$a f_{00} = b f_{00} = 0. \qquad \text{III 14}$$

The normalized solution of equation III 14 is

$$f_{00} = \frac{1}{\pi\hbar} e^{-2H/\hbar\omega}. \qquad \text{III 15}$$

The solutions $f_{n_1 n_2}$ are degenerate, but this degeneracy is removed by the requirement III 10. The most general solution of III 11 is

$$f = \sum_{n=-n_1}^{n_2} c_n f_{n_1+n,\, n_2-n} \qquad \text{III 16}$$

and the energy $E = \frac{\hbar\omega}{2}(n_1 + n_2 + 1)$. Since

$$a^{+} f_{n_1 n_2} = \sqrt{n_1+1}\; f_{n_1+1, n_2} \qquad \text{III 17}$$

$$a\, f_{n_1 n_2} = \sqrt{n_1}\; f_{n_1-1, n_2} \qquad \text{III 18}$$

$$b^{+} f_{n_1 n_2} = \sqrt{n_2+1}\; f_{n_1, n_2+1} \qquad \text{III 19}$$

and

$$b\, f_{n_1 n_2} = \sqrt{n_2}\; f_{n_1, n_2-1} \;, \qquad \text{III 20}$$

the condition III 10 may be expressed by the equation

$$a \sum_{n=-n_1}^{n_2} c_n \sqrt{n_2-n+1}\; f_{n_1+n\,;\, n_2-n+1} =$$

$$a^{+} \sum_{n=-n_1}^{n_2} c_n \sqrt{n_2-n}\; f_{n_1+n\,;\, n_2-n-1} \;, \qquad \text{III 21}$$

or by

$$\sum_{n=-n_1}^{n_2} c_n \sqrt{(n_1+n)(n_2-n+1)}\; f_{n_1+n-1\,;\, n_2-n+1} =$$

$$\sum_{n=-n_1}^{n_2} c_n \sqrt{(n_1+n+1)(n_2-n)}\; f_{n_1+n+1\,;\, n_2-n-1} =$$

$$\sum_{n=-n_1+2}^{n_2+2} c_{n-2} \sqrt{(n_1+n-1)(n_2-n+2)}\; f_{n_1+n-1\,;\, n_2-n+1} . \qquad \text{III 22}$$

The $f_{n_1 n_2}$ are independent. In fact, they are orthogonal

$$\langle f_{n_1 n_2} \,;\, f_{n_1' n_2'} \rangle = \delta_{n_1 n_1'}\, \delta_{n_2 n_2'} \,. \qquad \text{III 23}$$

Therefore,

$$c_{-n_1+1} = c_{n_2-1} = 0 \;, \qquad \text{III 24}$$

and

$$C_{n-2} = \sqrt{\frac{(n_1+n)(n_2-n+1)}{(n_1+n-1)(n_2-n+2)}}\; C_n \; . \qquad \text{III 25}$$

Hence $n_1 = n_2 = N$, say, and

$$C_{n-2} = \sqrt{\frac{(N+n)(N-n+1)}{(N+n-1)(N-n+2)}}\; C_n \; , \qquad \text{III 26}$$

while

$$E_n = \hbar\omega(N+1/2) \; , N=0,1,2,\ldots \qquad \text{III 27}$$

The coefficients C_n are all expressed in terms of C_N, which is determined by the normalization

$$\langle f_N, f_N \rangle = 1 \qquad \text{III 28}$$

The usual formula III 27 has been obtained. Ühlhorn found the solutions f_N in terms of Laguerre functions, while the solutions here are expressed in terms of Hermite functions $f_{n_1 n_2}$. That the two solutions are in fact the same follows from the addition theorem for Hermite polynomials,[62]

$$(-1)^N \sum_{K=0}^{N} \binom{N}{K} H_{2K}(x)\, H_{2N-2K}(y) = N!\, L_N(x^2+y^2) \qquad \text{III 29}$$

where L_N is the Laguerre polynomical.

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