A STATISTICAL DERIVATION OF THE HYDRODYNAMIC EQUATIONS OF CHANGE FOR A SYSTEM OF IONIZED MOLECULES*

by

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ABSTRACT

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Non-relativistic, classical statistical mechanics is used to describe a dense fluid of molecules composed of nuclei and electrons with a purely coulomb interaction potential. A general equation of change is derived for the time rate of change of any macroscopic (ensemble averaged) dynamical variable. From this general equation, Maxwell's equations in a medium and the hydrodynamic equations of change are derived and expressed in terms of molecular properties, e.g. polarization and magnetization densities. These equations are discussed in the limiting case of low density and compared with previous results.

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INTRODUCTION

A fluid system near equilibrium may be described either microscopically or macroscopically. Microscopically, the system is regarded as being composed of discrete particles, the state of each particle being described by its position and momentum coordinates. The time evolution of the state of the system is described by Newton's equations. From a macroscopic viewpoint, the system is considered as a continuous fluid, the state of each infinitesimal region of the fluid being described by its mass, momentum, and energy densities. The time evolution of these densities is described by the hydrodynamic equations. Naturally, a macroscopic description is the only practical one for a system of more than a few hundred particles. Using such a description, the fundamental problem of treating a fluid near equilibrium is that of obtaining the hydrodynamic equations of change and the phenomenological coefficients for the fluid.

For a dilute gas, these equations are particularly easy to derive.[1] The equation of continuity or mass density equation of change is

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \underline{r}} \cdot \rho \underline{v} = 0 , \tag{0.0.1}$$

the equation of motion or momentum density equation of change is

$$\frac{\partial \rho \underline{v}}{\partial t} + \frac{\partial}{\partial \underline{r}} \cdot \left(\rho \underline{v}\,\underline{v} + \underline{\underline{p}}_K \right) = 0, \tag{0.0.2}$$

and the equation of change for the energy density is

$$\frac{\partial \rho \left(U_K + \frac{1}{2} v^2 \right)}{\partial t} + \frac{\partial}{\partial \underline{r}} \cdot \left[\rho \left(U_K + \frac{1}{2} v^2 \right) + \underline{\underline{p}}_K \cdot \underline{v} + \underline{q}_K \right] = 0. \tag{0.0.3}$$

In the above, radiation effects and external forces are neglected. The quantity, ρ , is the macroscopic mass density, $\underline{v}$ is the stream velocity, $\underline{\underline{p}}_K$ is the kinetic pressure tensor, U_K is the kinetic energy density, and $\underline{q}_K$ is the kinetic energy flux.

Irving and Kirkwood have studied the more general problem and have derived the equations of change for a dense fluid.[2] Essentially, this derivation results in the addition of interaction or "collisional" terms to the pressure tensor, energy density, and energy flux of equations (0.0.2) and (0.0.3). However, this work was restricted to systems for which the interparticle potential approaches zero faster than the inverse square or higher power of the interparticle distance. Hence, the work is not applicable to coulomb systems for which the interparticle potential is proportional to the inverse first power of the interparticle distance. The equations of change for such a system are essential to the study of magnetohydrodynamics, plasma physics, and any field concerned with the behavior of ionized gases. Thus it is desirable to supplement the preceding development by deriving the equations of change for a dense coulomb gas.

The Irving and Kirkwood derivation of the equations of change is statistical, i.e. the macroscopic description of the system is obtained by statistically averaging over an ensemble of systems. (This procedure is discussed in detail in Chapter I of the present work.) Many of the derivations of the equations of change for a coulomb system, however, are non-statistical.[3,4] Starting with (0.0.1), (0.0.2), and (0.0.3), the equations for a dilute system, the derivations add terms to the energy, momentum, and flux densities. The added terms are macroscopic representations of the electromagnetic properties which arise from the microscopic coulomb interactions of the system. Although there is good agreement among various sources as to what these contributions are for a system of isolated point particles, there is disagreement when the particles are assumed to be grouped into molecules. From a purely classical viewpoint, the potential between two molecules is a result of the interactions between the nuclei and electrons composing the molecules. In view of the complexity of these interactions, the intermolecular potential is usually expanded in a Taylor series about the center of mass of the molecule so that the molecule is represented as a collection of superimposed multipoles (monopole, dipole, quadrapole, etc.). In the macroscopic equations of change for a molecular system, the electromagnetic contributions contain terms involving the multipole densities. The reasoning that is used to introduce these densities into the equations of change when they are non-statistically derived is not very satisfying and leads to the conflicting results among the various sources that we mentioned previously. Hence a statistical derivation of the equations of change for the coulomb system is extremely desirable.

In recent years several authors have in a limited way undertaken statistical derivations. Mazur has derived an equation of momentum change by such an approach.[5] He neglected magnetic effects, however, and treated only a system of neutral molecules. Britten included magnetic effects in his derivation of the mass and momentum. equations for a coulomb system but considered only point particles.[6] Kaufman derived an energy equation of change as well as mass and momentum equations of change, but again considered only point particles.[7]

It is the purpose of this work to derive, statistically, the equations of change for a system of molecules. In the development of the equations, expressions for the electromagnetic contributions to the energy and momentum densities are obtained. In Chapter I, a general equation of change for any macroscopic density is developed. This equation is then used in Chapter II to derive a set of Maxwell's equations for the macroscopic electric and magnetic field densities. (Maxwell's equations are a necessary addition to the hydrodynamic equations of a coulomb system.) Finally, the equations of change for the mass density, momentum density, and energy density are derived in Chapters III, IV, and V. Wherever it seems possible in these derivations, we interpret the quantities that arise in the resulting equations in terms of known physical entities such as current density, and polarization density.

Non-relativistic, classical mechanics is used throughout this work. In many applications, relativistic effects are completely negligible. These effects are only important in extremely high temperature plasma such as that existing in stars. For a system of molecules, of course, a classical treatment is not adequate. However, a quantum mechanical treatment would probably not alter the equations of change but only affect the detailed expressions for the densities. Since these expressions are not evaluated in this work, the quantum mechanical development is reserved for discussion at a later date.

I. THE GENERAL EQUATION OF CHANGE

In this chapter we use statistical techniques to derive a general equation of change for a system of N charged point particles. These particles may be considered as representing the nuclei and electrons in a real system. Although the molecular properties of the system do not concern us in this chapter, for convenience in succeeding chapters, we make use of a double subscript notation suggesting that the particles are clustered into groups representing molecules and ions. Assuming that the particles obey the laws of classical, non-relativistic mechanics, we begin by writing the classical equations for the microscopic interactions of the particles and the electromagnetic fields that they produce.

1.1 The Microscopic Equations

Newton's equation of motion for particle i of molecule or ion k is

$$F_{ki} = m_{ki} \frac{d^2 \underline{r}_{ki}}{dt^2} , \qquad (1.1.1)$$

where m_{ki} is the mass and $\underline{r}_{ki}$ is the position vector of particle ki. The force, $\underline{F}_{ki}$, on particle ki is given by the Lorentz expression,

$$\underline{F}_{ki} = e_{ki}\left[\underline{E}^{\mu}_{ki}(\underline{r}_{ki}) + \frac{1}{c}\left(\underline{u}_{ki} \times \underline{B}^{\mu}(\underline{r}_{ki})\right)\right], \qquad (1.1.2)$$

where e_{ki} is the charge and $\underline{u}_{ki}$ is the velocity of particle ki, and where $\underline{E}^{\mu}_{ki}(\underline{r}_{ki})$ is the electric field and $\underline{B}^{\mu}(\underline{r}_{ki})$ is the magnetic field at particle ki produced by the particles and by the external sources. The subscript ki on $\underline{E}^{\mu}_{ki}$ indicates that the coulombic effects of particle ki are not included in the expression for the electric field at particle ki. This point is clarified in section 1.3 where the expression for $\underline{E}^{\mu}_{ki}$ is developed.

Maxwell's equations for the system are

$$\frac{\partial}{\partial \underline{r}} \times \underline{E}^{\mu}(\underline{r}) + \frac{1}{c}\dot{\underline{B}}^{\mu}(\underline{r}) = 0, \qquad (1.1.3)$$

$$\frac{\partial}{\partial \underline{r}} \cdot \underline{B}^{\mu}(\underline{r}) = 0, \qquad (1.1.4)$$

$$\frac{\partial}{\partial \underline{r}} \times \underline{B}^{\mu}(\underline{r}) - \frac{1}{c}\dot{\underline{E}}^{\mu}(\underline{r}) = \frac{4\pi}{c}\sum_{ki} e_{ki}\,\underline{u}_{ki}\,\delta(\underline{r}_{ki} - \underline{r}), \qquad (1.1.5)$$

and

$$\frac{\partial}{\partial \underline{r}} \cdot \underline{E}^{\mu}(\underline{r}) = 4\pi \sum_{ki} e_{ki}\,\delta(\underline{r}_{ki} - \underline{r}), \qquad (1.1.6)$$

where $\delta(\underline{r})$ is the Dirac delta function.

The first two Maxwell equations, (1.1.3) and (1.1.4), are satisfied by the following expressions for $\underline{B}^{\mu}$ and $\underline{E}^{\mu}$:

$$\underline{B}^{\mu}(\underline{r}) = \frac{\partial}{\partial \underline{r}} \times \underline{A}(\underline{r}) \tag{1.1.7}$$

and

$$\underline{E}^{\mu}(\underline{r}) = -\frac{\partial}{\partial \underline{r}} \phi(\underline{r}) - \frac{1}{c} \dot{\underline{A}}(\underline{r}), \tag{1.1.8}$$

where $\underline{A}$ is an arbitrary vector function called the vector potential, and ϕ is an arbitrary scalar function called the scalar potential. Equations (1.1.7) and (1.1.8) are dquivalent to (1.1.3) and (1.1.4) and serve as partial definitions of $\underline{A}$ and ϕ .

In the next three sections, we derive Hamilton's equations for the system under consideration and show that these equations are equivalent to the microscopic equations just given. The treatment of these three sections follows closely a similar treatment of Heitler[8]. It is included here for the sake of completeness and to introduce the notation involved.

1.2 The Hamiltonian of the Particles

We first seek a Lagrangian of the system which leads to a set of equations of motion equivalent to (1.1.1). From this Lagrangian we obtain the desired Hamiltonian for the particles. Substituting

(1.1.2), (1.1.7), and (1.1.8) into (1.1.1) we obtain

$$e_{ki}\left\{-\frac{\partial\phi_{ki}(\underline{r}_{ki})}{\partial\underline{r}_{ki}}-\frac{1}{c}\dot{\underline{A}}(\underline{r}_{ki})+\frac{1}{c}\left[\underline{u}_{ki}\times\left(\frac{\partial}{\partial\underline{r}_{ki}}\times\underline{A}(\underline{r}_{ki})\right)\right]\right\}=m_{ki}\frac{d\underline{u}_{ki}}{dt}. \tag{1.2.1}$$

The notation, $\phi_{ki}(\underline{r}_{ki})$, represents the potential, $\phi(\underline{r})$, evaluated at the position $(\underline{r}=\underline{r}_{ki})$ of particle ki, but excluding the self-potential of this particle. The total time derivative of $\underline{A}(\underline{r}_{ki})$ is given by

$$\frac{d\underline{A}(\underline{r}_{ki})}{dt}=\dot{\underline{A}}(\underline{r}_{ki})+\underline{u}_{ki}\cdot\frac{\partial}{\partial\underline{r}_{ki}}\underline{A}(\underline{r}_{ki}). \tag{1.2.2}$$

In the above equation, the $(\dot{\ })$ above a function indicates partial differentiation of the function with respect to time holding constant only the parenthesized variables at the right of the function, i.e.,

$$\dot{f}(\underline{r}_{ki})\equiv\left(\frac{\partial f}{\partial t}\right)_{\underline{r}_{ki}}. \tag{1.2.3}$$

When there is no parenthesized variable, the variable held constant is taken to be $\underline{r}$.

Substituting (1.2.2) and the vector identity,

$$\underline{u}_{ki}\times\left(\frac{\partial}{\partial\underline{r}_{ki}}\times\underline{A}(\underline{r}_{ki})\right)=\left(\frac{\partial}{\partial\underline{r}_{ki}}\underline{A}(\underline{r}_{ki})\right)\cdot\underline{u}_{ki}-\underline{u}_{ki}\cdot\frac{\partial}{\partial\underline{r}_{ki}}\underline{A}(\underline{r}_{ki}), \tag{1.2.4}$$

into (1.2.1), we find that

$$e_{ki}\left[-\frac{\partial \phi_{ki}(\underline{r}_{ki})}{\partial \underline{r}_{ki}}+\frac{1}{c}\left(\frac{\partial \underline{A}(\underline{r}_{ki})}{\partial \underline{r}_{ki}}\right)\cdot\underline{u}_{ki}-\frac{1}{c}\frac{d\underline{A}(\underline{r}_{ki})}{dt}\right]=m_{ki}\frac{d\underline{u}_{ki}}{dt}. \tag{1.2.5}$$

Since ϕ and $\underline{A}$ are independent of $\underline{u}_{ki}$, the above relations may be rearranged to give

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \underline{u}_{ki}}-\frac{\partial \mathcal{L}}{\partial \underline{r}_{ki}}=0, \tag{1.2.6}$$

where

$$\mathcal{L}\equiv\sum_{ki}\left(\frac{1}{2}m_{ki}u_{ki}^{2}-e_{ki}\,\phi_{ki}(\underline{r}_{ki})+\frac{e_{ki}}{c}\underline{u}_{ki}\cdot\underline{A}(\underline{r}_{ki})\right) \tag{1.2.7}$$

is the Lagrangian. Equation (1.2.6) is equivalent to Newton's equations, (1.1.1), and Lorentz's equations, (1.1.2), combined, and represents a set of Lagrangian equations for the particles.

We now define, in the usual fashion, a momentum,

$$\underline{p}_{ki}\equiv\frac{\partial \mathcal{L}}{\partial \underline{u}_{ki}}=m_{ki}\underline{u}_{ki}+\frac{e_{ki}}{c}\underline{A}(\underline{r}_{ki}), \tag{1.2.8}$$

conjugate to $\underline{r}_{ki}$. Notice that $\underline{p}_{ki}$ is similar to the usual linear momentum, $m_{ki}\underline{r}_{ki}$, for particle ki except for an additional term involving the vector potential. Using (1.2.7) and (1.2.8), the particle Hamiltonian, which is defined as

$$\mathcal{H}_p \equiv \sum_{ki} \underline{u}_{ki} \cdot \underline{p}_{ki} - \mathcal{L} \,, \tag{1.2.9}$$

may be written as

$$\mathcal{H}_p = \sum_{ki} \frac{1}{2m_{ki}} \left| \underline{p}_{ki} - \frac{e_{ki}}{c} \underline{A}(\underline{r}_{ki}) \right|^2 + \sum_{ki} e_{ki} \phi_{ki}(\underline{r}_{ki}) . \tag{1.2.10}$$

Later, in section 1.4, it is confirmed that the above expression leads to a set of Hamiltonian equations for the particles, which are equivalent to Newton's and Lorentz's combined equations.

1.3 The Hamiltonian of the Fields

We now seek a Lagrangian and corresponding Hamiltonian which lead to the equations of motion of the fields. From Maxwell's last two equations, (1.1.5) and (1.1.6), and the definitions of the scalar and vector potentials, (1.1.7) and (1.1.8), we derive differential equations for $\underline{A}$ and ϕ. First we substitute (1.1.7) and (1.1.8) into (1.1.5) and (1.1.6). From (1.1.5) we obtain

$$\frac{\partial}{\partial \underline{r}} \times \left(\frac{\partial}{\partial \underline{r}} \times \underline{A} \right) + \frac{1}{c} \frac{\partial \dot{\phi}}{\partial \underline{r}} + \frac{1}{c^2} \ddot{\underline{A}} = \frac{4\pi}{c} \sum_{ki} e_{ki} \underline{u}_{ki} \delta(\underline{r}_{ki} - \underline{r}) . \tag{1.3.1}$$

Then, using the vector identity,

$$\frac{\partial}{\partial \underline{r}} \times \left(\frac{\partial}{\partial \underline{r}} \times \underline{A} \right) = \frac{\partial}{\partial \underline{r}} \left(\frac{\partial}{\partial \underline{r}} \cdot \underline{A} \right) - \frac{\partial^2 \underline{A}}{\partial r^2} \,, \tag{1.3.2}$$

we obtain one of the desired differential equations,

$$\frac{1}{c^2}\ddot{\underline{A}} - \frac{\partial^2 \underline{A}}{\partial r^2} + \frac{\partial}{\partial \underline{r}}\left(\frac{\partial}{\partial \underline{r}}\cdot\underline{A} + \frac{1}{c}\dot{\phi}\right) = \frac{4\pi}{c}\sum_{ki} e_{ki}\underline{u}_{ki}\,\delta\left(\underline{r}_{ki}-\underline{r}\right). \tag{1.3.3}$$

From (1.1.6) we obtain the second desired equation,

$$\frac{\partial^2 \phi}{\partial r^2} + \frac{1}{c}\frac{\partial}{\partial \underline{r}}\cdot\dot{\underline{A}} = -4\pi\sum_{ki} e_{ki}\,\delta\left(\underline{r}_{ki}-\underline{r}\right). \tag{1.3.4}$$

Equations (1.3.3) and (1.3.4) can be simplified by use of the Coulomb gauge. The vector and scalar potentials, $\underline{A}$ and ϕ are only partially defined by (1.1.7) and (1.1.8). As a further part of the definition, we require that $\underline{A}$ satisfy the relation

$$\frac{\partial}{\partial \underline{r}}\cdot\underline{A} = 0. \tag{1.3.5}$$

With this choice of the gauge condition, (1.3.3) and (1.3.4) become, respectively,

$$\frac{1}{c^2}\ddot{\underline{A}} - \frac{\partial^2 \underline{A}}{\partial r^2} + \frac{1}{c}\frac{\partial \dot{\phi}}{\partial \underline{r}} = \frac{4\pi}{c}\sum_{ki} e_{ki}\underline{u}_{ki}\,\delta\left(\underline{r}_{ki}-\underline{r}\right) \tag{1.3.6}$$

and

$$\frac{\partial^2 \phi}{\partial r^2} = -4\pi\sum_{ki} e_{ki}\,\delta\left(\underline{r}_{ki}-\underline{r}\right). \tag{1.3.7}$$

It is convenient to separate $\underline{A}$ and ϕ, each, into an external part, which arises from charges external to the system, and an internal part, which is produced by the system itself:

$$\underline{A} = \underline{A}^{(i)} + \underline{A}^{(e)}. \tag{1.3.8}$$

$$\phi = \phi^{(i)} + \phi^{(e)}. \tag{1.3.9}$$

The external contributions, $\underline{A}^{(e)}$ and $\phi^{(e)}$, have no sources inside the system and, hence, from (1.3.5), (1.3.6), and (1.3.7), satisfy the following set of equations:

$$\frac{\partial}{\partial \underline{r}} \cdot \underline{A}^{(e)} = 0. \tag{1.3.10}$$

$$\frac{1}{c^2} \ddot{\underline{A}}^{(e)} - \frac{\partial^2 \underline{A}^{(e)}}{\partial r^2} + \frac{1}{c} \frac{\partial \dot{\phi}^{(e)}}{\partial \underline{r}} = 0. \tag{1.3.11}$$

$$\frac{\partial^2 \phi^{(e)}}{\partial r^2} = 0. \tag{1.3.12}$$

The internal contributions, thus, satisfy the equations,

$$\frac{\partial}{\partial \underline{r}} \cdot \underline{A}^{(i)} = 0, \tag{1.3.13}$$

$$\frac{1}{c^2}\ddot{\underline{A}}^{(i)} - \frac{\partial^2 \underline{A}^{(i)}}{\partial r^2} + \frac{1}{c}\frac{\partial \dot{\phi}^{(i)}}{\partial \underline{r}} = \frac{4\pi}{c}\sum_{ki} e_{ki}\underline{u}_{ki}\,\delta(\underline{r}_{ki}-\underline{r}), \tag{1.3.14}$$

and

$$\frac{\partial^2 \phi^{(i)}}{\partial r^2} = -4\pi\sum_{ki} e_{ki}\,\delta(\underline{r}_{ki}-\underline{r}). \tag{1.3.15}$$

Equation (1.3.15) may readily be solved, to give

$$\phi^{(i)}(\underline{r}) = \sum_{ki}\frac{e_{ki}}{|\underline{r}_{ki}-\underline{r}|}\,. \tag{1.3.16}$$

Thus, in the coulomb gauge, $\phi^{(i)}$ is expressible solely in terms of the particle coordinates.

We now return to (1.3.13) and (1.3.14) to derive a set of Hamiltonian equations for $\underline{A}^{(i)}$. For this purpose we expand $\underline{A}^{(i)}$ in a series of orthogonal time independent functions, $A_\lambda(\underline{r})$. In order that there be an enumerable number of such functions, it is convenient to restrict the discussion to a system enclosed in a cubical box of side length L . Since the system as a whole has no net charge, we take the box large enough that $\phi^{(i)} = 0$ on its surfaces. We further assume that $\underline{A}^{(i)}$ is periodic on the surface of the box, i.e. that $\underline{A}^{(i)}$ and its derivatives have the same values at corresponding points on opposite planes. The $\underline{A}_\lambda$ are, then, defined by

$$\frac{\partial^2 \underline{A}_\lambda}{\partial r^2} + \frac{\omega_\lambda^2}{c^2} \underline{A}_\lambda = 0, \tag{1.3.17}$$

$$\frac{\partial}{\partial \underline{r}} \cdot \underline{A}_\lambda = 0, \tag{1.3.18}$$

and

$$\int_{L^3} \underline{A}_\lambda \cdot \underline{A}_\mu \, d\underline{r} = 4\pi c^2 L^3 \delta_{\lambda\mu} \quad ; \; \delta_{\lambda\mu} = \begin{cases} 0 & \text{if } \lambda \neq \mu \\ 1 & \text{if } \lambda = \mu . \end{cases} \tag{1.3.19}$$

Equation (1.3.18) ensures that the gauge condition, (1.3.13), is obeyed and (1.3.19) is a normality condition. In addition,[9] we require as a boundary condition on (1.3.17) that the $\underline{A}_\lambda$ be periodic on the surface of L^3.

Since the $\underline{A}_\lambda$ form a complete set of vector functions, the vector potential $\underline{A}^{(i)}$ may be expanded in the form,

$$\underline{A}^{(i)}(\underline{r},t) = \sum_\lambda q_\lambda(t) \underline{A}_\lambda(\underline{r}). \tag{1.3.20}$$

Substituting (1.3.20) into (1.3.14), taking the dot product of both sides with $\underline{A}_\mu$, and integrating over L^3, we obtain

$$\frac{1}{c^2}\sum_{\lambda}\ddot{q}_{\lambda}\int_{L^3}\underline{A}_{\lambda}\cdot\underline{A}_{\mu}\,d\underline{r}-\sum_{\lambda}q_{\lambda}\int_{L^3}\frac{\partial^2\underline{A}_{\lambda}}{\partial r^2}\cdot\underline{A}_{\mu}\,d\underline{r}+\frac{1}{c}\int_{L^3}\frac{\partial\phi^{(i)}}{\partial\underline{r}}\cdot\underline{A}_{\mu}\,d\underline{r}$$

$$=\frac{4\pi}{c}\sum_{ki}e_{ki}\underline{u}_{ki}\cdot\int_{L^3}\underline{A}_{\mu}\,\delta(\underline{r}_{ki}-\underline{r})\,d\underline{r}\,. \qquad (1.3.21)$$

The first term on the left of (1.3.21) is easily evaluated from the normality condition, the second term is evaluated from (1.3.17) and (1.3.19), while the term on the right is a familiar delta-function integral. Finally, the last term on the left is shown to be zero as follows:

$$\int_{L^3}\frac{\partial\dot{\phi}^{(i)}}{\partial\underline{r}}\cdot\underline{A}_{\mu}\,d\underline{r}=\int_{L^3}\frac{\partial}{\partial\underline{r}}\cdot\dot{\phi}^{(i)}\underline{A}_{\mu}\,d\underline{r}-\int_{L^3}\dot{\phi}^{(i)}\frac{\partial}{\partial\underline{r}}\cdot\underline{A}_{\mu}\,d\underline{r}$$

$$=\int_{S}\dot{\phi}^{(i)}\underline{A}_{\mu}\cdot\underline{dS}\,. \qquad (1.3.22)$$

The second term in the first line of (1.3.22) is zero due to the gauge condition, (1.3.18). The boundaries of the system of particles may be taken as the integration boundaries of the surface integral in (1.3.22). Since the system is charge neutral, i.e.

$$\sum_{ki}e_{ki}=0, \qquad (1.3.23)$$

$\phi^{(i)}$ is assumed to be zero on the boundaries of the system. Hence, the surface integral is also zero, and (1.3.22) may be written as

$$\int_{L^3}\frac{\partial\dot{\phi}^{(i)}}{\partial\underline{r}}\cdot\underline{A}_{\mu}\,d\underline{r}=0. \qquad (1.3.24)$$

In view of the above arguments, we may write (1.3.21) as

$$\ddot{q}_\lambda + \omega_\lambda^2 q_\lambda = \frac{1}{c}\sum_{ki} e_{ki}\, \underline{u}_{ki} \cdot \underline{A}_\lambda(\underline{r}_{ki}), \tag{1.3.25}$$

(where for convenience we have changed the index μ to λ).

The equations (1.3.25) are equivalent to Maxwell's equations and are also analogous to the equations of motion of a system of independent forced harmonic oscillators. Carrying this analogy further, we may take as the Hamiltonian for the fields, the Hamiltonian of the equivalent system of oscillators, namely:

$$\begin{aligned} \mathcal{H}_f &= -\sum_{ki} \frac{e_{ki}}{c}\, \underline{u}_{ki} \cdot \sum_\lambda q_\lambda \underline{A}_\lambda(\underline{r}_{ki}) + \frac{1}{2}\sum_\lambda \left(p_\lambda^2 + \omega_\lambda^2 q_\lambda^2\right) \\ &= -\sum_{ki} \frac{e_{ki}}{c}\, \underline{u}_{ki} \cdot \underline{A}(\underline{r}_{ki}) + \frac{1}{2}\sum_\lambda \left(p_\lambda^2 + \omega_\lambda^2 q_\lambda^2\right), \end{aligned} \tag{1.3.26}$$

where p_λ is the momentum conjugate to q_λ . In the following section, we confirm that the above Hamiltonian leads to a set of Hamiltonian equations for the fields. In view of the analysis in this section, these Hamiltonian equations are equivalent to Maxwell's equations, (1.1.3) to (1.1.6).

1.4 The Complete Hamiltonian and the Hamiltonian Equations of Motion.

A comparison of (1.2.10) and (1.3.26) suggests considering the particle Hamiltonian, $\mathcal{H}_p$, plus the last term of the field Hamiltonian, $\mathcal{H}_f$, as the Hamiltonian,

$$\mathcal{H} = \sum_{ki} \frac{1}{2m_{ki}} \left| \underline{p}_{ki} - \frac{e_{ki}}{c} \underline{A}(\underline{r}_{ki}) \right|^2 + \sum_{ki} e_{ki} \phi_{ki}(\underline{r}_{ki}) + \frac{1}{2} \sum_{\lambda} \left(p_\lambda^2 + \omega_\lambda^2 q_\lambda^2 \right), \tag{1.4.1}$$

for the complete system (both fields and particles). The first term $-\sum_{ki} \frac{e_{ki}}{c} \underline{u}_{ki} \cdot \underline{A}(\underline{r}_{ki})$, in the expression for $\mathcal{H}_f$ is already included in the first term of the expression for $\mathcal{H}_p$; hence this term should not be repeated in the expression for $\mathcal{H}$.

Since, from (1.2.8), the first term in (1.4.1) may be written as $\sum_{ki} \frac{1}{2} m_{ki} u_{ki}^2$, this term is the kinetic energy of the particles. The second term in (1.4.1) is the coulomb potential energy of the particles, and the final term is the energy of the electromagnetic fields.[10] Therefore, $\mathcal{H}$, as given by (1.4.1) is the total energy of the system. However, the only true criterion for deciding whether (1.4.1) is the correct form for the Hamiltonian of the system is to ascertain, as is done next, that $\mathcal{H}$ yields a set of Hamiltonian equations of motion consistent with the microscopic equations of motion for the system.

From Hamilton's equations of motion it follows directly that

$$\dot{\underline{r}}_{ki} = \frac{\partial \mathcal{H}}{\partial \underline{p}_{ki}},$$

or

$$\underline{u}_{ki} = \frac{1}{m_{ki}} \left[\underline{p}_{ki} - \frac{e_{ki}}{c} \underline{A}(\underline{r}_{ki}) \right]; \tag{1.4.2}$$

$$\dot{\underline{p}}_{ki} = -\frac{\partial \mathcal{H}}{\partial \underline{r}_{ki}}$$

$$= \frac{e_{ki}}{c\, m_{ki}} \frac{\partial \underline{A}(\underline{r}_{ki})}{\partial \underline{r}_{ki}} \cdot \left[\underline{p}_{ki} - \frac{e_{ki}}{c} \underline{A}(\underline{r}_{ki})\right] - \frac{\partial}{\partial \underline{r}_{ki}} e_{ki} \phi_{ki}(\underline{r}_{ki})$$

$$= \frac{e_{ki}}{c} \frac{\partial \underline{A}(\underline{r}_{ki})}{\partial \underline{r}_{ki}} \cdot \underline{u}_{ki} - e_{ki} \underline{E}_{ki}(\underline{r}_{ki}) ; \tag{1.4.3}$$

$$\dot{q}_\lambda = \frac{\partial \mathcal{H}}{\partial p_\lambda}$$

$$= p_\lambda ; \tag{1.4.4}$$

and

$$\dot{p}_\lambda = -\frac{\partial \mathcal{H}}{\partial q_\lambda}$$

$$= -\omega_\lambda^2 q_\lambda + \sum_{ki} \frac{e_{ki}}{c\, m_{ki}} \left[\underline{p}_{ki} - \frac{e_{ki}}{c} \underline{A}(\underline{r}_{ki})\right] \cdot \underline{A}_\lambda(\underline{r}_{ki})$$

$$= -\omega_\lambda^2 q_\lambda + \sum_{ki} \frac{e_{ki}}{c} \underline{u}_{ki} \cdot \underline{A}_\lambda(\underline{r}_{ki}) . \tag{1.4.5}$$

Equation (1.4.3) with a bit of rearrangement can be shown to be identical to (1.2.5), the particle equation of motion. In addition (1.4.5) can be seen to be identical to (1.3.25), the field equation of change. Hence $\mathcal{H}$ in (1.4.1) is the Hamiltonian of the complete system.

We now rewrite the expressions for the electric and magnetic fields in terms of the canonical coordinates, q_λ and p_λ. From (1.1.7), (1.3.8), and (1.3.20), we have

$$\underline{B}^{\mu}(\underline{r}) = \sum_{\lambda} q_\lambda \frac{\partial}{\partial \underline{r}} \times \underline{A}_\lambda(\underline{r}) + \frac{\partial}{\partial \underline{r}} \times \underline{A}^{(e)}(\underline{r})$$

$$= \sum_{\lambda} q_\lambda \frac{\partial}{\partial \underline{r}} \times \underline{A}_\lambda(\underline{r}) + \underline{B}^{(e)}(\underline{r}) . \qquad (1.4.6)$$

And from (1.1.8), (1.3.8), (1.3.9), (1.3.16), and (1.3.20), we have

$$\underline{E}^{\mu}(\underline{r}) = \sum_{ki} e_{ki} \frac{\underline{r} - \underline{r}_{ki}}{|\underline{r} - \underline{r}_{ki}|^3} - \frac{1}{c} \sum_{\lambda} p_\lambda \underline{A}_\lambda(\underline{r}) - \frac{\partial}{\partial \underline{r}} \phi^{(e)}(\underline{r}) - \frac{1}{c} \dot{\underline{A}}^{(e)}(\underline{r})$$

$$= \sum_{ki} e_{ki} \frac{\underline{r} - \underline{r}_{ki}}{|\underline{r} - \underline{r}_{ki}|^3} - \frac{1}{c} \sum_{\lambda} p_\lambda \underline{A}_\lambda(\underline{r}) + \underline{E}^{(e)}(\underline{r}) . \qquad (1.4.7)$$

Notice that while the magnetic field depends only on the field coordinates q_λ, the electric field depends on both the q_λ and the particle coordinates $\underline{r}_{ki}$. The part dependent on the $\underline{r}_{ki}$ is the electric field in a stationary system, while the part dependent on the q_λ describes the retarded potential and the radiative effects.

1.5 The General Equation of Change

The phase space of the system is an orthogonal, multi-dimensional space consisting of the position and momentum coordinates of the particles and the field oscillators. That is, the coordinates of the phase space are the set, ($\underline{r}_{ki}, p_{ki}, q_\lambda, p_\lambda$). If the point in phase space representing the state of the system at a given time, t, is known, we can, in principle, find the point representing the state at any other time by solving the set of Hamiltonian equations. From this information, the value of any property of the system at any time may be calculated.

However, it is, of course, an impossible task to determine at t the positions and momenta of all the particles and field oscillators or to solve a set of Hamiltonian equations. It is fortunate, therefore, that for practical applications detailed information about the exact state of the system is unnecessary. What we want to calculate are the macroscopically observable properties of the system such as the electric field, produced by the system at a point in space. For this purpose, we consider an ensemble of systems. This ensemble is represented by a cloud of points in phase space, the density of which at time, t, is proportional to $f^{(N)*}(\underline{r}_{ki}, p_{ki}, q_\lambda, p_\lambda)$, the N particle distribution function.

The function, $f^{(N)*}$, is normalized such that

$$\int f^{(N)*} \prod_{\substack{ki\\ \lambda}} d\underline{r}_{ki}\, d\underline{p}_{ki}\, dq_{\lambda}\, dp_{\lambda} \equiv 1 . \tag{1.5.1}$$

The value of this function at a point in phase space is the probability that a system chosen at random from the ensemble is in the state described by that point. The average or macroscopic value, $\langle g^* \rangle^*$, of any function, g^*, of the coordinates and momenta is

$$\langle g^* \rangle^* \equiv \int g^* f^{(N)*} \prod_{\substack{ki\\ \lambda}} d\underline{r}_{ki}\, d\underline{p}_{ki}\, dq_{\lambda}\, dp_{\lambda} . \tag{1.5.2}$$

For the macroscopic functions of interest, g^* has no explicit time dependence, i.e.

$$\frac{\partial g^*}{\partial t} = 0, \tag{1.5.3}$$

and depends on only one or two variables, of the set, $(\underline{r}_{ki}, \underline{p}_{ki}, q_{\lambda}, p_{\lambda})$. Hence, it is possible to write (1.5.2) in terms of reduced distribution functions involving only those variables on which g^* depends.[11] To obtain expressions for the macroscopic variables, therefore, we need information about only a small number of particles or field oscillators. Although, in our work, we do not develop expressions for the macroscopic variables, we do obtain expressions for the time derivatives of some of these variables in terms of other macroscopic quantities. In the remainder of this section, we show that this may be done without explicitly evaluating the integrals in (1.5.2).

It may be shown[12] that the function $f^{(N)*}$ obeys an equation of change known as the Liouville equation, which may be written as

$$\frac{\partial f^{(N)*}}{\partial t} + \Lambda^* f^{(N)*} = 0, \tag{1.5.4}$$

where Λ^* is the Liouville operator,

$$\Lambda^* = \sum_{ki}\left[\frac{\partial \mathcal{H}}{\partial \underline{p}_{ki}}\frac{\partial}{\partial \underline{r}_{ki}} - \frac{\partial \mathcal{H}}{\partial \underline{r}_{ki}}\frac{\partial}{\partial \underline{p}_{ki}}\right] + \sum_{\lambda}\left[\frac{\partial \mathcal{H}}{\partial p_{\lambda}}\frac{\partial}{\partial q_{\lambda}} - \frac{\partial \mathcal{H}}{\partial q_{\lambda}}\frac{\partial}{\partial p_{\lambda}}\right]. \tag{1.5.5}$$

From the Hamiltonian equations of motion, (1.4.2) through (1.4.5), it follows that this operator is

$$\Lambda^* = \sum_{ki} \underline{u}_{ki}\cdot\frac{\partial}{\partial \underline{r}_{ki}} + \sum_{ki}\left[\frac{e_{ki}}{c}\frac{\partial \underline{A}(\underline{r}_{ki})}{\partial \underline{r}_{ki}}\cdot\underline{u}_{ki} - e_{ki}\frac{\partial \phi_{ki}(\underline{r}_{ki})}{\partial \underline{r}_{ki}}\right]\cdot\frac{\partial}{\partial \underline{p}_{ki}}$$

$$+ \sum_{\lambda} p_{\lambda}\frac{\partial}{\partial q_{\lambda}} + \sum_{\lambda}\left[\sum_{ki}\frac{e_{ki}}{c}\underline{u}_{ki}\cdot\underline{A}_{\lambda}(\underline{r}_{ki}) - \omega_{\lambda}^{2} q_{\lambda}\right]\cdot\frac{\partial}{\partial p_{\lambda}}. \tag{1.5.6}$$

It is convenient in the later discussion to use $\underline{u}_{ki}$ rather than $\underline{p}_{ki}$ as an independent variable. The distribution function in this new coordinate system is defined by

$$f^{(N)} = J f^{(N)*}, \tag{1.5.7}$$

where

$$J = \frac{\partial(\underline{r}_{ki}, \underline{p}_{ki}, p_\lambda, q_\lambda)}{\partial(\underline{r}_{ki}, \underline{u}_{ki}, p_\lambda, q_\lambda)} = \prod_{ki} m_{ki} \tag{1.5.8}$$

is the Jacobian of the transformation $(\underline{r}_{ki}, \underline{p}_{ki}, p_\lambda, q_\lambda) \rightarrow (\underline{r}_{ki}, \underline{u}_{ki}, p_\lambda, q_\lambda)$. Substituting (1.5.7) into (1.5.4), we see that the new distribution function satisfies an equation similar to the Liouville equation,

$$\frac{\partial f^{(N)}}{\partial t} + \Lambda f^{(N)} = 0, \tag{1.5.9}$$

where Λ is the operator in the new coordinate system,

$$\Lambda = \sum_{ki} \underline{u}_{ki} \cdot \frac{\partial}{\partial \underline{r}_{ki}} + \sum_{ki} \frac{e_{ki}}{m_{ki}} \left[\underline{E}^{\mu}_{ki}(\underline{r}_{ki}) + \frac{1}{c} \underline{u}_{ki} \times \underline{B}^{\mu}(\underline{r}_{ki}) \right] \cdot \frac{\partial}{\partial \underline{u}_{ki}}$$
$$+ \sum_{\lambda} p_\lambda \frac{\partial}{\partial q_\lambda} + \sum_{\lambda} \left[\sum_{ki} \frac{e_{ki}}{c} \underline{u}_{ki} \cdot \underline{A}_\lambda(\underline{r}_{ki}) - \omega_\lambda^2 q_\lambda \right] \frac{\partial}{\partial p_\lambda} . \tag{1.5.10}$$

The derivation of this expression for the operator is discussed in Appendix 1.A1.

Finally, we derive an equation for the time derivative of the ensemble average of any dynamical variable $g(\underline{r}_{ki}, \underline{u}_{ki}, q_\lambda, p_\lambda)$ where

$$g(\underline{r}_{ki}, \underline{u}_{ki}, q_\lambda, p_\lambda) = g^*(\underline{r}_{ki}, \underline{p}_{ki}, q_\lambda, p_\lambda). \tag{1.5.11}$$

This is the general equation of change.

From (1.5.1), (1.5.7), and the well-known integral transformation relation, we write the normalization condition on $f^{(N)}$ as

$$\int f^{(N)} \prod_{\substack{ki \\ \lambda}} d\underline{r}_{ki}\, d\underline{u}_{ki}\, dq_\lambda\, dp_\lambda = \int J f^{(N)*} \frac{1}{J} \prod_{\substack{ki \\ \lambda}} d\underline{r}_{ki}\, d\underline{p}_{ki}\, dq_\lambda\, dp_\lambda = 1 . \tag{1.5.12}$$

Similarly, from (1.5.2), the ensemble average $\langle g^* \rangle^*$ may be written in the new system of coordinates as

$$\langle g^* \rangle^* = \int g \frac{1}{J} f^{(N)} J \prod_{\substack{ki \\ \lambda}} d\underline{r}_{ki}\, d\underline{u}_{ki}\, dq_\lambda\, dp_\lambda = \langle g \rangle , \tag{1.5.13}$$

where

$$\langle g \rangle \equiv \int g f^{(N)} \prod_{\substack{ki \\ \lambda}} d\underline{r}_{ki}\, d\underline{u}_{ki}\, dq_\lambda\, dp_\lambda . \tag{1.5.14}$$

The time rate of change of $\langle g \rangle$ is given by

$$\begin{aligned} \frac{\partial \langle g \rangle}{\partial t} &= \int g \frac{\partial f^{(N)}}{\partial t} \prod_{\substack{ki \\ \lambda}} d\underline{r}_{ki}\, d\underline{u}_{ki}\, dq_\lambda\, dp_\lambda \\ &= - \int g \Lambda f^{(N)} \prod_{\substack{ki \\ \lambda}} d\underline{r}_{ki}\, d\underline{u}_{ki}\, dq_\lambda\, dp_\lambda \\ &= \int f^{(N)} \Lambda g \prod_{\substack{ki \\ \lambda}} d\underline{r}_{ki}\, d\underline{u}_{ki}\, dq_\lambda\, dp_\lambda \end{aligned} \tag{1.5.15}$$

In writing the first two lines of (1.5.15), we use the explicit time independence of g [see (1.5.3)] and the equation of change for $f^{(N)}$, (1.5.9). The last line of (1.5.15) follows from the property that Λ is skew-symmetric with respect to integration over phase space (see Appendix 1.A2). The general equation of change may thus be written as

$$\frac{\partial\langle g\rangle}{\partial t}=\langle\Lambda g\rangle. \tag{1.5.16}$$

Starting with Newton's and Maxwell's equations, we have derived the Hamiltonian for a system of non-relativistic point charged particles. Using this Hamiltonian, we have derived a Liouville equation for the distribution function of the system in phase space, and, from this, a general equation of change for the ensemble average of any dynamical variable. This general equation of change forms, in the succeeding chapters, the basis of the derivation of the macroscopic Maxwell relations and the magnetohydrodynamic equations for the system.

Appendix 1.A1: The Transformation of Λ^* to Λ.

We discuss here the transformation of the Liouville operator Λ^* in phase space, the space of $(\underline{r}^*_{ki}, \underline{p}^*_{ki}, q^*_\lambda, p^*_\lambda)$, to the operator Λ in the space, $(\underline{r}_{ki}, \underline{u}_{ki}, q_\lambda, p_\lambda)$.

The equations of transformation from the stared to the unstared coordinates are [see (1.4.2)]

$$\underline{r}_{ki} = \underline{r}^*_{ki}, \tag{1.A1.1}$$

$$\underline{u}_{ki} = \frac{1}{m_{ki}}\left(\underline{p}^*_{ki} - \frac{e_{ki}}{c}\underline{A}(\underline{r}^*_{ki})\right), \tag{1.A1.2}$$

$$q_\lambda = q^*_\lambda, \tag{1.A1.3}$$

and

$$p_\lambda = p^*_\lambda. \tag{1.A1.4}$$

The general equation for the transformation of a partial derivative from the stared coordinates to the unstared is

$$\frac{\partial h^*}{\partial x^*_i} = \sum_j \frac{\partial x_j}{\partial x^*_i}\frac{\partial h}{\partial x_j}, \tag{1.A1.5}$$

where $h = h^*$. The function, h, is a function of x_i, the generalized coordinate in unstared space, and h^* is a function of x_j^*, the generalized coordinate in stared space.

Using (1.A1.1) through (1.A1.5), we write

$$\frac{\partial h^*}{\partial \underline{r}^*_{ki}} = \sum_{lj} \frac{\partial \underline{r}_{lj}}{\partial \underline{r}^*_{ki}} \cdot \frac{\partial h}{\partial \underline{r}_{lj}} + \sum_{lj} \frac{\partial \underline{u}_{lj}}{\partial \underline{r}^*_{ki}} \cdot \frac{\partial h}{\partial \underline{u}_{lj}}$$

$$+ \sum_{\lambda} \frac{\partial q_\lambda}{\partial \underline{r}^*_{ki}} \frac{\partial h}{\partial q_\lambda} + \sum_{\lambda} \frac{\partial p_\lambda}{\partial \underline{r}^*_{ki}} \frac{\partial h}{\partial p_\lambda}$$

$$= \frac{\partial h}{\partial \underline{r}_{ki}} - \frac{e_{ki}}{m_{ki} c} \frac{\partial \underline{A}(\underline{r}_{ki})}{\partial \underline{r}_{ki}} \cdot \frac{\partial h}{\partial \underline{u}_{ki}}, \qquad (1.A1.6)$$

$$\frac{\partial h^*}{\partial \underline{p}^*_{ki}} = \frac{1}{m_{ki}} \frac{\partial h}{\partial \underline{u}_{ki}}, \qquad (1.A1.7)$$

$$\frac{\partial h^*}{\partial q^*_\lambda} = -\sum_{ki} \frac{e_{ki}}{m_{ki} c} \underline{A}_\lambda(\underline{r}_{ki}) \cdot \frac{\partial h}{\partial \underline{u}_{ki}} + \frac{\partial h}{\partial q_\lambda}, \qquad (1.A1.8)$$

and

$$\frac{\partial h^*}{\partial p^*_\lambda} = \frac{\partial h}{\partial p_\lambda}. \qquad (1.A1.9)$$

Substituting (1.A1.6) through (1.A1.9) into the expression for Λ^*, (1.5.6), we obtain

$$\Lambda = \sum_{ki} \underline{u}_{ki} \cdot \frac{\partial}{\partial \underline{r}_{ki}} - \sum_{ki} \frac{e_{ki}}{m_{ki} c} \underline{u}_{ki} \cdot \frac{\partial \underline{A}(\underline{r}_{ki})}{\partial \underline{r}_{ki}} \cdot \frac{\partial}{\partial \underline{u}_{ki}}$$

$$- \sum_{ki} \frac{e_{ki}}{m_{ki} c} \left(\frac{\partial \underline{A}(\underline{r}_{ki})}{\partial \underline{r}_{ki}} \cdot \underline{u}_{ki} \right) \cdot \frac{\partial}{\partial \underline{u}_{ki}} - \sum_{ki} \frac{e_{ki}}{m_{ki}} \frac{\partial \phi_{ki}(\underline{r}_{ki})}{\partial \underline{r}_{ki}} \cdot \frac{\partial}{\partial \underline{u}_{ki}}$$

$$- \sum_{\lambda} p_{\lambda} \sum_{ki} \frac{e_{ki}}{m_{ki} c} \underline{A}_{\lambda}(\underline{r}_{ki}) \cdot \frac{\partial}{\partial \underline{u}_{ki}} + \sum_{\lambda} p_{\lambda} \frac{\partial}{\partial q_{\lambda}}$$

$$+ \sum_{\lambda} \left[\sum_{ki} \frac{e_{ki}}{c} \underline{u}_{ki} \cdot \underline{A}_{\lambda}(\underline{r}_{ki}) - \omega_{\lambda}^{2} q_{\lambda} \right] \frac{\partial}{\partial p_{\lambda}} . \qquad (1.A1.10)$$

Combining the second and third terms of (1.A1.10) and referring to (1.1.7) yields

$$\sum_{ki} \frac{e_{ki}}{m_{ki} c} \left[\frac{\partial \underline{A}(\underline{r}_{ki})}{\partial \underline{r}_{ki}} \cdot \underline{u}_{ki} - \underline{u}_{ki} \cdot \frac{\partial \underline{A}(\underline{r}_{ki})}{\partial \underline{r}_{ki}} \right] \cdot \frac{\partial}{\partial \underline{u}_{ki}}$$

$$= \sum_{ki} \frac{e_{ki}}{m_{ki} c} \left[\underline{u}_{ki} \times \left(\frac{\partial}{\partial \underline{r}_{ki}} \times \underline{A}(\underline{r}_{ki}) \right) \right] \cdot \frac{\partial}{\partial \underline{u}_{ki}}$$

$$= \sum_{ki} \frac{e_{ki}}{m_{ki} c} \left[\underline{u}_{ki} \times \underline{B}^{\mu}(\underline{r}_{ki}) \right] \cdot \frac{\partial}{\partial \underline{u}_{ki}} . \qquad (1.A1.11)$$

From the fourth and fifth terms of (1.A1.10) and referring to (1.1.8), we write

$$\sum_{ki} \frac{e_{ki}}{m_{ki}} \left[- \frac{\partial \phi_{ki}(\underline{r}_{ki})}{\partial \underline{r}_{ki}} - \frac{1}{c} \sum_{\lambda} p_{\lambda} \underline{A}_{\lambda}(\underline{r}_{ki}) \right] \cdot \frac{\partial}{\partial \underline{u}_{ki}} \qquad (1.A1.12)$$

$$= \sum_{ki} \frac{e_{ki}}{m_{ki}} \underline{E}^{\mu}_{ki}(\underline{r}_{ki}) \cdot \frac{\partial}{\partial \underline{u}_{ki}} .$$

Hence, we may write from (1.A1.10),

$$\Lambda = \sum_{ki} \underline{u}_{ki} \cdot \frac{\partial}{\partial \underline{r}_{ki}} + \sum_{ki} \frac{e_{ki}}{m_{ki}} \left[\underline{E}^{\mu}_{ki}(\underline{r}_{ki}) + \frac{1}{c} \underline{u}_{ki} \times \underline{B}^{\mu}(\underline{r}_{ki}) \right] \cdot \frac{\partial}{\partial \underline{u}_{ki}}$$

$$+ \sum_{\lambda} p_{\lambda} \frac{\partial}{\partial q_{\lambda}} + \sum_{\lambda} \left[\sum_{ki} \frac{e_{ki}}{c} \underline{u}_{ki} \cdot \underline{A}_{\lambda}(\underline{r}_{ki}) - \omega_{\lambda}^{2} q_{\lambda} \right] \frac{\partial}{\partial p_{\lambda}} \, . \qquad (1.\text{A}1.13)$$

This is the expression for Λ .

Appendix 1.A2: A Proof that Λ is a Skew-Symmetric Operator

From (1.5.9) it is readily seen that Λ is of the form

$$\Lambda = \sum_{\alpha} h_\alpha \frac{\partial}{\partial x_\alpha} \, , \tag{1.A2.1}$$

where the x_α are the independent variables, and h_α is a function of any of the independent variables except x_α. Using this form, we write

$$\begin{aligned}\int_{-\infty}^{\infty} \left(\Lambda f^{(N)}\right) g \prod_{\beta} dx_\beta &= \sum_{\alpha} \int_{-\infty}^{\infty} h_\alpha \frac{\partial f^{(N)}}{\partial x_\alpha} g \prod_{\beta} dx_\beta \\ &= \sum_{\alpha} \int_{-\infty}^{\infty} \frac{\partial \left(h_\alpha f^{(N)} g\right)}{\partial x_\alpha} \prod_{\beta} dx_\beta - \sum_{\alpha} \int_{-\infty}^{\infty} h_\alpha \frac{\partial g}{\partial x_\alpha} f^{(N)} \prod_{\beta} dx_\beta \, .\end{aligned} \tag{1.A2.2}$$

Using Leibnitz's rule, the first term in (1.A2.2) may be written

$$\begin{aligned}\sum_{\alpha} \int_{-\infty}^{\infty} \frac{\partial \left(h_\alpha f^{(N)} g\right)}{\partial x_\alpha} \prod_{\beta} dx_\beta &= \sum_{\alpha} \int_{-\infty}^{\infty} \frac{d}{dx_\alpha} \int_{-\infty}^{\infty} h_\alpha f^{(N)} g \prod_{\beta \neq \alpha} dx_\beta \, dx_\alpha \\ &= \sum_{\alpha} \int_{-\infty}^{\infty} h_\alpha f^{(N)} g \prod_{\beta \neq \alpha} dx_\beta \Bigg|_{x_\alpha = -\infty}^{x_\alpha = \infty} \\ &= 0 .\end{aligned} \tag{1.A2.3}$$

The last step in (1.A2.3) results from the condition that $f^{(N)}$ vanishes as each independent variable approaches the limit of its range. Using (1.A2.3), (1.A2.2) may be written

$$\int (\Lambda f^{(N)})\, g \prod_\beta dx_\beta = -\sum_\alpha \int h_\alpha \frac{\partial g}{\partial x_\alpha} f^{(N)} \prod_\beta dx_\beta$$

$$= -\int f^{(N)} \Lambda g \prod_\beta dx_\beta\,. \qquad (1.A2.4)$$

This is a statement of the skew symmetry of Λ.

II. THE MAXWELL EQUATIONS IN A MATERIAL MEDIUM

In the previous chapter, we defined the microscopic electric and magnetic fields, $\underline{E}^{\mu}$ and $\underline{B}^{\mu}$ [see (1.4.6) and (1.4.7)]. These fields fluctuate rapidly with time; the measurable quantities, however, are the macroscopic fields, $\underline{E}$ and $\underline{B}$, obtained by averaging $\underline{E}^{\mu}$ and $\underline{B}^{\mu}$ over a statistical ensemble. The fields, $\underline{E}$ and $\underline{B}$, are described by a set of equations analogous to the Maxwell equations for $\underline{E}^{\mu}$ and $\underline{B}^{\mu}$ [see (1.1.3) to (1.1.6)]. These Maxwell equations, in material media, may be derived by evaluating the quantities, $\frac{\partial}{\partial \underline{r}} \cdot \underline{E}$, $\frac{\partial}{\partial \underline{r}} \cdot \underline{B}$, $\frac{\partial \underline{E}}{\partial t}$, and $\frac{\partial \underline{B}}{\partial t}$.

2.1 The First Maxwell Equation

The derivation of the first Maxwell equation is trivial. Starting with the definition of $\underline{B}$,

$$\underline{B} \equiv \langle \underline{B}^{\mu} \rangle, \tag{2.1.1}$$

we take the divergence of both sides to obtain

$$\frac{\partial}{\partial \underline{r}} \cdot \underline{B} = \left\langle \frac{\partial}{\partial \underline{r}} \cdot \underline{B}^{\mu} \right\rangle, \tag{2.1.2}$$

or, since the divergence of $\underline{B}^{\mu}$ is zero [see (1.1.4)],

$$\frac{\partial}{\partial \underline{r}} \cdot \underline{B} = 0. \tag{2.1.3}$$

This is the usual equation for the magnetic field in a material medium.

2.2 The Second Maxwell Equation

We next consider $\frac{\partial \underline{B}}{\partial t}$. From the definition of $\underline{B}^{\mu}$, (1.4.6), and the general equation of change, (1.5.16), we have

$$\frac{\partial \underline{B}}{\partial t} = \left\langle \Lambda \sum_{\lambda} q_{\lambda} \frac{\partial}{\partial \underline{r}} \times \underline{A}_{\lambda} \right\rangle + \frac{\partial \underline{B}^{(e)}}{\partial t}, \tag{2.2.1}$$

where the last term is a consequence of the simple identity,

$$\left\langle \underline{B}^{(e)} \right\rangle \equiv \underline{B}^{(e)} \langle 1 \rangle \equiv \underline{B}^{(e)}. \tag{2.2.2}$$

Applying Maxwell's equations in vacuo to the second term on the right of (2.2.1) and carrying out the Λ operation [see (1.5.10)] in the first term, we obtain

$$\begin{aligned} \frac{\partial \underline{B}}{\partial t} &= \sum_{\lambda\mu} \left\langle p_{\mu} \frac{\partial q_{\lambda}}{\partial q_{\mu}} \frac{\partial}{\partial \underline{r}} \times \underline{A}_{\lambda} \right\rangle - c \frac{\partial}{\partial \underline{r}} \times \underline{E}^{(e)} \\ &= \sum_{\lambda} \left\langle p_{\lambda} \frac{\partial}{\partial \underline{r}} \times \underline{A}_{\lambda} \right\rangle - c \frac{\partial}{\partial \underline{r}} \times \underline{E}^{(e)}. \end{aligned} \tag{2.2.3}$$

Now from (1.4.7), the definition of $\underline{E}^{\mu}$, it is seen that

$$\begin{aligned} \underline{E} &\equiv \left\langle \underline{E}^{\mu} \right\rangle \\ &= -\frac{\partial}{\partial \underline{r}} \sum_{ki} \left\langle \frac{e_{ki}}{|\underline{r}_{ki} - \underline{r}|} \right\rangle - \frac{1}{c} \sum_{\lambda} \left\langle p_{\lambda} \underline{A}_{\lambda} \right\rangle + \underline{E}^{(e)}. \end{aligned} \tag{2.2.4}$$

where again we use a simple identity,

$$\langle \underline{E}^{(e)} \rangle = \underline{E}^{(e)}. \tag{2.2.5}$$

Taking the curl of both sides, (2.2.4) becomes

$$-c\frac{\partial}{\partial \underline{r}} \times \underline{E} = \sum_{\lambda} \left\langle p_{\lambda} \frac{\partial}{\partial \underline{r}} \times \underline{A}_{\lambda} \right\rangle - c\frac{\partial}{\partial \underline{r}} \times \underline{E}^{(e)}. \tag{2.2.6}$$

Finally, substituting (2.2.6) into (2.2.3), we arrive at the relation,

$$\frac{1}{c}\frac{\partial \underline{B}}{\partial t} = -\frac{\partial}{\partial \underline{r}} \times \underline{E}. \tag{2.2.7}$$

Once again this is well-known as a Maxwell equation in a material medium.

2.3 The Third Maxwell Equation

From (2.2.4), we write

$$\frac{\partial}{\partial \underline{r}} \cdot \underline{E} = -\frac{\partial^2}{\partial r^2} \sum_{ki} \left\langle \frac{e_{ki}}{|\underline{r}_{ki} - \underline{r}|} \right\rangle + \frac{\partial}{\partial \underline{r}} \cdot \underline{E}^{(e)}, \tag{2.3.1}$$

The second term on the right is zero by Maxwell's equations in vacuo, and by carrying out the differentiation in the first term on the right, we obtain

$$\frac{\partial}{\partial \underline{r}} \cdot E = 4\pi \sum_{ki} \langle e_{ki}\, \delta(\underline{r}_{ki} - \underline{r}) \rangle, \tag{2.3.2}$$

where $\sum_{ki}\langle e_{ki}\,\delta(\underline{r}_{ki}-\underline{r})\rangle$ can be interpreted as the macroscopic charge density at the point $\underline{r}$.

In the above paragraph, we have expressed $\frac{\partial}{\partial \underline{r}}\cdot\underline{E}$ in terms of an electron-nuclei centered density $\delta(\underline{r}_{ki}-\underline{r})$. We would like, however, to write $\frac{\partial}{\partial \underline{r}}\cdot\underline{E}$ in terms of a molecule-ion centered density, $\delta(\underline{r}_{k}-\underline{r})$, where $\underline{r}_k$ is the vector to the center of mass of molecule k,

$$\underline{r}_k \equiv \sum_i \frac{m_{ki}\,\underline{r}_{ki}}{m_k}, \tag{2.3.3}$$

and m_k is the mass of molecule k,

$$m_k = \sum_i m_{ki}\,. \tag{2.3.4}$$

To do this we expand each k subscripted term on the right of (2.3.2) in a Taylor series about $\underline{r}_k$,

$$\begin{aligned}\sum_{ki}\langle e_{ki}\,\delta(\underline{r}_{ki}-\underline{r})\rangle &= \sum_{ki}\langle e_{ki}\,\delta(\underline{r}_{k}-\underline{r})\rangle \\ &+\sum_{ki}\langle e_{ki}\,\underline{R}_{ki}\cdot\frac{\partial}{\partial \underline{r}_k}\delta(\underline{r}_{k}-\underline{r})\rangle+\frac{1}{2}\sum_{ki}\langle e_{ki}\,\underline{R}_{ki}\underline{R}_{ki}:\frac{\partial}{\partial \underline{r}_k}\frac{\partial}{\partial \underline{r}_k}\delta(\underline{r}_{k}-\underline{r})\rangle+\cdots\,.\end{aligned} \tag{2.3.5}$$

Here

$$\underline{R}_{ki} = \underline{r}_{ki}-\underline{r}_k \tag{2.3.6}$$

is the vector from the center of mass of molecule k, to particle i of molecule k .

Equation (2.3.5) may be written in the general form,

$$\sum_{ki}\left\langle e_{ki}\,\delta(\underline{r}_{ki}-\underline{r})\right\rangle = \sum_{n=0}^{\infty}\frac{1}{n!}\sum_{ki}\left\langle e_{ki}\,\underline{\underline{R}}_{ki}^{(n)}\cdot^{(n)}\left(\frac{\partial}{\partial\underline{r}_k}\right)^{(n)}\delta(\underline{r}_k-\underline{r})\right\rangle, \tag{2.3.7}$$

where the superscript n's have the obvious meaning, e.g.

$$\underline{\underline{R}}_{ki}^{(3)}\cdot^{(3)}\left(\frac{\partial}{\partial\underline{r}_k}\right)^{(3)} \equiv \underline{R}_{ki}\underline{R}_{ki}\underline{R}_{ki}\,\vdots\,\frac{\partial}{\partial\underline{r}_k}\frac{\partial}{\partial\underline{r}_k}\frac{\partial}{\partial\underline{r}_k}\;. \tag{2.3.8}$$

Now using the symmetry of the delta function,

$$\frac{\partial}{\partial\underline{r}_k}\delta(\underline{r}_k-\underline{r}) = -\frac{\partial}{\partial\underline{r}}\delta(\underline{r}_k-\underline{r}), \tag{2.3.9}$$

we write (2.3.7) as

$$\sum_{ki}\left\langle e_{ki}\,\delta(\underline{r}_{ki}-\underline{r})\right\rangle = \sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n)}\cdot^{(n)}\sum_{ki}\left\langle e_{ki}\,\underline{\underline{R}}_{ki}^{(n)}\delta(\underline{r}_k-\underline{r})\right\rangle. \tag{2.3.10}$$

We now define a tensor of order, n ,

$$\underline{\underline{Q}}^{(n)} \equiv \frac{1}{n!}\sum_{ki}\left\langle e_{ki}\,\underline{\underline{R}}_{ki}^{(n)}\delta(\underline{r}_k-\underline{r})\right\rangle, \tag{2.3.11}$$

where $\sum_{i} e_{ki}\,\underline{\underline{R}}_{ki}^{(n)}$ is the electric multipole moment of order n of molecule k . This quantity, $\underline{\underline{Q}}^{(n)}$, may be interpreted as the macroscopic molecular electric multipole density of order m . For example, $\underline{\underline{Q}}^{(0)}$ is the monopole or charge density, $\underline{\underline{Q}}^{(1)}$, the dipole density, etc.

Utilizing (2.3.10) and (2.3.11), we may write (2.3.2) as

$$\frac{\partial}{\partial \underline{r}}\cdot\underline{E} = 4\pi \underline{\underline{Q}}^{(0)} + 4\pi\sum_{m=0}^{\infty}(-1)^{m+1}\left(\frac{\partial}{\partial\underline{r}}\right)^{(m+1)}\cdot^{(m+1)}\underline{\underline{Q}}^{(m+1)}. \qquad (2.3.12)$$

It is convenient to define the "true" macroscopic charge density by

$$\rho_e \equiv \underline{\underline{Q}}^{(0)} = \sum_k \left\langle e_k\, \delta(\underline{r}_k - \underline{r})\right\rangle, \qquad (2.3.13)$$

where

$$e_k \equiv \sum_i e_{ki} \qquad (2.3.14)$$

is the charge of molecule k . It is also convenient to define the electric polarization, $\underline{P}$, by

$$\underline{P} \equiv \sum_{m=0}^{\infty}(-1)^{m}\left(\frac{\partial}{\partial\underline{r}}\right)^{(m)}\cdot^{(m)}\underline{\underline{Q}}^{(m+1)}, \qquad (2.3.15)$$

and the electric displacement, $\underline{D}$, as

$$\underline{D} \equiv \underline{E} + 4\pi\underline{P}. \qquad (2.3.16)$$

In terms of these quantities, equation (2.3.12) becomes

$$\frac{\partial}{\partial \underline{r}} \cdot \underline{D} = 4\pi \rho_e \,. \tag{2.3.17}$$

In form, this is a usual Maxwell equation for a material media, but our definition of $\underline{P}$ is a generalization of that usually given since we include moments of higher order than the dipole. From equation (2.3.17), it is clear that $\underline{D}$ is that field whose sources are the molecules of the system, in their ensemble averaged positions, regarded as ideal monopoles or point particles. In contrast to $\underline{D}$, it is seen from (2.3.2), that the field, $\underline{E}$, has as its source the "true" particles of the system, the nuclei and electrons regarded as point particles. From these arguments it can be seen intuitively that $\underline{D}$ is that quantity which $\underline{E}$ approaches as the average intermolecular distance increases. In dilute systems, therefore, $\underline{D}$ is a close approximation to $\underline{E}$, and $\underline{P}$ in (2.3.16) is negligible. As the density of the system increases, $\underline{P}$ has a greater effect, and more terms must be retained in its series representation, (2.3.15), to obtain accurate results.

2.4 The Fourth Maxwell Equation

To obtain the final Maxwell equation, we evaluate $\frac{\partial \underline{E}}{\partial t}$. From the general equation of change, (1.5.16), and the definitions of $\underline{E}$ and Λ, (2.2.4) and (1.5.10), we obtain

$$\frac{\partial \underline{E}}{\partial t} = -\frac{\partial}{\partial \underline{r}} \sum_{kilj} \left\langle e_{ki}\, \underline{u}_{lj} \cdot \frac{\partial}{\partial \underline{r}_{lj}} \frac{1}{|\underline{r}_{ki} - \underline{r}|} \right\rangle$$

$$-\frac{1}{c} \left\langle \sum_{\lambda\mu} \left[\sum_{ki} \frac{e_{ki}}{c}\, \underline{u}_{ki} \cdot \underline{A}_{\mu}(\underline{r}_{ki}) - \omega_{\lambda}^{2} q_{\lambda} \right] \frac{\partial p_{\lambda}}{\partial p_{\mu}} \underline{A}_{\lambda}(\underline{r}) \right\rangle + \frac{\partial \underline{E}^{(e)}}{\partial t}$$

$$= -\sum_{ki} \left\langle e_{ki}\, \underline{u}_{ki} \cdot \left[\frac{\partial}{\partial \underline{r}_{ki}} \frac{\partial}{\partial \underline{r}} \frac{1}{|\underline{r}_{ki} - \underline{r}|} + \frac{1}{c^{2}} \sum_{\lambda} \underline{A}_{\lambda}(\underline{r}_{ki})\, \underline{A}_{\lambda}(\underline{r}) \right\rangle \right.$$

$$+ \sum_{\lambda} \left\langle \frac{\omega_{\lambda}^{2}}{c}\, q_{\lambda}\, \underline{A}_{\lambda}(\underline{r}) \right\rangle + \frac{\partial \underline{E}^{(e)}}{\partial t} \, . \qquad (2.4.1)$$

In Appendix 2.A1, the first term in (2.4.1) is simplified. If the result from this appendix is substituted into the first term of (2.4.1), and the defining equation for $\underline{A}_{\lambda}$, (1.3.17), is substituted into the second term, we obtain

$$\frac{\partial \underline{E}}{\partial t} = -4\pi \sum_{ki} \left\langle e_{ki}\, \underline{u}_{ki}\, \delta(\underline{r}_{ki} - \underline{r}) \right\rangle - c \sum_{\lambda} \left\langle q_{\lambda} \frac{\partial^{2} \underline{A}_{\lambda}(\underline{r})}{\partial r^{2}} \right\rangle + \frac{\partial \underline{E}^{(e)}}{\partial t} \, . \qquad (2.4.2)$$

From a well-known vector identity and the condition that the divergence of $\underline{A}_{\lambda}$ is zero [see (1.3.18)] , it follows that

$$\frac{\partial}{\partial \underline{r}} \times \left(\frac{\partial}{\partial \underline{r}} \times \underline{A}_{\lambda} \right) \equiv \frac{\partial}{\partial \underline{r}} \left(\frac{\partial}{\partial \underline{r}} \cdot \underline{A}_{\lambda} \right) - \frac{\partial^{2} \underline{A}_{\lambda}}{\partial r^{2}} = -\frac{\partial^{2} \underline{A}_{\lambda}}{\partial r^{2}} \, . \qquad (2.4.3)$$

From Maxwell's equations in vacuo, it also follows that

$$\frac{\partial \underline{E}^{(e)}}{\partial t} = c \frac{\partial}{\partial \underline{r}} \times \underline{B}^{(e)} . \tag{2.4.4}$$

Thus, (2.4.2) may be written

$$\frac{\partial \underline{E}}{\partial t} = -4\pi \sum_{ki} \left\langle e_{ki} \underline{u}_{ki} \delta(\underline{r}_{ki} - \underline{r}) \right\rangle + c \frac{\partial}{\partial \underline{r}} \times \sum_{\lambda} \left\langle q_{\lambda} \frac{\partial}{\partial \underline{r}} \times \underline{A}_{\lambda}(\underline{r}) \right\rangle + c \frac{\partial}{\partial \underline{r}} \times \underline{B}^{(e)} . \tag{2.4.5}$$

Finally, from the definition of $\underline{B}$, (1.4.6), it follows that

$$\frac{\partial \underline{E}}{\partial t} = -4\pi \sum_{ki} \left\langle e_{ki} \underline{u}_{ki} \delta(\underline{r}_{ki} - \underline{r}) \right\rangle + c \frac{\partial}{\partial \underline{r}} \times \underline{B} , \tag{2.4.6}$$

where $\sum_{ki} \left\langle e_{ki} \underline{u}_{ki} \delta(\underline{r}_{ki} - \underline{r}) \right\rangle$ is the macroscopic total current density analogous to the macroscopic total charge density, $\sum_{ki} \left\langle e_{ki} \delta(\underline{r}_{ki} - \underline{r}) \right\rangle$. Equation (2.4.6) is the particle centered equation analogous to (2.3.2).

Again, as in section 2.3, we transform this equation to a molecule centered expression. To do this, we first evalute $\frac{\partial \underline{D}}{\partial t}$. From (2.3.16), it is easily seen that

$$\frac{\partial \underline{D}}{\partial t} = \frac{\partial \underline{E}}{\partial t} + 4\pi \frac{\partial \underline{P}}{\partial t} . \tag{2.4.7}$$

Substituting (2.4.6) into (2.4.7), we obtain

$$\frac{\partial \underline{D}}{\partial t} = -4\pi \sum_{ki} \left\langle e_{ki} \underline{u}_{ki} \delta(\underline{r}_{ki} - \underline{r}) \right\rangle + c \frac{\partial}{\partial \underline{r}} \times \underline{B} + 4\pi \frac{\partial \underline{P}}{\partial t} . \tag{2.4.8}$$

Expanding $\sum_{ki}\langle e_{ki}\underline{u}_{ki}\delta(\underline{r}_{ki}-\underline{r})\rangle$ in a Taylor series similar to (2.3.7), we obtain

$$\sum_{ki}\langle e_{ki}\underline{u}_{ki}\delta(\underline{r}_{ki}-\underline{r})\rangle=\sum_{n=0}^{\infty}\frac{1}{n!}\sum_{ki}\langle e_{ki}\underline{u}_{ki}\underline{\underline{R}}_{ki}^{(n)}\cdot^{(n)}\left(\frac{\partial}{\partial\underline{r}_k}\right)^{(n)}\delta(\underline{r}_k-\underline{r})\rangle$$

$$=\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n)}\cdot^{(n)}\sum_{ki}\langle e_{ki}\underline{\underline{R}}_{ki}^{(n)}\underline{u}_{ki}\delta(\underline{r}_k-\underline{r})\rangle. \tag{2.4.9}$$

In section 2.5, we evaluate the time derivative of the polarization, $\underline{P}$ [see (2.5.9)] . The result may be written as

$$\frac{\partial\underline{P}}{\partial t}=\sum_{n=0}^{\infty}\sum_{l=0}^{n}\frac{(-1)^n}{(n+1)!}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n)}\cdot^{(n)}\sum_{ki}\langle e_{ki}\underline{\underline{R}}_{ki}^{(l)}\underline{U}_{ki}\underline{\underline{R}}_{ki}^{(n-l)}\delta(\underline{r}_k-\underline{r})\rangle$$

$$-\sum_{n=0}^{\infty}\frac{(-1)^n}{(n+1)!}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n+1)}\cdot^{(n+1)}\sum_{ki}\langle e_{ki}\underline{u}_k\underline{\underline{R}}_{ki}^{(n+1)}\delta(\underline{r}_k-\underline{r})\rangle. \tag{2.4.10}$$

The quantity,

$$\underline{u}_k\equiv\frac{d\underline{r}_k}{dt}=\sum_i\frac{m_{ki}\underline{u}_{ki}}{m_k}, \tag{2.4.11}$$

is the velocity of molecule k , and

$$\underline{U}_{ki}\equiv\frac{d\underline{R}_{ki}}{dt}=\underline{u}_{ki}-\underline{u}_k \tag{2.4.12}$$

is the velocity of the "true" particle ki about the center of mass of molecule k . Substituting (2.4.9) and (2.4.10) into (2.4.8) allows (2.4.8) to be written as

$$
\begin{aligned}
\frac{\partial \underline{D}}{\partial t} = & -4\pi \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \left(\frac{\partial}{\partial \underline{\underline{r}}}\right)^{(n)} \cdot^{(n)} \sum_{ki} \left\langle e_{ki} \underline{\underline{R}}_{ki}^{(n)} \underline{u}_{ki}\, \delta(\underline{r}_{ki}-\underline{r}) \right\rangle \\
& + 4\pi \sum_{n=0}^{\infty} \sum_{r=0}^{n} \frac{(-1)^n}{(n+1)!} \left(\frac{\partial}{\partial \underline{\underline{r}}}\right)^{(n)} \cdot^{(n)} \sum_{ki} \left\langle e_{ki} \underline{\underline{R}}_{ki}^{(r)} \underline{U}_{ki} \underline{\underline{R}}_{ki}^{(n-r)} \delta(\underline{r}_{k}-\underline{r}) \right\rangle \\
& - 4\pi \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1)!} \left(\frac{\partial}{\partial \underline{\underline{r}}}\right)^{(n+1)} \cdot^{(n+1)} \sum_{ki} \left\langle e_{ki} \underline{u}_{k} \underline{\underline{R}}_{ki}^{(n+1)} \delta(\underline{r}_{k}-\underline{r}) \right\rangle + c \frac{\partial}{\partial \underline{r}} \times \underline{B} \\
= & \; 4\pi \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \left(\frac{\partial}{\partial \underline{\underline{r}}}\right)^{(n)} \cdot^{(n)} \Bigg[-\sum_{ki} \left\langle e_{ki} \underline{\underline{R}}_{ki}^{(n)} \underline{U}_{ki}\, \delta(\underline{r}_{k}-\underline{r}) \right\rangle \\
& + \frac{1}{n+1} \sum_{r=0}^{n} \sum_{ki} \left\langle e_{ki} \underline{\underline{R}}_{ki}^{(r)} \underline{U}_{ki} \underline{\underline{R}}_{ki}^{(n-r)} \delta(\underline{r}_{k}-\underline{r}) \right\rangle \Bigg] - 4\pi \sum_{ki} \left\langle e_{ki} \underline{u}_{k} \delta(\underline{r}_{k}-\underline{r}) \right\rangle \\
& + 4\pi \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1)!} \left(\frac{\partial}{\partial \underline{\underline{r}}}\right)^{(n+1)} \cdot^{(n+1)} \Bigg[\sum_{ki} \left\langle e_{ki} \underline{\underline{R}}_{ki}^{(n+1)} \underline{u}_{k}\, \delta(\underline{r}_{k}-\underline{r}) \right\rangle \\
& - \sum_{ki} \left\langle e_{ki} \underline{u}_{k} \underline{\underline{R}}_{ki}^{(n+1)} \delta(\underline{r}_{k}-\underline{r}) \right\rangle \Bigg] + c \frac{\partial}{\partial \underline{r}} \times \underline{B} \\
= & \; 4\pi \sum_{n=0}^{\infty} \sum_{r=0}^{n} \frac{(-1)^n}{(n+1)!} \left(\frac{\partial}{\partial \underline{\underline{r}}}\right)^{(n)} \cdot^{(n)} \sum_{ki} \left\langle e_{ki} \left[\underline{\underline{R}}_{ki}^{(r)} \underline{U}_{ki} \underline{\underline{R}}_{ki}^{(n-r)} - \underline{\underline{R}}_{ki}^{(n)} \underline{U}_{ki} \right] \delta(\underline{r}_{k}-\underline{r}) \right\rangle \\
& + 4\pi \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1)!} \left(\frac{\partial}{\partial \underline{r}}\right)^{(n+1)} \cdot^{(n+1)} \sum_{ki} \left\langle e_{ki} \left[\underline{\underline{R}}_{ki}^{(n+1)} \underline{u}_{k} - \underline{u}_{k} \underline{\underline{R}}_{ki}^{(n+1)} \right] \delta(\underline{r}_{k}-\underline{r}) \right\rangle \\
& - 4\pi \sum_{k} \left\langle e_{k} \underline{u}_{k} \delta(\underline{r}_{k}-\underline{r}) \right\rangle + c \frac{\partial}{\partial \underline{r}} \times \underline{B} \,. \qquad (2.4.13)
\end{aligned}
$$

Notice that the first term in the final expression for (2.4.13) is zero when n = 0 and also when r = n; hence we write

$$\frac{\partial \underline{D}}{\partial t} = 4\pi \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1)!} \left(\frac{\partial}{\partial \underline{\underline{r}}}\right)^{(n+1)} \cdot^{(n+1)} \Bigg\{ \sum_{ki} \Big\langle e_{ki} \Big[\underline{\underline{R}}_{ki}^{(n+1)} \underline{u}_k - \underline{u}_k \underline{\underline{R}}_{ki}^{(n+1)} \Big] \delta(\underline{r}_k - \underline{r}) \Big\rangle$$

$$+ \frac{1}{n+2} \sum_{r=0}^{n} \sum_{ki} \Big\langle e_{ki} \Big[\underline{\underline{R}}_{ki}^{(n+1)} \underline{U}_{ki} - \underline{\underline{R}}_{ki}^{(r)} \underline{U}_{ki} \underline{\underline{R}}_{ki}^{(n+1-r)} \Big] \delta(\underline{r}_k - \underline{r}) \Big\rangle \Bigg\}$$

$$- 4\pi \sum_{k} \big\langle e_k \underline{u}_k \delta(\underline{r}_k - \underline{r}) \big\rangle + c \frac{\partial}{\partial \underline{r}} \times \underline{B} . \tag{2.4.14}$$

From the usual vector identity,

$$\frac{\partial}{\partial \underline{r}} \cdot (\underline{a}\,\underline{b} - \underline{b}\,\underline{a}) \equiv - \frac{\partial}{\partial \underline{r}} \times (\underline{a} \times \underline{b}), \tag{2.4.15}$$

the identity,

$$\left(\frac{\partial}{\partial \underline{\underline{r}}}\right)^{(n)} \cdot^{(n)} \left(\underline{\underline{a}}^{(n)} \underline{b} - \underline{b}\, \underline{\underline{a}}^{(n)}\right) \equiv - \frac{\partial}{\partial \underline{r}} \times \left[\left(\frac{\partial}{\partial \underline{\underline{r}}}\right)^{(n-1)} \cdot^{(n-1)} \underline{\underline{a}}^{(n)} \times \underline{b} \right], \tag{2.4.16}$$

is derived, where n is a positive integer. Also from (2.4.15), we obtain

$$\left(\frac{\partial}{\partial \underline{\underline{r}}}\right)^{(n)} \cdot^{(n)} \left[\underline{\underline{a}}^{(n)} \underline{b} - \underline{\underline{a}}^{(r)} \underline{b}\, \underline{\underline{a}}^{(n-r)} \right] = - \frac{\partial}{\partial \underline{r}} \times \left[\left(\frac{\partial}{\partial \underline{\underline{r}}}\right)^{(n-1)} \cdot^{(n-1)} \underline{\underline{a}}^{(n)} \times \underline{b} \right], \tag{2.4.17}$$

where r is an integer such that $0 \leq r \leq n-1$. Using (2.4.16) in the first integral within the $\{\ \}$ in (2.4.14), and using (2.4.17) in the second integral, we obtain

$$\frac{\partial \underline{D}}{\partial t} = -4\pi \frac{\partial}{\partial \underline{r}} \times \left\{ \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1)!} \left(\frac{\partial}{\partial \underline{\underline{r}}}\right)^{(n)} \cdot^{(n)} \left[\sum_{ki} \left\langle e_{ki}\, \underline{\underline{R}}_{ki}^{(n+1)} \times \underline{u}_k\, \delta(\underline{r}_k - \underline{r}) \right\rangle \right.\right.$$

$$\left.\left. + \frac{n+1}{n+2} \sum_{ki} \left\langle e_{ki}\, \underline{\underline{R}}_{ki}^{(n+1)} \times \underline{U}_{ki}\, \delta(\underline{r}_k - \underline{r}) \right\rangle \right] \right\}$$

$$- 4\pi \sum_{k} \left\langle e_k \underline{u}_k\, \delta(\underline{r}_k - \underline{r}) \right\rangle + c \frac{\partial}{\partial \underline{r}} \times \underline{B} \,. \qquad (2.4.18)$$

For convenience we define a "magnetic multipole density",

$$\underline{\underline{M}}_U^{(n)} \equiv \frac{n}{(n+1)!} \frac{1}{c} \sum_{ki} \left\langle e_{ki}\, \underline{\underline{R}}_{ki}^{(n)} \times \underline{U}_{ki}\, \delta(\underline{r}_k - \underline{r}) \right\rangle , \qquad (2.4.19)$$

and an "equivalent magnetic multipole density",

$$\underline{\underline{M}}_u^{(n)} \equiv \frac{1}{n!} \frac{1}{c} \sum_{ki} \left\langle e_{ki}\, \underline{\underline{R}}_{ki}^{(n)} \times \underline{u}_k\, \delta(\underline{r}_k - \underline{r}) \right\rangle , \qquad (2.4.20)$$

where $\underline{\underline{M}}_U^{(n)}$ and $\underline{\underline{M}}_u^{(n)}$ are tensors of order n . To interpret these quantities, we regard the motion of the multipole moments of a molecule as being separated into two parts: The motion about the center of mass of the molecule gives rise to the $\underline{\underline{M}}_U^{(n)}$, while the motion with the center of mass gives rise to the $\underline{\underline{M}}_u^{(n)}$. Under this interpretation, the monopole term, $\underline{\underline{M}}_u^{(0)}$, is regarded as the current density and is designated by the symbol,

$$\underline{J} \equiv \underline{\underline{M}}_{u}^{(0)} = \sum_{k} \langle e_k \underline{u}_k \delta(\underline{r}_k - \underline{r}) \rangle . \qquad (2.4.21)$$

We further define a magnetization,

$$\underline{M} \equiv \sum_{n=0}^{\infty} (-1)^{n} \left(\frac{\partial}{\partial \underline{r}} \right)^{(n)} \cdot^{(n)} \left[\underline{\underline{M}}_{u}^{(n+1)} + \underline{\underline{M}}_{v}^{(n+1)} \right] , \qquad (2.4.22)$$

and a magnetic intensity,

$$\underline{H} \equiv \underline{B} - 4\pi \underline{M} . \qquad (2.4.23)$$

With these definitions, (2.4.18) may be written

$$\frac{\partial \underline{D}}{\partial t} = -4\pi \underline{J} + c \frac{\partial}{\partial \underline{r}} \times \underline{H} . \qquad (2.4.24)$$

This equation is a familiar Maxwell equation in a material media as are the equations derived in the previous sections. The quantity, $\underline{H}$, is analogous to $\underline{D}$ in that it is the magnetic field produced by the molecules regarded as point charges. This can be seen from (2.4.24) since $\underline{J}$ [see (2.4.21)] is due to the motion of the molecular charges assumed concentrated at the center of mass of the molecule. By reasoning analogous to that of section 2.3, $\underline{B}$ is interpreted as being produced by the "true" point charges (the nuclei and electrons). Hence, $\underline{H}$ is a close approximation to $\underline{B}$ for dilute systems, but, for more concentrated systems, $\underline{H}$ should be corrected by adding to it the magnetization, $\underline{M}$, which depends on the motions of the intramolecular charges. These terms are the $\underline{\underline{M}}_v^{(n)}$ and $\underline{\underline{M}}_u^{(n)}$ $\left[\text{see (2.4.19) and (2.4.20)}\right]$.

To clarify the interpretation of $\underline{M}$, we introduce the concept of a mass weighted macroscopic molecular velocity, the familiar "stream velocity",

$$\underline{v} \equiv \frac{\sum_k \langle m_k \underline{u}_k \delta(\underline{r}_k - \underline{r})\rangle}{\sum_k \langle m_k \delta(\underline{r}_k - \underline{r})\rangle}, \qquad (2.4.25)$$

and a "Brownian motion velocity",

$$\underline{v}_k \equiv \underline{u}_k - \underline{v} . \qquad (2.4.26)$$

Using these definitions, $\underline{\underline{M}}_u^{(n)}$ becomes

$$\underline{\underline{M}}_u^{(n)} \equiv \frac{1}{c} \underline{\underline{Q}}^{(n)} \times \underline{v} + \frac{1}{n!} \frac{1}{c} \sum_{ki} \langle e_{ki} \underline{\underline{R}}_{ki}^{(n)} \times \underline{v}_k \delta(\underline{r}_k - \underline{r})\rangle. \qquad (2.4.27)$$

If we write $\underline{M}$ including only the terms to the second order in $\underline{R}_{ki}$ and $\underline{U}_{ki}$, we obtain by using (2.4.27)

$$\underline{M} = \underline{\underline{M}}_v^{(1)} + \frac{1}{c}\left[\underline{\underline{Q}}^{(1)} \times \underline{v} - \frac{\partial}{\partial \underline{r}} \cdot \left(\underline{\underline{Q}}^{(2)} \times \underline{v}\right)\right]$$

$$+ \frac{1}{c} \sum_{ki} \left\langle e_{ki} \left[\underline{R}_{ki} \times \underline{v}_k - \frac{\partial}{\partial \underline{r}} \cdot \left(\underline{R}_{ki} \underline{R}_{ki} \times \underline{v}_k\right)\right] \delta(\underline{r}_k - \underline{r})\right\rangle,$$

(2.4.28)

where

$$\underline{\underline{M}}_V^{(1)} = \frac{1}{2c} \sum \langle e_{ki}\, \underline{R}_{ki} \times \underline{U}_{ki}\, \delta(\underline{r}_k - \underline{r}) \rangle . \qquad (2.4.29)$$

If we assume that the Brownian motion is small compared to the stream velocity, and neglect the quadrapole term, we may write (2.4.28) as

$$\underline{M} = \underline{\underline{M}}_V^{(1)} + \frac{1}{c}\, \underline{\underline{Q}}^{(1)} \times \underline{v} , \qquad (2.4.30)$$

a familiar result for "constant velocity" systems.[13] If we assume further that the system is stationary, (2.4.30) becomes

$$\underline{M} = \underline{\underline{M}}_V^{(1)} , \qquad (2.4.31)$$

which is another familiar expression.[14]

2.5 The General Conservation Equation

We next derive an expression for $\frac{\partial \underline{\underline{Q}}^{(n)}}{\partial t}$. For $n = 0$, the result is the familiar equation of charge conservation. The general result is frequently used in conjunction with Maxwell's equations. Use was made of this general result in deriving the fourth Maxwell equation in the previous section [see (2.4.10)].

From the general equation of change and the definition of $\underline{\underline{Q}}^{(n)}$, (1.5.16) and (2.3.11), it follows that

$$\frac{\partial \underline{\underline{Q}}^{(n)}}{\partial t} = \frac{1}{n!}\sum_{kilj}\left\langle e_{ki}\,\underline{u}_{lj}\cdot\frac{\partial}{\partial \underline{r}_{lj}}\,\underline{\underline{R}}_{ki}^{(n)}\,\delta(\underline{r}_k-\underline{r})\right\rangle$$

$$=\sum_{r=0}^{n-1}\frac{1}{n!}\sum_{kilj}\left\langle e_{ki}\,\underline{\underline{R}}_{ki}^{(r)}\,\underline{u}_{lj}\cdot\left(\frac{\partial \underline{R}_{ki}}{\partial \underline{r}_{lj}}\right)\underline{\underline{R}}_{ki}^{(n-1-r)}\,\delta(\underline{r}_k-\underline{r})\right\rangle$$

$$+\frac{1}{n!}\sum_{kilj}\left\langle e_{ki}\,\underline{\underline{R}}_{ki}^{(n)}\,\underline{u}_{lj}\cdot\frac{\partial}{\partial \underline{r}_{lj}}\,\delta(\underline{r}_k-\underline{r})\right\rangle . \qquad (2.5.1)$$

From the definitions of $\underline{r}_k$ and $\underline{R}_{ki}$, (2.3.3) and (2.3.6), we write

$$\frac{\partial}{\partial \underline{r}_{lj}}\,\delta(\underline{r}_k-\underline{r}) = \frac{m_{kj}}{m_k}\,\delta_{kl}\,\frac{\partial}{\partial \underline{r}_k}\,\delta(\underline{r}_k-\underline{r}) \qquad (2.5.2)$$

and

$$\frac{\partial \underline{R}_{ki}}{\partial \underline{r}_{lj}} = \left(\delta_{ij}-\frac{m_{kj}}{m_k}\right)\underline{\underline{I}}\;\delta_{kl}\,, \qquad (2.5.3)$$

where δ_{ij} is the Kronkeker delta [see (1.3.19)], and $\underline{\underline{I}}$ is the unit tensor. Substituting (2.5.2) and (2.5.3) into (2.5.1) and summing over lj, we obtain

$$\frac{\partial \underline{\underline{Q}}^{(n)}}{\partial t} = \sum_{r=0}^{n-1}\frac{1}{n!}\sum_{ki}\left\langle e_{ki}\,\underline{\underline{R}}_{ki}^{(r)}\,\underline{V}_{ki}\,\underline{\underline{R}}_{ki}^{(n-1-r)}\,\delta(\underline{r}_k-\underline{r})\right\rangle$$

$$-\frac{\partial}{\partial \underline{r}}\cdot\frac{1}{n!}\sum_{ki}\left\langle e_{ki}\,\underline{u}_k\,\underline{\underline{R}}_{ki}^{(n)}\,\delta(\underline{r}_k-\underline{r})\right\rangle . \qquad (2.5.4)$$

where $\underline{u}_k$ and $\underline{U}_{ki}$ are defined by (2.4.11) and (2.4.12), respectively.

Notice that (2.5.4) may also be written as

$$\frac{\partial \sum_{ki} \langle e_{ki}\, \underline{\underline{R}}_{ki}^{(m)}\, \delta(\underline{r}_k-\underline{r}) \rangle}{\partial t} + \frac{\partial}{\partial \underline{r}} \cdot \sum_{ki} \langle e_{ki}\, \underline{u}_k\, \underline{\underline{R}}_{ki}^{(m)}\, \delta(\underline{r}_k-\underline{r}) \rangle$$

$$= \sum_{ki} \langle e_{ki}\, \frac{d\underline{\underline{R}}_{ki}^{(m)}}{dt}\, \delta(\underline{r}_k-\underline{r}) \rangle . \qquad (2.5.5)$$

When $m = 0$, the above equation reduces to the familiar equation of charge conservation,

$$\frac{\partial \rho_e}{\partial t} + \frac{\partial}{\partial \underline{r}} \cdot \underline{J} = 0, \qquad (2.5.6)$$

where ρ_e is the macroscopic charge density and $\underline{J}$ is the macroscopic current density [see (2.3.13) and (2.4.21)] .

Furthermore, the form of (2.5.5) suggests the definition of two new quantities,

$$\underline{\underline{J}}_P \equiv \sum_{m=0}^{\infty} \frac{(-1)^m}{(m+1)!} \left(\frac{\partial}{\partial \underline{r}}\right)^{(m)} \cdot^{(m)} \sum_{ki} \langle e_{ki}\, \underline{u}_k\, \underline{\underline{R}}_{ki}^{(m+1)}\, \delta(\underline{r}_k-\underline{r}) \rangle \qquad (2.5.7)$$

and

$$\underline{\tilde{P}} \equiv \sum_{m=0}^{\infty} \frac{(-1)^m}{(m+1)!} \left(\frac{\partial}{\partial \underline{r}}\right)^{(m)} \cdot^{(m)} \sum_{ki} \langle e_{ki}\, \frac{d\underline{\underline{R}}_{ki}^{(m+1)}}{dt}\, \delta(\underline{r}_k-\underline{r}) \rangle . \qquad (2.5.8)$$

If (2.5.5), (2.5.7), and (2.5.8) are combined with the definition of $\underline{P}$, (2.3.15), the resulting equation is

$$\frac{\partial \underline{P}}{\partial t} + \frac{\partial}{\partial \underline{r}} \cdot \underline{\underline{J}}_P = \widetilde{\underline{P}} . \tag{2.5.9}$$

This has the form of a "conservation" equation for the polarization, $\underline{P}$. In this equation, $\underline{\underline{J}}_P$ may be interpreted as a polarization current and $\widetilde{\underline{P}}$, as a "source" of polarization.

We introduce in this chapter a device which we use throughout this work. By multiplying the dynamical variables by a molecular density function, $\delta(\underline{r}_k - \underline{r})$, rather than by a particle density function, $\delta(\underline{r}_{ki} - \underline{r})$, we introduce a set of macroscopic fields, $\underline{D}$ and $\underline{H}$, the sources of which are the molecules with internal structure neglected. We derive a set of Maxwell equations for these fields and a polarization and a magnetization, $\underline{P}$ and $\underline{M}$, which correct $\underline{D}$ and $\underline{H}$ for the internal structure of the molecules when this structure is important. Finally, a conservation equation for the polarization, $\underline{P}$, is derived.

Appendix 2.A1: A Proof of a Relation Involving the $\underline{A}_\lambda$

From the expression for $\phi^{(i)}$ in terms of the canonical variables, (1.3.16), we have, recalling the significance of the $(\,\dot{}\,)$ notation $\left[\text{ see (1.2.3)}\right]$,

$$\dot{\phi}^{(i)} = \sum_{ki} \dot{\underline{r}}_{ki} \cdot \frac{\partial}{\partial \underline{r}_{ki}} \frac{e_{ki}}{|\underline{r}_{ki} - \underline{r}|}$$

$$= \sum_{ki} e_{ki} \underline{u}_{ki} \cdot \frac{\partial}{\partial \underline{r}_{ki}} \frac{1}{|\underline{r}_{ki} - \underline{r}|} \; . \tag{2.A1.1}$$

Substituting (2.A1.1) and the expression for $\underline{A}^{(i)}$ in terms of the canonical variables, (1.3.20), into the equation relating $\phi^{(i)}$ and $\underline{A}^{(i)}$, (1.3.14), we write

$$\sum_{\lambda} \left[\frac{1}{c^2} \ddot{q}_\lambda \underline{A}_\lambda(\underline{r}) - q_\lambda \frac{\partial^2 \underline{A}_\lambda(\underline{r})}{\partial r^2} \right] + \frac{1}{c^2} \sum_{ki} e_{ki} \underline{u}_{ki} \cdot \frac{\partial}{\partial \underline{r}_{ki}} \frac{\partial}{\partial \underline{r}} \frac{1}{|\underline{r}_{ki} - \underline{r}|}$$

$$= \frac{4\pi}{c} \sum_{ki} e_{ki} \underline{u}_{ki} \, \delta(\underline{r}_{ki} - \underline{r}) \; . \tag{2.A1.2}$$

Finally, substituting the defining equation for $\underline{A}_\lambda$, (1.3.17), and the equation of motion for q_λ , (1.3.25), into (2.A1.2), we obtain

$$\sum_{ki} e_{ki} \underline{u}_{ki} \cdot \left[\frac{\partial}{\partial \underline{r}_{ki}} \frac{\partial}{\partial \underline{r}} \frac{1}{|\underline{r}_{ki} - \underline{r}|} + \frac{1}{c^2} \sum_{\lambda} \underline{A}_\lambda(\underline{r}_{ki}) \underline{A}_\lambda(\underline{r}) \right] = 4\pi \sum_{ki} e_{ki} \underline{u}_{ki} \, \delta(\underline{r}_{ki} - \underline{r}) , \tag{2.A1.3}$$

which is the desired result.

III. THE EQUATION OF CONTINUITY

In a fluid, the macroscopic quantities of interest are the mass, momentum, and energy. In the remaining chapters, we derive the equations of change of these quantities. We find it appropriate, as in the previous chapter, to define the macroscopic mass, momentum, and energy densities in terms of molecule centered integrals containing $\delta(\underline{r}_k-\underline{r})$. The particular equations of change are obtained by using the general equation of change, (1.5.16), to obtain the time derivatives of these densities. In this chapter, we obtain, in particular, the equation of continuity.

A molecule centered macroscopic mass density is defined as

$$\rho=\sum_k\langle m_k\,\delta(\underline{r}_k-\underline{r})\rangle. \tag{3.0.1}$$

To obtain the conservation equation for ρ, the general equation of change, (1.5.16) is used to find the time derivative,

$$\frac{\partial\rho}{\partial t}=\sum_k\langle\Lambda\, m_k\,\delta(\underline{r}_k-\underline{r})\rangle$$

$$=\sum_{k\ell j}\langle m_k\,\underline{u}_{\ell j}\cdot\frac{\partial}{\partial\underline{r}_{\ell j}}\delta(\underline{r}_k-\underline{r})\rangle. \tag{3.0.2}$$

Using (2.5.2) and summing over ℓ, it is found that

$$\frac{\partial \rho}{\partial t} = \sum_{kj} \left\langle m_{kj}\, \underline{u}_{kj} \cdot \frac{\partial}{\partial \underline{r}_k} \delta(\underline{r}_k - \underline{r}) \right\rangle$$

$$= - \frac{\partial}{\partial \underline{r}} \cdot \sum_{k} \left\langle m_k\, \underline{u}_k\, \delta(\underline{r}_k - \underline{r}) \right\rangle. \qquad (3.0.3)$$

The quantity on the right of the last equation is the macroscopic molecular momentum density, in terms of which the stream velocity, $\underline{v}$, is defined [see (2.4.25)],

$$\rho \underline{v} \equiv \sum_{k} \left\langle m_k\, \underline{u}_k\, \delta(\underline{r}_k - \underline{r}) \right\rangle. \qquad (3.0.4)$$

Hence (3.0.3) may be rewritten

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \underline{r}} \cdot \rho \underline{v} = 0. \qquad (3.0.5)$$

This equation of continuity for an ionized fluid is the usual equation of continuity for a non-ionized fluid.[15]

IV. THE EQUATION OF MOTION

In a manner analogous to that of the previous chapter, we now develop an equation of change for the macroscopic momentum density, $\rho\underline{v}$. This equation of motion contains force terms arising from the electromagnetic properties of the medium. In the usual treatment of molecules interacting according to a potential, these force terms are expressed as a collisional contribution to the pressure tensor, and this contribution is obtained as an integral involving the radial distribution function. In the electromagnetic case, because of the long-range nature of the coulomb potential, this integral diverges. The essential problem of this chapter is that of separating the effect of the electromagnetic forces into short-range terms leading to a non-divergent collisional contribution to the pressure tensor and long-range terms involving functions of the macroscopic electric and magnetic fields introduced in Chapter II.

4.1 The Time Derivative of the Momentum Density

As in Chapter III, we take the time derivative of the macroscopic momentum density (3.0.4), using the general equation of change, (1.5.16), and obtain

$$\frac{\partial \rho\underline{v}}{\partial t} = \sum_{kli} \left\langle m_k \underline{u}_{li} \cdot \frac{\partial}{\partial \underline{r}_{li}} \underline{u}_k \, \delta(\underline{r}_k - \underline{r}) \right\rangle \tag{4.1.1}$$

$$+ \sum_{kli} \left\langle m_k \frac{e_{li}}{m_{li}} \left[\underline{E}^{\mu}_{li}(\underline{r}_{li}) + \frac{1}{c}\underline{u}_{li} \times \underline{B}^{\mu}(\underline{r}_{li}) \right] \cdot \frac{\partial}{\partial \underline{u}_{li}} \underline{u}_k \, \delta(\underline{r}_k - \underline{r}) \right\rangle .$$

Using the previously derived expression for $\frac{\partial}{\partial \underline{r}_{\ell i}} \delta(\underline{r}_k - \underline{r})$ [see (2.5.2)] and the definition of $\underline{u}_k$, (2.4.11), we can, upon summing over ℓ, bring the first term on the right of the equation to the left, and write (4.1.1) as

$$\frac{\partial \rho \underline{v}}{\partial t} + \frac{\partial}{\partial \underline{r}} \cdot \sum_k \langle m_k \underline{u}_k \underline{u}_k \delta(\underline{r}_k - \underline{r}) \rangle$$
$$= \sum_{ki} \left\langle e_{ki} \left[\underline{E}^{\mu}_{ki}(\underline{r}_{ki}) + \frac{1}{c} \underline{u}_{ki} \times \underline{B}^{\mu}(\underline{r}_{ki}) \right] \delta(\underline{r}_k - \underline{r}) \right\rangle . \tag{4.1.2}$$

We consider first the second term on the left of (4.1.2) and use the definition of $\underline{v}_k$, (2.4.26), to write

$$\sum_k \langle m_k \underline{u}_k \underline{u}_k \delta(\underline{r}_k - \underline{r}) \rangle = \sum_k \langle m_k \underline{v}_k \underline{v}_k \delta(\underline{r}_k - \underline{r}) \rangle$$
$$+ \sum_k \left[\langle m_k \underline{v}_k \delta(\underline{r}_k - \underline{r}) \rangle \underline{v} + \underline{v} \langle m_k \underline{v}_k \delta(\underline{r}_k - \underline{r}) \rangle \right] \tag{4.1.3}$$
$$+ \rho \underline{v} \underline{v} .$$

Since, from the definition of $\underline{v}_k$,

$$\sum_k \langle m_k \underline{v}_k \delta(\underline{r}_k - \underline{r}) \rangle \equiv 0 , \tag{4.1.4}$$

the second term on the right of the last equation vanishes. The first term,

$$\underline{\underline{P}}_K \equiv \sum_k \langle m_k \underline{v}_k \underline{v}_k \delta(\underline{r}_k - \underline{r}) \rangle , \tag{4.1.5}$$

is the usual kinetic contribution to the pressure tensor. Substituting (4.1.3) and (4.1.5) into (4.1.2), we obtain

$$\frac{\partial \rho \underline{v}}{\partial t} + \frac{\partial}{\partial \underline{r}} \cdot \rho \underline{v}\, \underline{v} = - \frac{\partial}{\partial \underline{r}} \cdot \underline{\underline{p}}_K + \sum_{ki} \left\langle e_{ki} \left[\underline{E}^{\mu}_{ki} (\underline{r}_{ki}) + \frac{1}{c} \underline{u}_{ki} \times \underline{B}^{\mu} (\underline{r}_{ki}) \right] \delta (\underline{r}_k - \underline{r}) \right\rangle. \tag{4.1.6}$$

The last equation, except for the last term on the right, is the usual equation of motion of a non-ionized gas at low density. The last term, then, describes the effects of external fields on the charged particles and the effects of the collisional transfer of momentum through the interactions among the particles. To examine this term in more detail, we write

$$\sum_{ki} \left\langle e_{ki} \left[\underline{E}^{\mu}_{ki} (\underline{r}_{ki}) + \frac{1}{c} \underline{u}_{ki} \times \underline{B}^{\mu} (\underline{r}_{ki}) \right] \delta (\underline{r}_k - \underline{r}) \right\rangle \equiv \underline{X} + \underline{\Delta}\,, \tag{4.1.7}$$

where

$$\underline{X} \equiv \sum_{ki} \langle e_{ki} [\underline{E}_{ki} (\underline{r}_{ki}) + \frac{1}{c} \underline{u}_{ki} \times \underline{B} (\underline{r}_{ki}) \delta (\underline{r}_k - \underline{r}) \rangle \tag{4.1.8}$$

and

$$\Delta \equiv \sum_{ki} \left\langle e_{ki} \left\{ \left[\underline{E}^{\mu}_{ki} (\underline{r}_{ki}) - \underline{E}_{ki} (\underline{r}_{ki}) \right] + \frac{1}{c} \underline{u}_{ki} \times \left[\underline{B}^{\mu} (\underline{r}_{ki}) - \underline{B} (\underline{r}_{ki}) \right] \right\} \delta (\underline{r}_k - \underline{r}) \right\rangle. \tag{4.1.9}$$

In (4.1.8) and (4.1.9), $\underline{B}(\underline{r}_{ki})$ is the macroscopic magnetic field density at $\underline{r}_{ki}$ as defined by (2.1.1) and $\underline{E}_{ki}(\underline{r}_{ki})$ is the macroscopic electric field density defined by (2.2.4) excluding the effects of particle ki.

Explicitly,

$$\mathbf{E}_{ki}(\mathbf{r}_{ki}) = \int \mathbf{E}^{\mu'}_{ki}(\mathbf{r}_{ki})\, f(\mathbf{r}'_{lj}, \mathbf{u}'_{lj}, q'_\lambda, p'_\lambda) \prod_{lj\lambda} d\mathbf{r}'_{lj}\, d\mathbf{u}'_{lj}\, dq'_\lambda\, dp'_\lambda$$

$$= \left\langle \mathbf{E}^{\mu'}_{ki}(\mathbf{r}_{ki}) \right\rangle'$$

$$= \left\langle \sum_{\substack{lj \\ (lj \neq ki)}} e_{lj} \frac{\mathbf{r}_{ki} - \mathbf{r}'_{lj}}{|\mathbf{r}_{ki} - \mathbf{r}'_{lj}|^3} - \frac{1}{c} \sum_\lambda p'_\lambda \mathbf{A}_\lambda(\mathbf{r}_{ki}) \right\rangle' + \mathbf{E}^{(e)}(\mathbf{r}_{ki}), \tag{4.1.10}$$

where the ($'$) on the brackets in the second and third lines of (4.1.10) indicates that the average is to be carried out over the primed variables only.

From (4.1.10), it is clear that we may also write

$$\mathbf{E}_{ki}(\mathbf{r}_{ki}) = \left\langle \sum_{lj} e_{lj} \frac{\mathbf{r}_{ki} - \mathbf{r}'_{lj}}{|\mathbf{r}_{ki} - \mathbf{r}'_{lj}|^3} - e_{ki} \frac{\mathbf{r}_{ki} - \mathbf{r}'_{ki}}{|\mathbf{r}_{ki} - \mathbf{r}'_{ki}|^3} - \frac{1}{c} \sum_\lambda p'_\lambda \mathbf{A}_\lambda(\mathbf{r}_{ki}) \right\rangle' + \mathbf{E}^{(e)}(\mathbf{r}_{ki}). \tag{4.1.11}$$

The first term inside the brackets in the above equation is a double sum over all the particles, while the second term involves only one particle. The first term may, therefore, be expected to be larger than the second by a factor of the order of magnitude of N^2, where N is the number of particles in the system. Thus, since

N is taken to be large, the second term inside the brackets in (4.1.11) is negligible. Consequently, using the definition of $\underline{E}(\underline{r}_{ki})$, (2.2.4), we may write (4.1.11) as

$$\underline{E}_{ki}(\underline{r}_{ki}) = \underline{E}(\underline{r}_{ki}). \tag{4.1.12}$$

Thus, from (4.1.8), $\underline{X}$ may be expressed as

$$\underline{X} = \sum_{ki} \left\langle e_{ki} \left[\underline{E}(\underline{r}_{ki}) + \frac{1}{c}\underline{u}_{ki} \times \underline{B}(\underline{r}_{ki}) \right] \delta(\underline{r}_k - \underline{r}) \right\rangle. \tag{4.1.13}$$

Substituting the definitions of $\underline{X}$ and $\underline{\Delta}$ into (4.1.6), we obtain for the equation of motion

$$\frac{\partial \rho \underline{v}}{\partial t} + \frac{\partial}{\partial \underline{r}} \cdot \rho \underline{v}\,\underline{v} = -\frac{\partial}{\partial \underline{r}} \cdot \underline{\underline{p}}_K + \underline{X} + \underline{\Delta}. \tag{4.1.14}$$

From (4.1.9), $\underline{\Delta}$ is seen to be dependent on the difference between the microscopic fields, $\underline{E}^{\mu}_{ki}$ and $\underline{B}^{\mu}$, and the macroscopic fields, $\underline{E}_{ki}$ and $\underline{B}$. This difference is appreciable only for dense systems. For low density systems, then, $\underline{X}$ is the primary contribution to the force term in (4.1.14). Hence, because $\underline{X}$ represents the interparticle interaction when the interparticle distance is large, $\underline{X}$ is the "long range" contribution to the electromagnetic force. The term $\underline{\Delta}$, which is a correction to $\underline{X}$ when the interparticle distance is small, is, consequently, the "short range" contribution to the force term. More is said about the interpretation of $\underline{\Delta}$ at the end of section 4.2.

4.2 The Short Range Term

Next we consider the short range term, $\underline{\Delta}$, in greater detail. For this purpose it is convenient to define a double average of a function, $g(\underline{r}_{ki},\underline{u}_{ki},q_\lambda,p_\lambda,\underline{r}'_{ki},\underline{u}'_{ki},q'_\lambda,p'_\lambda)$, of two sets (primed and unprimed) of independent variables as

$$\langle\langle g\rangle\rangle \equiv \int g\, f^{(N)}(\underline{r}_{ki},\underline{u}_{ki},q_\lambda,p_\lambda)\, f^{(N)}(\underline{r}'_{ki},\underline{u}'_{ki},q'_\lambda,p'_\lambda)$$

$$\times \prod_{ki\lambda} d\underline{r}_{ki}\, d\underline{u}_{ki}\, dq_\lambda\, dp_\lambda\, d\underline{r}'_{ki}\, d\underline{u}'_{ki}\, dq'_\lambda\, dp'_\lambda, \qquad (4.2.1)$$

where $f^{(N)}$ [see (1.5.7)] is the distribution function in the phase space of the system. In view of the normalization condition, $\langle 1\rangle = 1$ [see (1.5.12)] , we find that

$$\langle x(\underline{r}_{ki},\underline{u}_{ki},q_\lambda,p_\lambda)\rangle + \langle y'(\underline{r}'_{ki},\underline{u}'_{ki},q'_\lambda,p'_\lambda)\rangle = \langle x + \langle y'\rangle' = \langle\langle x+y'\rangle\rangle. \qquad (4.2.2)$$

Using this double average notation, we write from (4.1.9) and the definition of $\underline{E}_{ki}(\underline{r}_{ki})$ and $\underline{E}^{\mu}_{ki}(\underline{r}_{ki})$ [see (4.1.10) and (1.4.7)]

$$\underline{\Delta} = \underline{\Delta}_c + \underline{\Delta}_M . \qquad (4.2.3)$$

The first term in (4.2.3),

$$\underline{\Delta}_c \equiv \sum_{ki\neq lj} \left\langle\!\left\langle e_{ki}\, e_{lj} \left[\frac{\underline{r}_{ki}-\underline{r}_{lj}}{|\underline{r}_{ki}-\underline{r}_{lj}|^3} - \frac{\underline{r}_{ki}-\underline{r}'_{lj}}{|\underline{r}_{ki}-\underline{r}'_{lj}|^3} \right] \delta(\underline{r}_k-\underline{r}) \right\rangle\!\right\rangle , \qquad (4.2.4)$$

is the coulombic interaction term. The second term,

$$\underline{\Delta}_M \equiv -\frac{1}{c} \sum_{ki} \left\langle\!\left\langle e_{ki} \left[\underline{E}^T(\underline{r}_{ki}) - \underline{E}^{T\prime}(\underline{r}_{ki}) \right] \delta(\underline{r}_k-\underline{r}) \right\rangle\!\right\rangle$$

$$+ \frac{1}{c} \sum_{ki} \left\langle\!\left\langle e_{ki}\, \underline{u}_{ki} \times \left[\underline{B}(\underline{r}_{ki}) - \underline{B}'(\underline{r}_{ki}) \right] \delta(\underline{r}_k-\underline{r}) \right\rangle\!\right\rangle , \qquad (4.2.5)$$

where $\underline{E}^T(\underline{r}_{ki})$ is defined by

$$\underline{E}^T(\underline{r}_{ki}) \equiv \sum_{\lambda} p_\lambda\, \underline{A}_\lambda(\underline{r}_{ki}) , \qquad (4.2.6)$$

is the transverse or retardation correction to the coulombic interaction plus the short range magnetic interaction term. For the non-relativistic systems we consider, the particles have low velocity and these last effects are small.

In casting $\underline{\Delta}$ into a more significant form, we first treat the coulombic term. For $l \neq k$, a Taylor series expansion results in

$$\frac{\underline{r}_{ki}-\underline{r}_{lj}}{|\underline{r}_{ki}-\underline{r}_{lj}|^3} = \frac{\underline{r}_k-\underline{r}_l}{|\underline{r}_k-\underline{r}_l|^3} + \underline{R}_{lj} \cdot \frac{\partial}{\partial \underline{r}_l} \left(\frac{\underline{r}_k-\underline{r}_l}{|\underline{r}_k-\underline{r}_l|^3} \right)$$

$$+ \underline{R}_{ki} \cdot \frac{\partial}{\partial \underline{r}_k} \left(\frac{\underline{r}_k-\underline{r}_l}{|\underline{r}_k-\underline{r}_l|^3} \right) + \underline{R}_{ki}\, \underline{R}_{lj} : \frac{\partial}{\partial \underline{r}_l} \frac{\partial}{\partial \underline{r}_k} \left(\frac{\underline{r}_k-\underline{r}_l}{|\underline{r}_k-\underline{r}_l|^3} \right) \qquad (4.2.7)$$

$$+ \frac{1}{2} \underline{R}_{lj}\, \underline{R}_{lj} : \frac{\partial}{\partial \underline{r}_l} \frac{\partial}{\partial \underline{r}_l} \left(\frac{\underline{r}_k-\underline{r}_l}{|\underline{r}_k-\underline{r}_l|^3} \right) + \frac{1}{2} \underline{R}_{ki}\, \underline{R}_{ki} : \frac{\partial}{\partial \underline{r}_k} \frac{\partial}{\partial \underline{r}_k} \left(\frac{\underline{r}_k-\underline{r}_l}{|\underline{r}_k-\underline{r}_l|^3} \right) + \cdots ,$$

which, since

$$\frac{\underline{r}_k-\underline{r}_\ell}{|\underline{r}_k-\underline{r}_\ell|} \equiv \frac{\partial}{\partial \underline{r}_\ell}\frac{1}{|\underline{r}_k-\underline{r}_\ell|} \equiv -\frac{\partial}{\partial \underline{r}_k}\frac{1}{|\underline{r}_k-\underline{r}_\ell|}, \tag{4.2.8}$$

may be written in general as

$$\frac{\underline{r}_{ki}-\underline{r}_{\ell j}}{|\underline{r}_{ki}-\underline{r}_{\ell j}|^3} = \sum_{m=0}^{\infty}\sum_{\lambda=0}^{m}\frac{(-1)^{(m-\lambda)}}{\lambda!(m-\lambda)!}\,\underline{\underline{R}}_{ki}^{(m-\lambda)}\,\underline{\underline{R}}_{\ell j}^{(\lambda)}\cdot^{(m)}\left(\frac{\partial}{\partial\underline{r}_\ell}\right)^{(m+1)}\frac{1}{|\underline{r}_k-\underline{r}_\ell|} \qquad (\ell\neq k). \tag{4.2.9}$$

Using (4.2.9), we write the first term of (4.2.3) as

$$\begin{aligned}\underline{\Delta}_c = {} & \sum_{\substack{k\\ i\neq j}}\left\langle\!\left\langle e_{ki}e_{kj}\left[\frac{\underline{r}_{ki}-\underline{r}_{kj}}{|\underline{r}_{ki}-\underline{r}_{kj}|^3}-\frac{\underline{r}_{ki}-\underline{r}'_{kj}}{|\underline{r}_{ki}-\underline{r}'_{kj}|^3}\right]\delta(\underline{r}_k-\underline{r})\right\rangle\!\right\rangle \\ & + \sum_{m=0}^{\infty}\sum_{\lambda=0}^{m}\sum_{\substack{k\neq\ell\\ ij}}\left\langle\!\left\langle e_{ki}e_{\ell j}\frac{(-1)^{(m-\lambda)}}{\lambda!(m-\lambda)!}\left[\underline{\underline{R}}_{ki}^{(m-\lambda)}\,\underline{\underline{R}}_{\ell j}^{(\lambda)}\cdot^{(m)}\left(\frac{\partial}{\partial\underline{r}_\ell}\right)^{(m+1)}\frac{1}{|\underline{r}_k-\underline{r}_\ell|}\right.\right.\right. \\ & \left.\left.\left. -\underline{\underline{R}}_{ki}^{(m-\lambda)}\,\underline{\underline{R}}_{\ell j}^{\prime(\lambda)}\cdot^{(m)}\left(\frac{\partial}{\partial\underline{r}'_\ell}\right)^{(m+1)}\frac{1}{|\underline{r}_k-\underline{r}'_\ell|}\right]\delta(\underline{r}_k-\underline{r})\right\rangle\!\right\rangle.\end{aligned} \tag{4.2.10}$$

The second term in (4.2.10) involves a sum over k and ℓ whereas the first term involves a sum over k only. Therefore the second term is larger than the first by a factor of the order of magnitude of M, where M is the number of molecules in the system. Since M is assumed to be large, we neglect the first term of (4.2.10) and write

$$\underline{\Delta}_c = \iint \Bigg(\sum_{m=0}^{\infty}\underline{\underline{N}}^{(m)}(\underline{r}',\underline{r}'')\cdot^{(m)}\left(\frac{\partial}{\partial\underline{r}''}\right)^{(m+1)}\frac{1}{|\underline{r}'-\underline{r}''|}\,\delta(\underline{r}'-\underline{r})\,d\underline{r}'\,d\underline{r}'', \tag{4.2.11}$$

where

$$\underline{\underline{N}}^{(n)}(\underline{r}', \underline{r}'') \equiv \sum_{\lambda=0}^{n} \frac{(-1)^{(n-\lambda)}}{\lambda!\,(n-\lambda)!} \sum_{\substack{k\neq l\\ i\ j}} \left\langle\!\left\langle e_{ki}\, e_{lj} \left[\underline{\underline{R}}_{ki}^{(n-\lambda)}\, \underline{\underline{R}}_{lj}^{(\lambda)}\, \delta(\underline{r}_k - \underline{r}')\, \delta(\underline{r}_l - \underline{r}'') \right.\right.\right.$$

$$\left.\left.\left. - \underline{\underline{R}}_{ki}^{(n-\lambda)}\, \underline{\underline{R}}_{lj}^{\prime(\lambda)}\, \delta(\underline{r}_k - \underline{r}')\, \delta(\underline{r}_l' - \underline{r}'') \right] \right\rangle\!\right\rangle . \tag{4.2.12}$$

The quantity, $\underline{\underline{N}}^{(n)}(\underline{r}', \underline{r}'')$ is related to the pair distribution function. If we look at the zeroth order term of (4.2.12), we obtain

$$\underline{\underline{N}}^{(0)}(\underline{r}', \underline{r}'') \equiv \sum_{k\neq l} e_k e_l \left\langle\!\left\langle \delta(\underline{r}_k - \underline{r}')\, \delta(\underline{r}_l - \underline{r}'') - \delta(\underline{r}_k - \underline{r}')\, \delta(\underline{r}_l' - \underline{r}'') \right\rangle\!\right\rangle . \tag{4.2.13}$$

This is closely related to the difference between the pair distribution function and the product of single particle distribution functions. The higher order terms describe the effects of molecular structure.

The following relation involving the $\underline{\underline{N}}^{(n)}(\underline{r}', \underline{r}'')$ and any tensor, $\underline{\underline{T}}^{(n)}$, of order n is useful:

$$\underline{\underline{N}}^{(n)}(\underline{r}', \underline{r}'') \cdot^{(n)} \underline{\underline{T}}^{(n)} = \sum_{r=0}^{n} \frac{(-1)^{(n-r)}}{r!\,(n-r)!} \sum_{\substack{k\neq l\\ ij}} \Big\langle\!\Big\langle e_{ki} e_{lj} \Big[\underline{\underline{R}}_{ki}^{(n-r)} \underline{\underline{R}}_{lj}^{(r)} \delta(\underline{r}_k - \underline{r}')\,\delta(\underline{r}_l - \underline{r}'')$$

$$- \underline{\underline{R}}_{ki}^{(n-r)} \underline{\underline{R}}_{lj}'^{(r)} \delta(\underline{r}_k - \underline{r}')\,\delta(\underline{r}_l' - \underline{r}'') \Big] \Big\rangle\!\Big\rangle \cdot^{(n)} \underline{\underline{T}}^{(n)}$$

$$= \sum_{r=0}^{n} \frac{(-1)^{r}}{r!\,(n-r)!} \sum_{\substack{k\neq l\\ ij}} \Big\langle\!\Big\langle e_{ki} e_{lj} \Big[\underline{\underline{R}}_{ki}^{(r)} \underline{\underline{R}}_{lj}^{(n-r)} \delta(\underline{r}_k - \underline{r}')\,\delta(\underline{r}_l - \underline{r}'')$$

$$- \underline{\underline{R}}_{ki}^{(r)} \underline{\underline{R}}_{lj}'^{(n-r)} \delta(\underline{r}_k - \underline{r}')\,\delta(\underline{r}_l' - \underline{r}'') \Big] \Big\rangle\!\Big\rangle \cdot^{(n)} \underline{\underline{T}}^{(n)}$$

$$= \sum_{r=0}^{n} \frac{(-1)^{n}(-1)^{(n-r)}}{r!\,(n-r)!} \sum_{\substack{k\neq l\\ ij}} \Big\langle\!\Big\langle e_{ki} e_{lj} \Big[\underline{\underline{R}}_{lj}^{(n-r)} \underline{\underline{R}}_{ki}^{(r)} \delta(\underline{r}_l - \underline{r}'')\,\delta(\underline{r}_k - \underline{r}')$$

$$- \underline{\underline{R}}_{lj}^{(n-r)} \underline{\underline{R}}_{ki}'^{(r)} \delta(\underline{r}_l - \underline{r}'')\,\delta(\underline{r}_k' - \underline{r}') \Big] \Big\rangle\!\Big\rangle \cdot^{(n)} \underline{\underline{T}}^{(n)}$$

$$= \sum_{r=0}^{n} \frac{(-1)^{n}(-1)^{(n-r)}}{r!\,(n-r)!} \sum_{\substack{k\neq l\\ ij}} \Big\langle\!\Big\langle e_{ki} e_{lj} \Big[\underline{\underline{R}}_{ki}^{(n-r)} \underline{\underline{R}}_{lj}^{(r)} \delta(\underline{r}_k - \underline{r}'')\,\delta(\underline{r}_l - \underline{r}')$$

$$- \underline{\underline{R}}_{ki}^{(n-r)} \underline{\underline{R}}_{lj}'^{(r)} \delta(\underline{r}_k - \underline{r}'')\,\delta(\underline{r}_l' - \underline{r}') \Big] \Big\rangle\!\Big\rangle \cdot^{(n)} \underline{\underline{T}}^{(n)}$$

$$= (-1)^{n}\, \underline{\underline{N}}^{(n)}(\underline{r}'', \underline{r}') \cdot^{(n)} \underline{\underline{T}}^{(n)}. \qquad (4.2.14)$$

The second line in (4.2.14) follows from the first line upon interchanging λ and $n-\lambda$, which is equivalent to reversing the order of the summation over λ. The third line follows from the second upon interchanging the order of factors in the supervector, $\underline{\underline{R}}^{(\lambda)}_{ki}\,\underline{\underline{R}}^{(n-\lambda)}_{lj}$, a valid operation when the supervector multiplies n times a symmetric tensor of order n. In writing the third line we have interchanged the primes on the variables of integration in the second term and made use of the identity,

$$(-1)^{\lambda} \equiv (-1)^{n}(-1)^{(\lambda-n)} \equiv (-1)^{n}(-1)^{(n-\lambda)}. \tag{4.2.15}$$

Finally the fourth line results from interchanging the dummy indices ki and lj.

Now we are in a position to write from (4.2.11)

$$\underline{\Delta}_c = \iint \sum_{n=0}^{\infty} \underline{\underline{N}}^{(n)}(\underline{r}'',\underline{r}') \cdot^{(n)} \left(\frac{\partial}{\partial \underline{r}'}\right)^{(n+1)} \frac{1}{|\underline{r}''-\underline{r}'|}\, \delta(\underline{r}''-\underline{r})\, d\underline{r}''\, d\underline{r}'$$

$$= -\iint \sum_{n=0}^{\infty} \underline{\underline{N}}^{(n)}(\underline{r}',\underline{r}'') \cdot^{(n)} \left(\frac{\partial}{\partial \underline{r}''}\right)^{(n+1)} \frac{1}{|\underline{r}'-\underline{r}''|}\, \delta(\underline{r}''-\underline{r})\, d\underline{r}'\, d\underline{r}''$$

$$(4.2.16)$$

$$= \frac{1}{2}\iint \sum_{n=0}^{\infty} \underline{\underline{N}}^{(n)}(\underline{r}',\underline{r}'') \cdot^{(n)} \left(\frac{\partial}{\partial \underline{r}''}\right)^{(n+1)} \frac{1}{|\underline{r}'-\underline{r}''|} \left[\delta(\underline{r}'-\underline{r}) - \delta(\underline{r}''-\underline{r})\right] d\underline{r}'\, d\underline{r}''$$

In going from (4.2.11) to the first line of the above equation, we have interchanged the dummy variables $\underline{r}'$ and $\underline{r}''$. In writing the second line use has been made of (4.2.14) and the relation

$$\left(\frac{\partial}{\partial \underline{\underline{r}}'}\right)^{(m+1)} \frac{1}{|\underline{r}''-\underline{r}'|} \equiv (-1)^{(m+1)} \left(\frac{\partial}{\partial \underline{\underline{r}}''}\right)^{(m+1)} \frac{1}{|\underline{r}'-\underline{r}''|} \, . \tag{4.2.17}$$

Finally, we obtain the last line of (4.2.17) by adding the first line to the second and dividing by 2.

Next we expand $\delta(\underline{r}'-\underline{r})-\delta(\underline{r}''-\underline{r})$ in a Taylor series about $\underline{r}'$,

$$\delta(\underline{r}'-\underline{r}) - \delta(\underline{r}''-\underline{r}) = -\sum_{s=0}^{\infty} \frac{1}{(s+1)!} (\underline{r}''-\underline{r})^{(s+1)} \cdot^{(s+1)} \left(\frac{\partial}{\partial \underline{\underline{r}}'}\right)^{(s+1)} \delta(\underline{r}'-\underline{r}), \tag{4.2.18}$$

and write (4.2.16) as

$$\begin{aligned}
\underline{\Delta}_c = & -\frac{1}{2} \sum_{\substack{m=0 \\ s=0}}^{\infty} \frac{1}{(s+1)!} \iint \underline{\underline{N}}^{(m)}(\underline{r}',\underline{r}'') \cdot^{(m)} \left[\left(\frac{\partial}{\partial \underline{\underline{r}}''}\right)^{(m+1)} \frac{1}{|\underline{r}'-\underline{r}''|} \right] \\
& \times \left[(\underline{r}''-\underline{r}')^{(s+1)} \cdot^{(s+1)} \left(\frac{\partial}{\partial \underline{\underline{r}}'}\right)^{(s+1)} \delta(\underline{r}'-\underline{r}) \right] d\underline{r}' d\underline{r}'' \\
= & -\frac{1}{2} \sum_{\substack{m=0 \\ s=0}}^{\infty} \frac{1}{(s+1)!} \iint \left(\frac{\partial}{\partial \underline{\underline{r}}}\right)^{(s+1)} \cdot^{(s+1)} (\underline{r}'-\underline{r}'')^{(s+1)} \underline{\underline{N}}^{(m)}(\underline{r}',\underline{r}'') \\
& \cdot^{(m)} \left(\frac{\partial}{\partial \underline{\underline{r}}''}\right)^{(m+1)} \frac{1}{|\underline{r}'-\underline{r}''|} \, \delta(\underline{r}'-\underline{r}) \, d\underline{r}' d\underline{r}'' \\
= & -\frac{\partial}{\partial \underline{r}} \cdot \frac{1}{2} \sum_{\substack{m=0 \\ s=0}}^{\infty} \frac{1}{(s+1)!} \int \left(\frac{\partial}{\partial \underline{\underline{r}}}\right)^{(s)} \cdot^{(s)} (\underline{r}-\underline{r}')^{(s+1)} \underline{\underline{N}}^{(m)}(\underline{r},\underline{r}') \\
& \cdot^{(m)} \left(\frac{\partial}{\partial \underline{r}'}\right)^{(m+1)} \frac{1}{|\underline{r}-\underline{r}'|} \, d\underline{r}' ,
\end{aligned} \tag{4.2.19}$$

where, in writing the last line, we have integrated over $\underline{r}'$ and have then dropped one of the primes from $\underline{r}''$.

We now define the collisional contribution to the pressure tensor as

$$\underline{\underline{p}}_\phi \equiv \frac{1}{2}\sum_{s=0}^{\infty}\frac{1}{(s+1)!}\left(\frac{\partial}{\partial \underline{r}}\right)^{(s)}\cdot^{(s)}\sum_{n=0}^{\infty}\int(\underline{r}-\underline{r}')^{(s+1)}\,\underline{\underline{N}}^{(n)}(\underline{r},\underline{r}')\cdot^{(n)}\left(\frac{\partial}{\partial \underline{r}'}\right)^{(n+1)}\frac{1}{|\underline{r}-\underline{r}'|}\,d\underline{r}'. \tag{4.2.20}$$

Using this definition of $\underline{\underline{p}}_\phi$, we write from (4.2.19) and (4.2.3)

$$\underline{\Delta} = -\frac{\partial}{\partial \underline{r}}\cdot\underline{\underline{p}}_\phi + \underline{\Delta}_M . \tag{4.2.21}$$

The term, $\underline{\Delta}_M$ $\left[\text{see (4.2.5)}\right]$, contains the contribution to the short range force, $\underline{\Delta}$, which, apparently, cannot be written as the divergence of a contribution to the pressure tensor. As mentioned earlier in this section, $\underline{\Delta}_M$ depends on the transverse fields and retardation effects, while $\underline{\Delta}_c$ and, consequently, $\underline{\underline{p}}_\phi$ depends on the coulombic effects. When the interparticle distance is small enough for $\underline{\Delta}$ to contribute significantly to the electromagnetic force, the coulombic effects are more important than the transverse field and retardation effects, especially for a non-relativistic system; hence, for most applications, $\underline{\Delta}_M$ can be neglected in comparison to $-\frac{\partial}{\partial \underline{r}}\cdot\underline{\underline{p}}_\phi$.

As a further aid to understanding the "short range" nature of

$\underline{\Delta}$, we now discuss the dependence of $\underline{\underline{\not\Delta}}_{\phi}$ and $\underline{\Delta}_{M}$ upon interparticle correlation. In the absence of correlation between the states of any two particles, we can factor the distribution function into a product of functions each involving the position and momentum coordinates of only one particle:

$$f^{(N)}\left(\underline{r}_{ki}^{(N)}, \underline{u}_{ki}^{(N)}, q_{\lambda}, p_{\lambda}\right) \longrightarrow \prod_{ki} f^{(1)}\left(\underline{r}_{ki}, \underline{u}_{ki}, q_{\lambda}, p_{\lambda}\right). \qquad (4.2.22)$$

Now, instead of the distribution function on the left of (4.2.22), the distribution function on the right may be used in performing the integration in (4.2.12). In this case, the primes on the $\underline{r}_{\ell}$ in (4.2.12) may be interchanged without interchanging those on the $\underline{r}_{k}$. The result is

$$\underline{\underline{N}}^{(n)}(\underline{r}', \underline{r}'') \longrightarrow \sum_{r=0}^{n} \frac{(-1)^{(n-r)}}{r!\,(n-r)!} \sum_{\substack{k \neq \ell \\ i\, j}} \left\langle\!\left\langle e_{ki} e_{\ell j} \left[\underline{\underline{R}}_{ki}^{(n-r)} \underline{\underline{R}}_{\ell j}^{\prime (r)} \delta(\underline{r}_{k} - \underline{r}') \, \delta(\underline{r}'_{\ell} - \underline{r}'') \right.\right.\right.$$

$$\left.\left.\left. - \underline{\underline{R}}_{ki}^{(n-r)} \underline{\underline{R}}_{\ell j}^{(r)} \delta(\underline{r}_{k} - \underline{r}') \, \delta(\underline{r}_{\ell} - \underline{r}'') \right] \right\rangle\!\right\rangle$$

$$\longrightarrow -\underline{N}^{(n)}(\underline{r}', \underline{r}'') \longrightarrow 0. \qquad (4.2.23)$$

By substituting (4.2.23) into (4.2.20), we see that in the absence of correlation between particles $\underline{\underline{\not\Delta}}_{\phi}$ vanishes.

A similar treatment applies to $\underline{\Delta}_M$. From the definition of $\underline{E}^T(\underline{r}_{ki})$ and $\underline{B}(\underline{r}_{ki})$ [see (4.2.6), (2.1.1) and (1.4.6)], we write $\underline{\Delta}_M$ as [see (4.2.5)]

$$\underline{\Delta}_M = -\frac{1}{c}\sum_{ki\lambda}\langle\langle e_{ki}\,(p_\lambda - p'_\lambda)\,\underline{A}_\lambda(\underline{r}_{ki})\,\delta(\underline{r}_k - \underline{r})\rangle\rangle$$

$$+\frac{1}{c}\sum_{ki\lambda}\langle\langle e_{ki}\,(q_\lambda - q'_\lambda)\,\underline{u}_{ki}\times\underline{A}_\lambda(\underline{r}_{ki})\,\delta(\underline{r}_k - \underline{r})\rangle\rangle. \qquad (4.2.24)$$

Written in this way $\underline{\Delta}_M$ is seen to depend on correlation between the field coordinates and the particle coordinates; for if there is no correlation, the distribution function can be factored into a product of a function involving just the field coordinates and a function involving just the particle coordinates,

$$f^{(N)}(\underline{r}_{ki}, \underline{u}_{ki}, q_\lambda, p_\lambda) \longrightarrow f_p^{(N)}(\underline{r}_{ki}, \underline{u}_{ki})\, f_f(q_\lambda, p_\lambda). \qquad (4.2.25)$$

If (4.2.25) is substituted into (4.2.24), the primes on the field coordinates may be interchanged without interchanging them on the particle coordinates; hence

$$\underline{\Delta}_M \longrightarrow -\frac{1}{c}\sum_{ki\lambda}\langle\langle e_{ki}\,(p'_\lambda - p_\lambda)\,\underline{A}_\lambda(\underline{r}_{ki})\,\delta(\underline{r}_k - \underline{r})\rangle\rangle$$

$$+\frac{1}{c}\sum_{ki\lambda}\langle\langle e_{ki}\,(q'_\lambda - q_\lambda)\,\underline{u}_{ki}\times\underline{A}_\lambda(\underline{r}_{ki})\,\delta(\underline{r}_k - \underline{r})\rangle\rangle$$

$$\longrightarrow -\underline{\Delta}_M \longrightarrow 0. \qquad (4.2.26)$$

Thus in the absence of correlation between particles and fields, $\underline{\Delta}_M$ vanishes as did $\not{\underline{\Delta}}_{\phi}$ in the absence of interparticle correlation.

This analysis gives another insight into the nature of the short range term $\underline{\Delta}$. It also explains what we mean by the term "collision" in connection with a coulombic system. Since the coulombic potential is a long range potential, one molecule is always influenced by the other molecules in the system sufficiently to regard all the molecules as being in continuous "collision" with one another. But we divide the coulombic force into two parts. One part, $\underline{X}$ in (4.1.14), depends on the macroscopic fields. The other part, $\underline{\Delta}$, depends on the correlation between the particles. It is in the sense of this correlation that we may now think of a "collision". Two particles have "collided" when they become correlated. A particle has "collided" with a field when it becomes correlated with one of the field oscillators. Since correlation is short-range, the term "collision" becomes meaningful. It is in this sense, too, that $\underline{\Delta}$ is regarded as a short range collisional force.

4.3 The Long Range Term

Now we discuss in more detail the long range force term, $\underline{X}$ From (4.1.13) we write

$$\underline{X} = \underline{X}_E + \underline{X}_B , \tag{4.3.1}$$

where

$$\underline{X}_E \equiv \sum_{ki} \left\langle e_{ki}\, \underline{E}(\underline{r}_{ki})\, \delta(\underline{r}_k - \underline{r}) \right\rangle \tag{4.3.2}$$

is the electric term, and

$$\underline{X}_B \equiv \frac{1}{c} \sum_{ki} \left\langle e_{ki}\, \underline{u}_{ki} \times \underline{B}(\underline{r}_{ki})\, \delta(\underline{r}_k - \underline{r}) \right\rangle \tag{4.3.3}$$

is the magnetic term.

We treat the term $\underline{X}_E$ first. Expanding $\underline{E}(\underline{r}_{ki})$ in a Taylor series about $\underline{r}_k$, we write

$$\begin{aligned}
\underline{X}_E &= \sum_{n=0}^{\infty} \frac{1}{n!} \sum_{ki} \left\langle e_{ki}\, \underline{\underline{R}}_{ki}^{(n)} \cdot^{(n)} \left[\left(\frac{\partial}{\partial \underline{r}_k} \right)^{(n)} \underline{E}(\underline{r}_k) \right] \delta(\underline{r}_k - \underline{r}) \right\rangle \\
&= \sum_{n=0}^{\infty} \frac{1}{n!} \sum_{ki} \left\langle e_{ki}\, \underline{\underline{R}}_{ki}^{(n)} \delta(\underline{r}_k - \underline{r}) \right\rangle \cdot^{(n)} \left(\frac{\partial}{\partial \underline{r}} \right)^{(n)} \underline{E}(\underline{r}) \\
&= \rho_e \underline{E} + \sum_{n=0}^{\infty} \underline{\underline{Q}}^{(n+1)} \cdot^{(n+1)} \left(\frac{\partial}{\partial \underline{r}} \right)^{(n+1)} \underline{E} \, ,
\end{aligned} \tag{4.3.4}$$

where ρ_e and $\underline{\underline{Q}}^{(n+1)}$ are defined by (2.3.13) and (2.3.11). Since $\underline{\underline{Q}}^{(n)}$ is a symmetric tensor, it can be shown in a straightforward manner that

$$\underline{\underline{Q}}^{(m)} \cdot_{(m)} \left(\frac{\partial}{\partial \underline{r}}\right)^{(m)} \underline{E} \equiv \sum_{r=0}^{m} \frac{(-1)^{r}\, m!}{r!\,(m-r)!} \left(\frac{\partial}{\partial \underline{r}}\right)^{(m-r)} \cdot_{(m-r)} \left[\left(\frac{\partial}{\partial \underline{r}}\right)^{(r)} \cdot_{(r)} \underline{\underline{Q}}^{(m)}\right] \underline{E} \,. \qquad (4.3.5)$$

Using this relation, (4.3.4) is written

$$\underline{X}_E = \rho_e \underline{E} + \sum_{m=0}^{\infty} \sum_{r=0}^{m+1} (-1)^{r} \frac{(m+1)!}{r!\,(m+1-r)!} \left(\frac{\partial}{\partial \underline{r}}\right)^{(m+1-r)} \cdot_{(m+1-r)} \left[\left(\frac{\partial}{\partial \underline{r}}\right)^{(r)} \cdot_{(r)} \underline{\underline{Q}}^{(m+1)}\right] \underline{E}$$

$$= \rho_e \underline{E} + \sum_{m=0}^{\infty} \sum_{r=0}^{m} (-1)^{r} \frac{(m+1)!}{r!\,(m+1-r)!} \left(\frac{\partial}{\partial \underline{r}}\right)^{(m+1-r)} \cdot_{(m+1-r)} \left[\left(\frac{\partial}{\partial \underline{r}}\right)^{(r)} \cdot_{(r)} \underline{\underline{Q}}^{(m+1)}\right] \underline{E}$$

$$+ \sum_{m=0}^{\infty} (-1)^{(m+1)} \left[\left(\frac{\partial}{\partial \underline{r}}\right)^{(m+1)} \cdot_{(m+1)} \underline{\underline{Q}}^{(m+1)}\right] \underline{E}$$

$$= \rho_e \underline{E} + \frac{\partial}{\partial \underline{r}} \cdot \sum_{m=0}^{\infty} \sum_{r=0}^{m} (-1)^{r} \frac{(m+1)!}{r!\,(m+1-r)!} \left(\frac{\partial}{\partial \underline{r}}\right)^{(m-r)} \cdot_{(m-r)} \left[\left(\frac{\partial}{\partial \underline{r}}\right)^{(r)} \cdot_{(r)} \underline{\underline{Q}}^{(m+1)}\right] \underline{E}$$

$$- \left[\frac{\partial}{\partial \underline{r}} \cdot \sum_{m=0}^{\infty} (-1)^{m} \left(\frac{\partial}{\partial \underline{r}}\right)^{(m)} \cdot_{(m)} \underline{\underline{Q}}^{(m+1)}\right] \underline{E}$$

$$= \rho_e \underline{E} - \left(\frac{\partial}{\partial \underline{r}} \cdot \underline{P}\right) \underline{E} + \frac{\partial}{\partial \underline{r}} \cdot \underline{\mathcal{P}}_1 \underline{E} \,. \qquad (4.3.6)$$

where $\underline{P}$ is defined by (2.3.15) and $\underline{\mathcal{P}}_1$ is an operator defined by

$$\underline{\mathcal{P}}_1 \equiv \sum_{m=0}^{\infty} \sum_{r=0}^{m} (-1)^{r} \frac{(m+1)!}{r!\,(m+1-r)!} \left(\frac{\partial}{\partial \underline{r}}\right)^{(m-r)} \cdot_{(m-r)} \left[\left(\frac{\partial}{\partial \underline{r}}\right)^{(r)} \cdot_{(r)} \underline{\underline{Q}}^{(m+1)}\right] . \qquad (4.3.7)$$

In this definition, the operator $\left(\frac{\partial}{\partial \underline{r}}\right)^{(m-n)}$ operates not only on $\left[\left(\frac{\partial}{\partial \underline{r}}\right)^{(n)} \cdot^{(n)} \underline{\underline{Q}}^{(m+1)}\right]$, but also on any function of $\underline{r}$ on the right of $\underline{\mathcal{P}}_1$. The symbol $\underline{\mathcal{P}}_1$ is used for the quantity defined by (4.3.7) because of the analogy between this operator and the polarization $\underline{P}$.

We next consider the magnetic term, $\underline{X}_B$, in (4.3.1) [see (4.3.3)] . For convenience, we first introduce the antisymmetric tensor $\underline{\underline{B}}$, defined by

$$(\underline{\underline{B}})_{\alpha\beta} \equiv \sum_{\gamma} \epsilon_{\alpha\beta\gamma} (\underline{B})_{\gamma} , \tag{4.3.8}$$

where $\epsilon_{\alpha\beta\gamma}$ is the Levi-Civita density. With this definition, it is easily shown that

$$\underline{u} \times \underline{B} = -\underline{u} \cdot \underline{\underline{B}} . \tag{4.3.9}$$

Thus $\underline{X}_B$ becomes

$$\underline{X}_B \equiv -\frac{1}{c} \sum_{ki} \left\langle e_{ki} \underline{u}_{ki} \cdot \underline{\underline{B}}(\underline{r}_{ki}) \delta(\underline{r}_k - \underline{r}) \right\rangle . \tag{4.3.10}$$

Expanding this term in a Taylor series about $\underline{r}_k$, we obtain

$$\begin{aligned}
\underline{X}_B &= -\frac{1}{c} \sum_{m=0}^{\infty} \frac{1}{m!} \sum_{ki} \left\langle e_{ki} \underline{u}_{ki} \underline{\underline{R}}_{ki}^{(m)} \cdot^{(m+1)} \left(\frac{\partial}{\partial \underline{r}_k}\right)^{(m)} \underline{\underline{B}}(\underline{r}_k) \delta(\underline{r}_k - \underline{r}) \right\rangle \\
&= -\frac{1}{c} \sum_{m=0}^{\infty} \frac{1}{m!} \sum_{ki} \left\langle e_{ki} \underline{u}_{ki} \underline{\underline{R}}_{ki}^{(m)} \delta(\underline{r}_k - \underline{r}) \right\rangle \cdot^{(m+1)} \left(\frac{\partial}{\partial \underline{r}}\right)^{(m)} \cdot \underline{\underline{B}} .
\end{aligned} \tag{4.3.11}$$

In order to rewrite the last expression in a more significant form, we first break $\underline{u}_{ki}$ into its two components $\underline{u}_k$ and $\underline{U}_{ki}$. Then by adding and subtracting terms (the reason for the choice of which will become clear later) we write

$$
\begin{aligned}
\underline{X}_B = {} & \frac{1}{c}\sum_{n=0}^{\infty}\sum_{r=0}^{n}\frac{1}{(n+1)!}\sum_{ki}\left\langle e_{ki}\left(\underline{\underline{R}}_{ki}^{(n-r)}\,\underline{U}_{ki}\,\underline{\underline{R}}_{ki}^{(r)} - \underline{U}_{ki}\,\underline{\underline{R}}_{ki}^{(n)}\right)\delta(\underline{r}_k-\underline{r})\right\rangle {\cdot}^{(n+1)}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n)}\underline{\underline{B}} \\
& + \frac{1}{c}\sum_{n=0}^{\infty}\frac{1}{n!}\sum_{ki}\left\langle e_{ki}\left(\underline{\underline{R}}_{ki}^{(n)}\,\underline{u}_k - \underline{u}_k\,\underline{\underline{R}}_{ki}^{(n)}\right)\delta(\underline{r}_k-\underline{r})\right\rangle {\cdot}^{(n+1)}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n)}\underline{\underline{B}} \\
& - \frac{1}{c}\sum_{n=0}^{\infty}\sum_{r=0}^{n}\frac{1}{(n+1)!}\sum_{ki}\left\langle e_{ki}\,\underline{\underline{R}}_{ki}^{(n-r)}\,\underline{U}_{ki}\,\underline{\underline{R}}_{ki}^{(r)}\,\delta(\underline{r}_k-\underline{r})\right\rangle {\cdot}^{(n+1)}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n)}\underline{\underline{B}} \\
& - \frac{1}{c}\sum_{n=0}^{\infty}\frac{1}{n!}\sum_{ki}\left\langle e_{ki}\,\underline{\underline{R}}_{ki}^{(n)}\,\underline{u}_k\,\delta(\underline{r}_k-\underline{r})\right\rangle {\cdot}^{(n+1)}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n)}\underline{\underline{B}} \\
= {} & \frac{1}{c}\sum_{n=0}^{\infty}\frac{n+1}{(n+2)!}\left\{\left[\sum_{ki}\left\langle e_{ki}\,\underline{U}_{ki}\times\underline{\underline{R}}_{ki}^{(n+1)}\delta(\underline{r}_k-\underline{r})\right\rangle {\cdot}^{(n)}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n)}\right]\times\frac{\partial}{\partial\underline{r}}\right\}\cdot\underline{\underline{B}} \\
& + \frac{1}{c}\sum_{n=0}^{\infty}\frac{1}{(n+1)!}\left\{\left[\sum_{ki}\left\langle e_{ki}\,\underline{u}_k\times\underline{\underline{R}}_{ki}^{(n+1)}\delta(\underline{r}_k-\underline{r})\right\rangle {\cdot}^{(n)}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n)}\right]\times\frac{\partial}{\partial\underline{r}}\right\}\cdot\underline{\underline{B}} \\
& - \frac{1}{c}\sum_{n=0}^{\infty}\frac{1}{(n+1)!}\sum_{ki}\left\langle e_{ki}\,\frac{d\,\underline{\underline{R}}_{ki}^{(n+1)}}{dt}\,\delta(\underline{r}_k-\underline{r})\right\rangle {\cdot}^{(n+1)}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n)}\underline{\underline{B}} \\
& - \frac{1}{c}\sum_{n=0}^{\infty}\frac{1}{(n+1)!}\sum_{ki}\left\langle e_{ki}\,\underline{\underline{R}}_{ki}^{(n+1)}\,\underline{u}_k\,\delta(\underline{r}_k-\underline{r})\right\rangle {\cdot}^{(n+2)}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n+1)}\underline{\underline{B}} \\
& - \frac{1}{c}\,\underline{J}\cdot\underline{\underline{B}}\ . \qquad (4.3.12)
\end{aligned}
$$

In writing the last form, we have eliminated the zero subterms of the first two main terms of the previous form and made use of the identities, (2.4.16) and (2.4.17), to introduce the cross product into these terms. In the third main term, we have replaced $\underline{U}_{ki}$ by $\frac{d\underline{R}_{ki}}{dt}$. Finally we have used the definition of $\underline{J}$ [see (2.4.21)] to rewrite the last term.

Now applying a relation similar to (4.3.5), we obtain from the above

$$\underline{X}_B = -\frac{1}{c}\underbrace{\frac{\partial}{\partial\underline{r}}\times\sum_{n=0}^{\infty}\sum_{\lambda=0}^{n}(-1)^{\lambda}\frac{(n+1)!}{\lambda!\,(n+1-\lambda)!}\left(\frac{\partial}{\partial\underline{\underline{r}}}\right)^{(n-\lambda)}\cdot^{(n-\lambda)}\left[\left(\frac{\partial}{\partial\underline{\underline{r}}}\right)^{(\lambda)}\cdot^{(\lambda)}\left(\underline{\underline{M}}_u^{(n+1)}+\underline{\underline{M}}_v^{(n+1)}\right)\right]}\times\underline{B}$$

$$+\frac{1}{c}\sum_{n=0}^{\infty}(-1)^{n}\left[\frac{\partial}{\partial\underline{r}}\times\left(\frac{\partial}{\partial\underline{\underline{r}}}\right)^{(n)}\cdot^{(n)}\left(\underline{\underline{M}}_u^{(n+1)}+\underline{\underline{M}}_v^{(n+1)}\right)\right]\times\underline{B}$$

$$+\frac{1}{c}\sum_{n=0}^{\infty}\sum_{\lambda=0}^{n}\frac{(-1)^{\lambda}}{(n+1)\lambda!\,(n-\lambda)!}\left(\frac{\partial}{\partial\underline{\underline{r}}}\right)^{(n-\lambda)}$$

$$\cdot^{(n-\lambda)}\left[\left(\frac{\partial}{\partial\underline{\underline{r}}}\right)^{(\lambda)}\cdot^{(\lambda)}\sum_{ki}\left\langle e_{ki}\frac{d\,\underline{\underline{R}}_{ki}^{(n+1)}}{dt}\delta(\underline{r}_k-\underline{r})\right\rangle\right]\times\underline{B}$$

$$+\frac{1}{c}\sum_{n=0}^{\infty}\sum_{\lambda=0}^{n+1}\frac{(-1)^{\lambda}}{\lambda!\,(n+1-\lambda)!}\left(\frac{\partial}{\partial\underline{\underline{r}}}\right)^{(n+1-\lambda)}$$

$$\cdot^{(n+1-\lambda)}\left[\left(\frac{\partial}{\partial\underline{\underline{r}}}\right)^{(\lambda)}\cdot^{(\lambda)}\sum_{ki}\left\langle e_{ki}\underline{u}_k\,\underline{\underline{R}}_{ki}^{(n+1)}\delta(\underline{r}_h-\underline{r})\right\rangle\right]\times\underline{B}$$

$$+\frac{1}{c}\,\underline{J}\times\underline{B}\,. \qquad (4.3.13)$$

In this equation, we have replaced $\cdot\underline{\underline{B}}$ by $-(\times\underline{B})$ and have simplified the first two main terms by the introduction of $\underline{\underline{M}}_u^{(n)}$ and $\underline{\underline{M}}_v^{(n)}$ [see (2.4.20) and (2.4.19)]. The $\lfloor\quad\rfloor$ bracket indicates that the vector operation so enclosed should be performed before any other vector operation in the term. The symbol, $\lfloor\quad\rfloor$, does not affect differentiation.

Applying the general conservation equation [see (2.5.5)] to the second term in (4.3.13), we write

$$\begin{aligned}
\underline{X}_B = & -\frac{1}{c}\frac{\partial}{\partial\underline{r}}\times\sum_{n=0}^{\infty}\sum_{r=0}^{n}\frac{(-1)^r(n+1)!}{r!(n+1-r)!}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n-r)}\cdot^{(n-r)}\left\lfloor\left(\frac{\partial}{\partial\underline{r}}\right)^{(r)}\cdot^{(r)}\left(\underline{\underline{M}}_u^{(n+1)}+\underline{\underline{M}}_v^{(n+1)}\right)\right\rfloor\times\underline{B} \\
& +\frac{1}{c}\sum_{n=0}^{\infty}(-1)^n\left\lfloor\frac{\partial}{\partial\underline{r}}\times\left(\frac{\partial}{\partial\underline{r}}\right)^{(n)}\cdot^{(n)}\left(\underline{\underline{M}}_u^{(n+1)}+\underline{\underline{M}}_v^{(n+1)}\right)\right\rfloor\times\underline{B} \\
& +\frac{1}{c}\sum_{n=0}^{\infty}\sum_{r=0}^{n}\frac{(-1)^r n!}{r!(n-r)!}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n-r)}\cdot^{(n-r)}\left\lfloor\left(\frac{\partial}{\partial\underline{r}}\right)^{(r)}\cdot^{(r)}\frac{\partial\underline{\underline{Q}}^{(n+1)}}{\partial t}\right\rfloor\times\underline{B} \\
& +\frac{1}{c}\sum_{n=0}^{\infty}\sum_{r=0}^{n}\frac{(-1)^r}{(n+2)r!(n+1-r)!}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n+1-r)} \\
& \qquad\cdot^{(n+1-r)}\left\lfloor\left(\frac{\partial}{\partial\underline{r}}\right)^{(r+1)}\cdot^{(r+1)}\sum_{ki}\left\langle e_{ki}\underline{u}_k\underline{\underline{R}}_{ki}^{(n+2)}\delta(\underline{r}_k-\underline{r})\right\rangle\right\rfloor\times\underline{B} \\
& +\frac{1}{c}\sum_{n=0}^{\infty}\sum_{r=0}^{n}\frac{(-1)^r}{r!(n+1-r)!}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n+1-r)} \\
& \qquad\cdot^{(n+1-r)}\left\lfloor\left(\frac{\partial}{\partial\underline{r}}\right)^{(r)}\cdot^{(r)}\sum_{ki}\left\langle e_{ki}\underline{u}_k\underline{\underline{R}}_{ki}^{(n+1)}\delta(\underline{r}_k-\underline{r})\right\rangle\right\rfloor\times\underline{B} \\
& +\frac{1}{c}\underline{J}\times\underline{B}\,, \qquad (4.3.14)
\end{aligned}$$

where the $\lambda = n+1$ terms in the fourth main term of (4.3.13) have been included in the fourth main term of (4.3.14).

Next, we define several new quantities,

$$\underline{\mathfrak{M}} \equiv \frac{1}{c}\sum_{n=0}^{\infty}\sum_{\lambda=0}^{n}\frac{(-1)^{\lambda}(n+1)!}{\lambda!\,(n+1-\lambda)!}\left(\frac{\partial}{\partial \underline{r}}\right)^{(n-\lambda)}\cdot^{(n-\lambda)}\left[\left(\frac{\partial}{\partial \underline{r}}\right)^{(\lambda)}\cdot^{(\lambda)}\left(\underline{\underline{M}}_{v}^{(n+1)}+\underline{\underline{M}}_{u}^{(n+1)}\right)\right], \tag{4.3.15}$$

$$\underline{\mathfrak{P}}_{2} \equiv -\sum_{n=0}^{\infty}\sum_{\lambda=0}^{n}\frac{(-1)^{\lambda}(n+1)!}{\lambda!\,(n+1-\lambda)!}\left(\frac{\partial}{\partial \underline{r}}\right)^{(n-\lambda)}\cdot^{(n-\lambda)}\left[\left(\frac{\partial}{\partial \underline{r}}\right)^{(\lambda)}\cdot^{(\lambda)}\underline{\underline{Q}}^{(n+2)}\right], \tag{4.3.16}$$

$$\mathfrak{J}_{P_1} \equiv \sum_{n=0}^{\infty}\sum_{\lambda=0}^{n}\frac{(-1)^{\lambda}}{\lambda!\,(n+1-\lambda)!}\left(\frac{\partial}{\partial \underline{r}}\right)^{(n-\lambda)}$$

$$\cdot^{(n-\lambda)}\left[\left(\frac{\partial}{\partial \underline{r}}\right)^{(\lambda)}\cdot^{(\lambda)}\sum_{ki}\left\langle e_{ki}\underline{u}_{k}\,\underline{\underline{R}}_{ki}^{(n+1)}\delta(\underline{r}_{k}-\underline{r})\right\rangle\right], \tag{4.3.17}$$

and

$$\mathfrak{J}_{P_2} \equiv \sum_{n=0}^{\infty}\sum_{\lambda=0}^{n}\frac{(-1)^{\lambda}}{(n+2)\lambda!\,(n+1-\lambda)!}\left(\frac{\partial}{\partial \underline{r}}\right)^{(n-\lambda)}$$

$$\cdot^{(n-\lambda)}\left[\left(\frac{\partial}{\partial \underline{r}}\right)^{(\lambda+1)}\cdot^{(\lambda+1)}\sum_{ki}\left\langle e_{ki}\underline{u}_{k}\,\underline{\underline{R}}_{ki}^{(n+2)}\delta(\underline{r}_{k}-\underline{r})\right\rangle\right]. \tag{4.3.18}$$

As in the definition of $\underline{\mathfrak{P}}_{1}$, (4.3.7), the above quantities are operators, with the $\left(\frac{\partial}{\partial \underline{r}}\right)^{(n-\lambda)}$ indicating differentiation not only of the square bracket in the operator, but also of any function of $\underline{r}$ to the right of the operator. The operators, $\underline{\mathfrak{M}}$, $\underline{\mathfrak{P}}_{2}$, and $\mathfrak{J}_{P_1}$ and $\mathfrak{J}_{P_2}$, are related, respectively to the magnetization, $\underline{M}$, the polarization, $\underline{P}$, and the polarization current, $\underline{J}_{P}$. Substituting the above definitions and the definitions of $\underline{P}$ and $\underline{M}$ [see (2.3.15) and (2.4.22)] into (4.3.14), we write

$$\underline{X}_B = -\underbrace{\frac{\partial}{\partial \underline{r}} \times \underline{\mathfrak{M}}}_{} \times \underline{B} + \left(\frac{\partial}{\partial \underline{r}} \times \underline{M}\right) \times \underline{B} + \frac{1}{c}\frac{\partial \underline{P}}{\partial t} \times \underline{B}$$

$$-\frac{1}{c}\frac{\partial}{\partial \underline{r}} \cdot \frac{\partial \underline{\underline{\mathcal{P}}}_2}{\partial t} \times \underline{B} + \frac{1}{c}\frac{\partial}{\partial \underline{r}} \cdot \left(\underline{\underline{\ell}}_{P_1} + \underline{\underline{\ell}}_{P_2}\right) \times \underline{B} + \frac{1}{c}\underline{J} \times \underline{B}. \tag{4.3.19}$$

Combining (4.3.19) and (4.3.6) with (4.3.1), we obtain

$$\underline{X} = \underbrace{\rho_e - \left(\frac{\partial}{\partial \underline{r}} \cdot \underline{P}\right) + \frac{\partial}{\partial \underline{r}} \cdot \underline{\underline{\mathcal{P}}}_1}_{} \underline{E}$$

$$+\underbrace{\frac{1}{c}\underline{J} + \frac{1}{c}\frac{\partial \underline{P}}{\partial t} + \left(\frac{\partial}{\partial \underline{r}} \times \underline{M}\right) - \frac{\partial}{\partial \underline{r}} \times \underline{\mathfrak{M}} + \frac{1}{c}\frac{\partial}{\partial \underline{r}} \cdot \left(\underline{\underline{\ell}}_{P_1} + \underline{\underline{\ell}}_{P_2} - \frac{\partial \underline{\underline{\mathcal{P}}}_2}{\partial t}\right)}_{} \times \underline{B}. \tag{4.3.20}$$

The bracketed quantity in the first term of this expression is analogous to a charge distribution and that in the second term is analogous to a current. The additions to ρ_e in the first term and $\underline{J}$ in the second are, of course, due to the internal structure of the molecules.

The force, $\underline{X}$, may also be written in a different form. From Maxwell's third and fourth equations [see (2.3.17) and (2.4.24)] , we write

$$\rho_e - \frac{\partial}{\partial \underline{r}} \cdot \underline{P} = \frac{1}{4\pi}\frac{\partial}{\partial \underline{r}} \cdot \underline{E} \tag{4.3.21}$$

and

$$\frac{\partial}{\partial \underline{r}} \times \underline{M} + \frac{1}{c}\underline{J} + \frac{1}{c}\frac{\partial \underline{P}}{\partial t} = \frac{1}{4\pi}\frac{\partial}{\partial \underline{r}} \times \underline{B} - \frac{1}{4\pi c}\frac{\partial \underline{E}}{\partial t} . \tag{4.3.22}$$

It is also easily shown that

$$-\underbrace{\frac{\partial}{\partial \underline{r}} \times \underline{\mathfrak{m}}}_{} \times \underline{B} = \frac{\partial}{\partial \underline{r}}\left(\underline{\mathfrak{m}} \cdot \underline{B}\right) - \frac{\partial}{\partial \underline{r}} \cdot \left(\underline{\mathfrak{m}}\,\underline{B}\right)^{\dagger}, \tag{4.3.23}$$

where $\dagger$ indicates the transpose tensor. Using these relations, (4.3.20) may be written

$$\underline{X} = \frac{1}{4\pi}\left(\frac{\partial}{\partial \underline{r}} \cdot \underline{E}\right)\underline{E} + \frac{\partial}{\partial \underline{r}} \cdot \underline{\underline{\mathcal{P}}}_1 \underline{E} + \frac{1}{4\pi}\left(\frac{\partial}{\partial \underline{r}} \times \underline{B}\right) \times \underline{B} - \frac{1}{4\pi c}\frac{\partial \underline{E}}{\partial t} \times \underline{B}$$

$$+ \frac{\partial}{\partial \underline{r}}\left(\underline{\mathfrak{m}} \cdot \underline{B}\right) - \frac{\partial}{\partial \underline{r}} \cdot \left(\underline{\mathfrak{m}}\,\underline{B}\right)^{\dagger} + \frac{1}{c}\frac{\partial}{\partial \underline{r}} \cdot \left(\underline{\underline{\mathcal{Q}}}_{p_1} + \underline{\underline{\mathcal{Q}}}_{p_2}\right) \times \underline{B} - \frac{1}{c}\frac{\partial}{\partial \underline{r}} \cdot \frac{\partial \underline{\underline{\mathcal{P}}}_2}{\partial t} \times \underline{B} . \tag{4.3.24}$$

Now we use the second Maxwell equation, (2.2.7), to rewrite the time derivatives in the above. This results in the expression,

$$\underline{X} = \frac{1}{4\pi}\left(\frac{\partial}{\partial \underline{r}} \cdot \underline{E}\right)\underline{E} + \frac{\partial}{\partial \underline{r}} \cdot \underline{\underline{\mathcal{P}}}_1 \underline{E} + \frac{1}{4\pi}\left(\frac{\partial}{\partial \underline{r}} \times \underline{B}\right) \times \underline{B} + \frac{\partial}{\partial \underline{r}}\left(\underline{\mathfrak{m}} \cdot \underline{B}\right) - \frac{\partial}{\partial \underline{r}} \cdot \left(\underline{\mathfrak{m}}\,\underline{B}\right)^{\dagger}$$

$$- \frac{1}{4\pi c}\frac{\partial}{\partial t}\left(\underline{D}_2 \times \underline{B}\right) - \frac{1}{4\pi}\underline{E} \times \left(\frac{\partial}{\partial \underline{r}} \times \underline{E}\right) + \frac{1}{c}\frac{\partial}{\partial \underline{r}} \cdot \left(\underline{\underline{\mathcal{Q}}}_{p_1} + \underline{\underline{\mathcal{Q}}}_{p_2}\right) \times \underline{B} - \frac{\partial}{\partial \underline{r}} \cdot \underline{\underline{\mathcal{P}}}_2 \times \left(\frac{\partial}{\partial \underline{r}} \times \underline{E}\right), \tag{4.3.25}$$

where

$$\underline{D}_2 \equiv \underline{E} + 4\pi\frac{\partial}{\partial \underline{r}} \cdot \underline{\underline{\mathcal{P}}}_2 \tag{4.3.26}$$

is an operator related to the displacement, $\underline{D}$ [see (2.3.16)]. Using the identity

$$\left(\frac{\partial}{\partial \underline{r}} \times \underline{B}\right) \times \underline{B} \equiv \underline{B} \cdot \frac{\partial \underline{B}}{\partial \underline{r}} - \frac{\partial \underline{B}}{\partial \underline{r}} \cdot \underline{B} , \tag{4.3.27}$$

with a similar expression for $\underline{E} \times \left(\frac{\partial}{\partial \underline{r}} \times \underline{E}\right)$, we obtain from (4.3.25)

$$\underline{X} = -\frac{1}{4\pi c} \frac{\partial}{\partial t} \left(\underline{D}_2 \times \underline{B}\right) - \frac{\partial}{\partial \underline{r}} \cdot \left[\frac{1}{8\pi} \underline{\underline{I}} \left(B^2 + E^2\right) - \frac{1}{4\pi} \left(\underline{B}\,\underline{B} + \underline{E}\,\underline{E}\right)\right.$$

$$\left. + \left(\underline{m}\,\underline{B}\right)^{+} - \underline{p}_1 \underline{E} - \underline{\underline{I}} \left(\underline{m} \cdot \underline{B}\right) + \underline{p}_2 \times \left(\frac{\partial}{\partial \underline{r}} \times \underline{E}\right) - \frac{1}{c} \left(\mathcal{J}_{p_1} + \mathcal{J}_{p_2}\right) \times \underline{B}\right]$$

$$= -\frac{1}{4\pi c} \frac{\partial}{\partial t} \left(\underline{D}_2 \times \underline{B}\right) \tag{4.3.28}$$

$$- \frac{\partial}{\partial \underline{r}} \cdot \left[\underline{\underline{T}} - \frac{1}{2} \underline{\underline{I}} \left(\underline{m} \cdot \underline{B} + \underline{p}_1 \cdot \underline{E}\right) + \underline{p}_2 \times \left(\frac{\partial}{\partial \underline{r}} \times \underline{E}\right) - \frac{1}{c} \left(\mathcal{J}_{p_1} + \mathcal{J}_{p_2}\right) \times \underline{B}\right],$$

where

$$\underline{\underline{T}} \equiv \frac{1}{4\pi} \left[\frac{1}{2} \underline{\underline{I}} \left(\underline{H} \cdot \underline{B} - \underline{D}_1 \cdot \underline{E}\right) - \left(\underline{H}\,\underline{B}\right)^{+} - \underline{D}_1 \underline{E}\right], \tag{4.3.29}$$

$$\underline{D}_1 \equiv \underline{E} + 4\pi \underline{p}_1 , \tag{4.3.30}$$

and

$$\underline{H} \equiv \underline{B} - 4\pi \underline{m} . \tag{4.3.31}$$

In the above $\underline{\mathcal{D}}_1$ is related to the displacement, $\underline{D}$, and $\underline{\mathcal{H}}$ to the magnetic intensity, $\underline{H}$, so that $\underline{\underline{T}}$ may be thought of as a generalized Maxwell stress tensor.

Finally, defining the quantities,

$$\underline{N} \equiv \frac{1}{4\pi c} \underline{\mathcal{P}}_2 \times \underline{B} \tag{4.3.32}$$

and

$$\underline{\underline{\mathcal{P}}}_L \equiv \underline{\underline{T}} - \frac{1}{2} \underline{\underline{I}} \left(\underline{m} \cdot \underline{B} + \underline{\mathcal{P}}_1 \cdot \underline{E} \right) - \frac{1}{c} \left(\underline{\underline{\Phi}}_{P_1} + \underline{\underline{\Phi}}_{P_2} \right) \times \underline{B} + \underline{\underline{\mathcal{P}}}_2 \times \left(\frac{\partial}{\partial \underline{r}} \times \underline{E} \right), \tag{4.3.33}$$

we write

$$\underline{X} \equiv - \frac{\partial \underline{N}}{\partial t} - \frac{\partial}{\partial \underline{r}} \cdot \underline{\underline{\mathcal{P}}}_L \, . \tag{4.3.34}$$

Thus the long range electromagnetic force in (4.1.14) is written as the time derivative of an electromagnetic contribution to the momentum density plus the divergence of an electromagnetic contribution to the pressure tensor.

4.4 Two Forms of the Equation of Motion

For a gas in which the molecules interact according to a short range potential, the equation of motion may be written as[15]

$$\frac{\partial \rho \underline{v}}{\partial t} + \frac{\partial}{\partial \underline{r}} \cdot \rho \underline{v} \underline{v} = - \frac{\partial}{\partial \underline{r}} \cdot \left(\underline{\underline{\mathcal{P}}}_K + \underline{\underline{\mathcal{P}}}'_\phi \right) + \underline{F} \, , \tag{4.4.1}$$

where $\underline{F}$ is an external body force and where the collisional pressure, $\underline{\underline{p}}'_{\phi}$, is similar to, but not identical with the $\underline{\underline{p}}_{\phi}$ of the present work. This point is amplified in section 4.5.

From (4.1.14) and (4.2.21) we write the equation of motion of our system in a form similar to (4.4.1),

$$\frac{\partial \rho \underline{v}}{\partial t} + \frac{\partial}{\partial \underline{r}} \cdot \rho \underline{v}\,\underline{v} = -\frac{\partial}{\partial \underline{r}} \cdot \underline{\underline{p}} + \underline{\Delta}_M + \underline{X} , \tag{4.4.2}$$

where

$$\underline{\underline{p}} = \underline{\underline{p}}_K + \underline{\underline{p}}_{\phi} . \tag{4.4.3}$$

The effects of the long range electromagnetic fields are contained in $\underline{X}$ $\left[\text{see (4.3.20)}\right]$ in the form of a "pondermotive" force addition to the equation of motion.

Substituting the expression for $\underline{X}$ given by (4.3.34) into (4.4.2), we arrive at an alternate form of the equation of motion,

$$\frac{\partial}{\partial t}\left(\rho \underline{v} + \underline{N}\right) + \frac{\partial}{\partial \underline{r}} \cdot \rho \underline{v}\,\underline{v} = -\frac{\partial}{\partial \underline{r}} \cdot \left(\underline{\underline{p}} + \underline{\underline{p}}_L\right) + \underline{\Delta}_M , \tag{4.4.4}$$

In this form, the long range electromagnetic effects are contained in $\underline{N}$, the electromagnetic "momentum", and $\underline{\underline{p}}_L$, the electromagnetic "pressure".

Both (4.4.2) and (4.4.4) should be useful in dealing with practical problems involving the equation of motion.

4.5 Limiting Forms of the Electromagnetic Terms

As an indication of the interpretation of the electromagnetic terms in the equation of motion, we consider the explicit expressions for $\underline{X}$, $\underline{N}$, $\underline{\underline{k}}_{L}$, and $\underline{\underline{k}}_{\phi}$ retaining only terms of first order in $\underline{R}_{ki}$ and $\underline{U}_{ki}$.

In the limit just outlined, we write the "pondermotive" force [see (4.3.20)] as

$$\underline{X} = \rho_e \underline{E} - \left(\frac{\partial}{\partial \underline{r}} \cdot \underline{P}\right) \underline{E} + \frac{\partial}{\partial \underline{r}} \cdot \underline{P}\,\underline{E} + \frac{1}{c} \underline{J} \times \underline{B} \tag{4.5.1}$$

$$+ \frac{1}{c} \frac{\partial \underline{P}}{\partial t} \times \underline{B} + \left(\frac{\partial}{\partial \underline{r}} \times \underline{M}\right) \times \underline{B} - \underbrace{\frac{\partial}{\partial \underline{r}} \times \underline{M}} \times \underline{B} + \frac{1}{c} \frac{\partial}{\partial \underline{r}} \cdot \underline{\underline{J}}_{p} \times \underline{B} ,$$

where we retain only the dipole terms in the expressions for $\underline{P}$, $\underline{M}$, and $\underline{\underline{J}}_{p}$ [see (2.3.15), (2.4.22), and (2.5.7)] ,

$$\underline{P} = \underline{\underline{Q}}^{(1)} = \sum_{ki} \langle e_{ki} \underline{R}_{ki} \delta(\underline{r}_k - \underline{r}) \rangle , \tag{4.5.2}$$

$$\underline{M} = \underline{\underline{M}}_{u}^{(1)} = \frac{1}{c} \sum_{ki} \langle e_{ki} \underline{R}_{ki} \times \underline{u}_k \delta(\underline{r}_k - \underline{r}) \rangle \tag{4.5.3}$$

$$= \frac{1}{c} \underline{P} \times \underline{v} ,$$

and

$$\underline{\underline{J}}_{p} = \sum_{ki} \langle e_{ki} \underline{u}_k \underline{R}_{ki} \delta(\underline{r}_k - \underline{r}) \rangle \tag{4.5.4}$$

$$= \underline{v}\,\underline{P} .$$

The final forms for the expressions for $\underline{M}$ and $\underline{\underline{J}}_p$ are a result of introducing the stream velocity, $\underline{v}$ [see (2.4.25)], into the preceding forms and ignoring the effects of the Brownian motion velocity, $\underline{v}_k$ [see (2.4.26)]. These equations give a further insight into the origin of $\underline{M}$ and $\underline{\underline{J}}_p$. In the limit of this section these quantities are due to the motion of $\underline{P}$ with the molecular stream.

Returning to (4.5.1) and summing the second, third and fifth terms, we find that

$$-\left(\frac{\partial}{\partial \underline{r}}\cdot\underline{P}\right)\underline{E} + \frac{\partial}{\partial \underline{r}}\cdot\underline{P}\,\underline{E} + \frac{1}{c}\,\frac{\partial \underline{P}}{\partial t}\times\underline{B} = \underline{P}\cdot\frac{\partial \underline{E}}{\partial \underline{r}} + \frac{1}{c}\,\frac{\partial \underline{P}}{\partial t}\times\underline{B}$$

$$= \left(\frac{\partial}{\partial \underline{r}}\times\underline{E}\right)\times\underline{P} + \frac{\partial \underline{E}}{\partial \underline{r}}\cdot\underline{P} + \frac{1}{c}\,\frac{\partial \underline{P}}{\partial t}\times\underline{B}$$

$$= \frac{\partial \underline{E}}{\partial \underline{r}}\cdot\underline{P} + \frac{1}{c}\,\frac{\partial}{\partial t}\left(\underline{P}\times\underline{B}\right). \qquad (4.5.5)$$

In deriving the above relations, we have used standard vector identities and Maxwell's second equation, (2.2.7). Adding the sixth term in (4.5.1) to the seventh term gives

$$\left(\frac{\partial}{\partial \underline{r}}\times\underline{M}\right)\times\underline{B} - \underbracket{\frac{\partial}{\partial \underline{r}}\times\underline{M}}\times\underline{B} = \left(\underline{M}\times\frac{\partial}{\partial \underline{r}}\right)\times\underline{B}$$

$$= \frac{\partial \underline{B}}{\partial \underline{r}}\cdot\underline{M} - \underline{M}\,\frac{\partial}{\partial \underline{r}}\cdot\underline{B} \qquad (4.5.6)$$

$$= \frac{\partial \underline{B}}{\partial \underline{r}}\cdot\underline{M},$$

where we have used standard vector identities and Maxwell's first equation, (2.1.3). Substituting (4.5.5), and (4.5.6) into (4.5.1), we obtain

$$\underline{X} = \rho_e \underline{E} + \frac{1}{c} \underline{J} \times \underline{B} + \frac{\partial \underline{E}}{\partial \underline{r}} \cdot \underline{P} + \frac{\partial \underline{B}}{\partial \underline{r}} \cdot \underline{M} + \frac{1}{c} \frac{\partial}{\partial t} \left(\underline{P} \times \underline{B} \right) + \frac{1}{c} \frac{\partial}{\partial \underline{r}} \cdot \left(\underline{\underline{J}}_{p} \times \underline{B} \right). \tag{4.5.7}$$

The first two terms in (4.5.7) are the usual electrostatic and magnetostatic volume forces and are the primary terms. The third and fourth terms represent forces due to the effect of the inhomogeneity of the fields on the polarization and magnetization of the system. The final terms represent time dependent forces.

Applying the limit discussed in this section to the second form of the equation of motion, (4.4.4), the expression for the electromagnetic momentum [see (4.3.32)] becomes

$$\underline{N} = \frac{1}{4\pi c} \underline{E} \times \underline{B} . \tag{4.5.8}$$

In purely macroscopic derivations of the equation of motion[3], the term, $\underline{D} \times \underline{B}$, (or $\underline{E} \times \underline{H}$, if $\underline{D}$ is assumed linearly related to $\underline{E}$ and $\underline{H}$ is assumed linearly related to $\underline{B}$) arises and is identified as the electromagnetic momentum. For a system of isolated point charges in a vacuum, $\underline{D} \times \underline{B}$, of course, reduces to $\underline{E} \times \underline{B}$; thus the difference between our results and those derived by a purely macroscopic treatment consists only of the manner in which the internal structure of the particles is taken into account. We now examine this in more detail.

The macroscopic derivation of the equation of motion consists of forming the divergence of the Maxwell stress tensor

$$\underline{\underline{T}} = \frac{1}{4\pi}\left[\frac{1}{2}\,\underline{\underline{I}}\left(\underline{H}\cdot\underline{B} - \underline{D}\cdot\underline{E}\right) - \underline{B}\,\underline{H} - \underline{D}\,\underline{E}\right]. \tag{4.5.9}$$

This quantity is also the $\underline{\underline{T}}$ of section 4.3 in the limit being considered in this section [see (4.3.29)]. Using Maxwell's equations, the divergence of $\underline{\underline{T}}$ is written as

$$\frac{\partial}{\partial \underline{r}}\cdot\underline{\underline{T}} = \underline{F} + \frac{1}{4\pi c}\,\frac{\partial\left(\underline{D}\times\underline{B}\right)}{\partial t}, \tag{4.5.10}$$

where

$$\underline{F} = \rho_e\underline{E} + \frac{1}{c}\,\underline{J}\times\underline{B} + \frac{1}{8\pi}\left[\frac{\partial \underline{E}}{\partial \underline{r}}\cdot\underline{D} - \frac{\partial \underline{D}}{\partial \underline{r}}\cdot\underline{E} + \frac{\partial \underline{H}}{\partial \underline{r}}\cdot\underline{B} - \frac{\partial \underline{B}}{\partial \underline{r}}\cdot\underline{H}\right] \tag{4.5.11}$$

is interpreted as the total force on the particles in a small element of volume about the point $\underline{r}$. Following this interpretation, $\underline{F}$ is written as

$$\underline{F} = \frac{\partial \rho\underline{v}}{\partial t}, \tag{4.5.12}$$

where $\rho\underline{v}$ is the momentum density of the material medium at $\underline{r}$. Assuming the validity of (4.5.11) and (4.5.12), (4.5.10) becomes

$$\frac{\partial}{\partial t}\left[\rho \underline{v} + \frac{1}{4\pi c}\left(\underline{D} \times \underline{B}\right)\right] = \frac{\partial}{\partial \underline{r}} \cdot \underline{\underline{T}} , \tag{4.5.13}$$

which has the form of a conservation equation for $\rho \underline{v} + \frac{1}{4\pi c}(\underline{D} \times \underline{B})$; hence $\frac{1}{4\pi c}(\underline{D} \times \underline{B})$ is interpreted as the electromagnetic contribution to the momentum density.

Our major criticism of the preceding derivation is that the assumption, that $\underline{F}$ is the total force on the material medium at $\underline{r}$, is a point not adequately demonstrated. This assumption seems to be made largely becuase it allows (4.5.10) to be written in the desired form of a momentum conservation equation, (4.5.13). It is, of course, difficult to determine the correct expression for the force on the medium at $\underline{r}$. This is one of the reasons that we abandon the macroscopic approach in our development and resort to the statistical treatment outlined in this chapter. Equation (4.4.4), contained in this work, is a conservation equation of the form of (4.5.13) if the term $\underline{\Delta}_M$ is neglected. For most applications neglecting $\underline{\Delta}_M$ is valid as is indicated in the discussion following (4.2.21). Regarding (4.4.4) as a conservation equation, then, makes it reasonable to interpret $\underline{N}$ [see (4.5.8)] as the electromagnetic contribution to the momentum. Since we have more confidence in a statistical development than we do in a macroscopic one, we feel that $\underline{N}$ is the correct momentum expression.

Again introducing the simplifying assumptions outlined at the beginning of this section, we write the electromagnetic pressure [see (4.3.33)] in (4.4.4) as

$$\underline{\underline{p}}_L = \underline{\underline{T}} - \frac{1}{2}\underline{\underline{I}}\left(\underline{M}\cdot\underline{B} + \underline{P}\cdot\underline{E}\right) - \frac{1}{c}\underline{v}\,\underline{P}\times\underline{B}, \tag{4.5.14}$$

where $\underline{\underline{T}}$ in the limiting form given by (4.5.9) is the usual expression for the Maxwell stress tensor in a material medium.

The collisional pressure may be written, keeping only the $s = 0$, $n = 0$, and $n = 1$ terms in (4.2.20), as

$$\underline{\underline{p}}_\phi = \frac{1}{2}\int(\underline{r}-\underline{r}')\frac{\partial}{\partial\underline{r}'}\frac{1}{|\underline{r}-\underline{r}'|}\,\underline{\underline{N}}^{(0)}(\underline{r},\underline{r}')\,d\underline{r}'$$

$$+\frac{1}{2}\int(\underline{r}-\underline{r}')\left(\frac{\partial}{\partial\underline{r}'}\frac{\partial}{\partial\underline{r}'}\frac{1}{|\underline{r}-\underline{r}'|}\right)\cdot\underline{\underline{N}}^{(1)}(\underline{r},\underline{r}')\,d\underline{r}'.$$

As an aid to the interpretation of $\underline{\underline{p}}_\phi$, we rewrite the expressions for $\underline{\underline{N}}^{(0)}(\underline{r},\underline{r}')$ and $\underline{\underline{N}}^{(1)}(\underline{r},\underline{r}')$. From (4.2.12), we have

$$\underline{\underline{N}}^{(0)}(\underline{r},\underline{r}') = \sum_{k\neq l}\left\langle\!\left\langle e_k e_l\,\delta(\underline{r}_k-\underline{r})\,\delta(\underline{r}_l-\underline{r}')\right\rangle\!\right\rangle - \rho_e(\underline{r})\,\rho_e(\underline{r}'),$$

where $\rho_e(\underline{r})$ is the charge density at $\underline{r}$ [see (2.3.13)] . In writing the last term of the above equation, we make use of the relation,

$$\sum_{k=l} \langle\langle e_k e_l \, \delta(\underline{r}_k - \underline{r}) \, \delta(\underline{r}'_l - \underline{r}') \rangle\rangle$$

$$= \sum_{k} \langle e_k \, \delta(\underline{r}_k - \underline{r}) \rangle \sum_{l} \langle e_l \, \delta(\underline{r}_l - \underline{r}) \rangle - \sum_{k} \langle e_k \, \delta(\underline{r}_k - \underline{r}) \rangle^2$$

$$= \rho_e(\underline{r}) \, \rho_e(\underline{r}'). \tag{4.5.17}$$

The second term in the second line of (4.5.17) is of the order of magnitude of N, while the first term is of order N^2, where N is the number of particles in the system. For a statistically significant sample, where N is assumed large, we neglect this second term in comparison with the first; this leads to the third line of the equation. Using a relation for $\underline{P}(\underline{r})$ and $\underline{P}(\underline{r}')$ similar to (4.5.17), we further write from (4.2.12)

$$\underline{\underline{N}}^{(1)}(\underline{r}, \underline{r}') = \sum_{\substack{k \neq l \\ i\,j}} \langle\langle e_{ki} e_{lj} (\underline{R}_{lj} - \underline{R}_{ki}) \, \delta(\underline{r}_k - \underline{r}) \, \delta(\underline{r}_l - \underline{r}') \rangle\rangle + \rho_e(\underline{r}') \, \underline{P}(\underline{r}) - \rho_e(\underline{r}) \, \underline{P}(\underline{r}'). \tag{4.5.18}$$

Making use of the expressions, (4.5.16) and (4.5.18), we may interpret the first term in (4.5.15) as arising from "charge-charge" forces and the second from "charge-dipole" forces.

To obtain a clearer idea of the nature of $\not{k}_{\phi}$, the first term in (4.5.15) is examined in more detail. First, the molecules of the system under consideration are divided into various types. The non-equilibrium radial distribution function for particles of type α and type β is then defined as

$$g_{\alpha\beta}(\underline{r},\underline{R}) \equiv \frac{1}{n_\alpha(\underline{r})\, n_\beta(\underline{r}+\underline{R})} \sum_{k_\alpha \neq l_\beta} \langle\langle \delta(\underline{r}_{k_\alpha}-\underline{r})\, \delta(\underline{r}_{l_\beta}-\underline{r}') \rangle\rangle, \tag{4.5.19}$$

where

$$\underline{R} = \underline{r}' - \underline{r}. \tag{4.5.20}$$

The quantity,

$$n_\alpha(\underline{r}) = \sum_{k_\alpha} \langle \delta(\underline{r}_{k_\alpha} - \underline{r}) \rangle, \tag{4.5.21}$$

is the number density evaluated at point $\underline{r}$ of particles of kind α. An expression similar to (4.5.21) may be written for $n_\beta(\underline{r}+\underline{R})$. The symbol k_α in (4.5.19) indicates that the summation over k is to be taken only over molecules of type α ; the symbol l_β has a similar meaning. Introducing the radial distribution function into the first term of (4.5.16) and the number densities into the second term, makes it possible to write

$$\underline{\underline{N}}^{(0)}(\underline{r},\underline{r}') = \sum_{\alpha\beta} e_\alpha n_\alpha(\underline{r})\, e_\beta n_\beta(\underline{r}+\underline{R}) \left[g_{\alpha\beta}(\underline{r},\underline{R}) - 1 \right]. \tag{4.5.22}$$

Neglecting the second term of (4.5.15) and introducing (4.5.22) into the first term allows the collisional pressure to be written as

$$\underline{\underline{p}}_\phi = \frac{1}{2} \sum_{\alpha\beta} \int e_\alpha n_\alpha(\underline{r})\, e_\beta n_\beta(\underline{r}+\underline{R}) \frac{\underline{R}\,\underline{R}}{R^3} \left[g_{\alpha\beta}(\underline{r},\underline{R}) - 1 \right] d\underline{R}. \tag{4.5.23}$$

In the limits of low density and high temperatures, the radial distribution function may be written as[16]

$$g_{\alpha\beta}(\underline{r},\underline{R}) = g_{\alpha\beta}(R)$$

$$= e^{-\phi_{\alpha\beta}(R)/kT}$$

$$= 1 - \frac{\phi_{\alpha\beta}(R)}{kT} + \cdots, \qquad (4.5.24)$$

where

$$\phi_{\alpha\beta}(R) = \frac{e_\alpha e_\beta e^{-R/\mathscr{H}}}{R} \qquad (4.5.25)$$

is the coulombic potential between a molecule of type α and one of type β a distance R apart. The factor, $e^{-R/\mathscr{H}}$, where $\mathscr{H}$ is the Debye radius, is included in the expression for the potential to represent the shielding effect due to other molecules. If (4.5.24) and (4.5.25) are substituted into (4.5.23), $\underline{\underline{p}}_\phi$ may be written as

$$\underline{\underline{p}}_\phi = -\frac{1}{2}\sum_{\alpha\beta} \frac{e_\alpha^2 e_\beta^2}{kT} \int n_\alpha(\underline{r})\, n_\beta(\underline{r}+\underline{R})\, \frac{\underline{R}\,\underline{R}}{R^4}\, e^{-R/\mathscr{H}}\, d\underline{R}$$

$$= -\frac{1}{2}\sum_{\alpha\beta} \frac{e_\alpha^2 e_\beta^2}{kT} n_\alpha(\underline{r})\, n_\beta(\underline{r}) \int \frac{\underline{R}\,\underline{R}}{R^4}\, e^{-R/\mathscr{H}}\, d\underline{R} \qquad (4.5.26)$$

In the last line of the above equation, we have assumed

$$n_\beta(\underline{r}+\underline{R}) = n_\beta(\underline{r}). \tag{4.5.27}$$

This is valid for small R, and, for large R, the term, $e^{-R/h}$ approaches zero rapidly enough to render negligible the error introduced by assuming (4.5.27).

In the usual treatment of gases with a short range intermolecular potential, the collisional pressure is given by (see the discussion at the beginning of section 4.4.)[15]

$$\underline{\underline{P}}'_\phi = -\frac{1}{2}\sum_{\alpha\beta} n_\alpha(\underline{r})\, n_\beta(\underline{r}) \int \frac{d\Phi_{\alpha\beta}(R)}{dR}\, \frac{\underline{R}\,\underline{R}}{R}\, g_{\alpha\beta}(\underline{r},\underline{R})\, d\underline{R}, \tag{4.5.28}$$

where the introduction of the α and β subscripts corresponds to the grouping of molecules into various charge types. If the unshielded coulomb potential,

$$\Phi_{\alpha\beta}(R) = \frac{e_\alpha e_\beta}{R}, \tag{4.5.29}$$

is substituted into (4.5.28), $\underline{\underline{P}}'_\phi$ becomes

$$\underline{\underline{P}}'_\phi = \frac{1}{2}\sum_{\alpha\beta} e_\alpha n_\alpha(\underline{r})\, e_\beta n_\beta(\underline{r}) \int \frac{\underline{R}\,\underline{R}}{R^3}\, g_{\alpha\beta}(\underline{r},\underline{R})\, d\underline{R}. \tag{4.5.30}$$

Finally substituting the expression for $g_{\alpha\beta}(\underline{r},\underline{R})$ given by (4.5.24) and (4.5.25) into (4.5.30) gives

$$\underline{\underline{p}}'_\phi = \frac{1}{2}\sum_{\alpha\beta}{}' e_\alpha n_\alpha(\underline{r}) e_\beta n_\beta(\underline{r}) \left[\int \frac{\underline{R}\,\underline{R}}{R^3}\, d\underline{R} - \frac{e_\alpha e_\beta}{kT} \int \frac{\underline{R}\,\underline{R}}{R^4} e^{-R/\mu} d\underline{R} \right]. \tag{4.5.31}$$

The integral in the second term of (4.5.31) is the same as the integral in the final expression, (4.5.26) for $\underline{\underline{p}}_\phi$. This integral converges while the integral in the first term of (4.5.31) diverges. Hence, the expression developed in this work for the collisional pressure of a coulombic system is convergent while the usual expression is not. This convergence is due to the introduction of -1 into the integrand of $\underline{\underline{p}}_\phi$ [compare (4.5.30) with (4.5.23)] as a result of the separation of the electromagnetic term in (4.1.6) into a long and a short range part. In essence, the divergent portion of $\underline{\underline{p}}'_\phi$ has been removed and written in terms of the macroscopic electric and magnetic fields as $\underline{\underline{p}}_L$ or $\underline{X}$.

4.6 Comparisons with Previous Results

In this section, we compare our form of the equation of motion with those obtained in earlier developments. First, we compare our results with those of Mazur.[17] Mazur carried out a statistical study of a system of molecules with internal structure, neglecting magnetic and retardation effects. He also neglected electric multipoles of higher order than the dipole (or quadrapole when the dipole is zero). In addition, intramolecular effects are neglected and Mazur restricted his study to molecules which are electrically neutral.

With these restrictions, our equation (4.4.2) may be written

$$\frac{\partial \rho \underline{v}}{\partial t} + \frac{\partial}{\partial \underline{r}} \cdot \rho \underline{v}\,\underline{v} = - \frac{\partial}{\partial \underline{r}} \cdot \underline{\underline{p}} + \underline{X}. \tag{4.6.1}$$

The $\underline{\underline{\Delta}}_M$ of (4.4.2) disappears because of the neglect of magnetic effects and retardation. The electric force is obtained in this limit from (4.5.1), as

$$\underline{X} = \underline{P} \cdot \frac{\partial \underline{E}}{\partial \underline{r}}, \tag{4.6.2}$$

where $\underline{P}$ is given by (4.5.2). The charge density ρ_e is absent in (4.6.2) due to the neutrality of the molecules. The collisional pressure, $\underline{\underline{p}}_\phi$, in Mazur's case is obtained from (4.2.20) by keeping only the $\Delta = 0$ terms. The $n = 0$ and $n = 1$ terms disappear since the molecules are neutral. Hence only the $n = 2$ terms containing $\underline{R}_{ki} \underline{R}_{lj}$, but not those containing $\underline{R}_{ki} \underline{R}_{ki}$, are retained. Under these conditions $\underline{\underline{p}}_\phi$ is given by

$$\underline{\underline{p}}_\phi = -\frac{1}{2} \sum_{\substack{k \neq l \\ i\, j}} e_{ki} e_{lj} \int (\underline{r} - \underline{r}') \langle\langle \underline{R}_{ki} \underline{R}_{lj}\, \delta(\underline{r}_k - \underline{r})\, \delta(\underline{r}_l - \underline{r}')$$
$$- \underline{R}_{ki} \underline{R}'_{lj}\, \delta(\underline{r}_k - \underline{r})\, \delta(\underline{r}'_l - \underline{r}') \rangle\rangle \vdots \frac{\partial}{\partial \underline{r}'} \frac{\partial}{\partial \underline{r}'} \frac{\partial}{\partial \underline{r}'} \frac{1}{|\underline{r} - \underline{r}'|}\, d\underline{r}'. \tag{4.6.3}$$

On comparing with Mazur's expressions, we see that the above expression for $\underline{\underline{p}}_\phi$ is identical to his $\underline{\underline{\sigma}}_v$, our $\underline{\underline{p}}$ in (4.6.1) is his $\underline{\underline{\sigma}}$, and our $\underline{X}$ in (4.6.2) is his $\underline{F}^{(p)}$; hence our (4.6.1) is identical with his (III.14).

Next we compare our results with those of Kaufman[7], whose work is also a statistical study. Kaufman also ignored magnetic effects. In addition he restricted his study to particles without structure. Under these restrictions, equation (4.4.4) becomes

$$\frac{\partial \rho \underline{v}}{\partial t} = -\frac{\partial}{\partial \underline{r}} \cdot \left(\underline{\underline{p}} + \underline{\underline{p}}_L + \rho \underline{v}\,\underline{v} \right). \tag{4.6.4}$$

Applying Kaufman's restrictions to (4.3.33), we obtain for the electromagnetic pressure

$$\underline{\underline{p}}_L = \underline{\underline{T}} = \frac{1}{8\pi} \underline{\underline{I}}\, E^2 - \frac{1}{4\pi} \underline{E}\,\underline{E}. \tag{4.6.5}$$

Again under Kaufman's restrictions, the collisional pressure is given by [see (4.2.20)]

$$\underline{\underline{p}}_\phi = \frac{1}{2} \sum_{s=0}^{\infty} \frac{1}{(s+1)!} \int \left(\frac{\partial}{\partial \underline{r}} \right)^{(s)} \cdot_{(s)} \frac{(\underline{r} - \underline{r}')^{(s+2)}}{|r - r'|^3}\, \underline{\underline{N}}^{(0)}\, d\underline{r}', \tag{4.6.6}$$

where $\underline{\underline{N}}^{(0)}$ is given by (4.2.13). By comparing the above equations with Kaufman's results, we see that, with the exception of one term, contained in his expression and not in ours, our $\underline{\underline{p}} + \underline{\underline{p}}_L + \rho \underline{v}\,\underline{v}$ is his $\underline{\underline{\Pi}}$ and our equation (4.6.4) is his (43). The missing term can be shown to be related to the "self-field" terms we discarded in developing (4.1.12) from (4.1.11) and in developing (4.2.11) from (4.2.10). In dropping these terms, we pointed out that for a large system, they are negligible. In keeping these same terms, Kaufman pointed out that they are important only for a system of molecular size; hence there is no conflict between the two results.

Finally, we compare our work to that of Chu.[4] In contrast to the statistical methods used by Mazur, Kaufman and in this work, Chu uses a macroscopic, "thermodynamic" approach. Chu obtains as his equation of motion

$$\frac{\partial \rho \underline{v}}{\partial t} + \frac{\partial}{\partial \underline{r}} \cdot \left(\rho \underline{v}\,\underline{v} \right) = - \frac{\partial}{\partial \underline{r}} \cdot \underline{\underline{p}}_K + \underline{f} , \tag{4.6.7}$$

where

$$f = \rho_e \underline{E} + \frac{1}{c} \underline{J} \times \underline{B} + \frac{1}{2} \left[\frac{\partial \underline{E}}{\partial \underline{r}} \cdot \underline{P} - \frac{\partial \underline{P}}{\partial \underline{r}} \cdot \underline{E} + \frac{\partial \underline{B}}{\partial \underline{r}} \cdot \underline{M} - \frac{\partial \underline{M}}{\partial \underline{r}} \cdot \underline{B} \right]$$
$$+ \frac{\partial}{\partial \underline{r}} \left[\frac{1}{2} \rho E^2 \frac{\partial \epsilon}{\partial \rho} + \frac{1}{2} \rho H^2 \frac{\partial \mu}{\partial \rho} \right] . \tag{4.6.8}$$

In the above expression ϵ, μ, and ρ are, respectively, the dielectric constant, the magnetic permeability, and the density of the system. From our equation of motion,

$$\frac{\partial \rho \underline{v}}{\partial t} + \frac{\partial}{\partial \underline{r}} \cdot \left(\rho \underline{v}\,\underline{v} \right) = - \frac{\partial}{\partial \underline{r}} \cdot \underline{\underline{p}} + \underline{X} + \underline{\Delta}_M , \tag{4.4.2}$$

we see that we must compare Chu's $\underline{f}$ with our

$$\underline{X} - \frac{\partial}{\partial \underline{r}} \cdot \underline{\underline{k}}_{\phi} + \underline{\Delta}_M = \rho_e \underline{E} + \frac{1}{c} \underline{J} \times \underline{B} + \frac{\partial \underline{E}}{\partial \underline{r}} \cdot \underline{P} + \frac{\partial \underline{B}}{\partial \underline{r}} \cdot \underline{M}$$

$$+ \frac{1}{c} \frac{\partial}{\partial t} \left(\underline{P} \times \underline{B} \right) + \frac{1}{c} \frac{\partial}{\partial \underline{r}} \cdot \left(\underline{v} \underline{P} \times \underline{B} \right) - \frac{\partial}{\partial \underline{r}} \cdot \underline{\underline{k}}_{\phi} + \underline{\Delta}_M \, , \tag{4.6.9}$$

where $\underline{X}$ has been evaluated in the limiting case discussed in section 4.5 [see (4.5.7)]. The result Chu obtains for $\underline{f}$ agrees with the above equation for $\underline{X}$ in the expression for the volume force, $\rho_e \underline{E} + \frac{1}{c} \underline{J} \times \underline{B}$, but does not have the same form for the inhomogeneous field terms [compare the third term in (4.6.8) with the third and fourth terms in (4.6.9)] and does not include the time dependent terms,

$$\frac{1}{c} \frac{\partial}{\partial t} \left(\underline{P} \times \underline{B} \right) + \frac{1}{c} \frac{\partial}{\partial \underline{r}} \cdot \left(\underline{v} \underline{P} \times \underline{B} \right),$$

at all. The collision terms, $-\frac{\partial}{\partial \underline{r}} \cdot \underline{\underline{k}}_{\phi} + \underline{\Delta}_M$, that appear in the expression for $\underline{X}$ are replaced in $\underline{f}$ by the "magnetostriction" term,

$$\frac{\partial}{\partial \underline{r}} \left[\frac{1}{2} \rho E^2 \frac{\partial \epsilon}{\partial \rho} + \frac{1}{2} \rho H^2 \frac{\partial \mu}{\partial \rho} \right];$$

thus the short range forces between molecules that are expressed in this work in terms of the correlation quantities $\underline{\underline{k}}_{\phi}$ and $\underline{\Delta}_M$ are treated in Chu's work in terms of derivatives of ϵ and μ . If the "magnetostriction" terms are neglected in (4.6.8), $\underline{f}$ reduces to the expression for $\underline{F}$ [see (4.5.11)] discussed in section 4.5 in connection with a more common macroscopic development of an equation of motion. The comments in section 4.5 regarding the desirability of a statistical approach over a purely macroscopic development, hence, apply to Chu's work also.

The essential point in the present derivation of the equation of motion is the separation of the effect of the electromagnetic force into long-range and short-range terms. We write the coulomb portion of the short-range term as a collisional contribution, $\underline{\underline{p}}_{\phi}$, to the pressure tensor, while the portion describing retardation and magnetic effects is left as a force term, $\underline{\Delta}_{M}$. The long-range force is written in two ways. Writing it as a "pondermotive" force, $\underline{X}$, gives rise to one form, (4.4.2), of the equation of motion, and writing it as an electromagnetic contribution, $\underline{\underline{p}}_{L}$, to the pressure tensor plus an electromagnetic contribution, $\underline{N}$, to the momentum density gives rise to a second form, (4.4.4). Heretofore, there has been some confusion concerning the nature of the electromagnetic pressure and momentum, and we hope that the statistical definitions of these quantities developed in this discussion clarify the situation. On comparing the present work with that of other authors, we find good agreement with the statistical derivations and significant disagreement with the macroscopic derivations. This, perhaps, is to be expected.

V. THE ENERGY EQUATION OF CHANGE

The final quantity for which we develop an equation of change is the macroscopic energy density of the system, $\frac{1}{2}\rho v^2 + \rho U_K + \rho U_\phi$. In this expression, $\frac{1}{2}\rho v^2$ is the kinetic energy of the system regarded as a continuum moving with the "stream" velocity, $\underline{v}$, and

$$\rho U_K \equiv \frac{1}{2}\sum_k m_k \langle v_k^2 \delta(\underline{r}_k - \underline{r})\rangle \tag{5.0.1}$$

is the energy density of the random motion of the molecules relative to the stream velocity. From the definition of the stream velocity, $\underline{v}$, and the random velocity, $\underline{v}_k$ [see (2.4.25) and (2.4.26)], we write

$$\rho U_K + \frac{1}{2}\rho v^2 = \frac{1}{2}\sum_k m_k \langle u_k^2 \delta(\underline{r}_k - \underline{r})\rangle. \tag{5.0.2}$$

From the above, we see that the first two terms in the energy expression are the ensemble average of the microscopic kinetic energy of the particles. The final term in the expression for the energy,

$$\rho U_\phi \equiv \frac{1}{2}\sum_{ki \neq \ell j} \langle\langle e_{ki} e_{\ell j} \left[\frac{1}{|\underline{r}_{ki} - \underline{r}_{\ell j}|} - \frac{1}{|\underline{r}_{ki} - \underline{r}'_{\ell j}|}\right] \delta(\underline{r}_k - \underline{r})\rangle\rangle, \tag{5.0.3}$$

is shown later (in section 5.2) to be a correlation energy density in the same sense that $\not{p}_\phi$ (see section 4.2) is a correlation pressure. The introduction of ρU_ϕ into the expression for the energy density is suggested by a similar term in the Irving Kirkwood development of the equation of change.[2] The inclusion of this term is further justified by (as is shown later, in section 5.2) the cancellation of terms arising from the time derivative of ρU_ϕ with terms arising from the time derivative of $\frac{1}{2}\rho v^2 + \rho U_K$. This considerably simplifies the equation of change of the energy.

5.1 The Time Derivative of the Energy Density

We develop an expression for the time derivative of the energy density using methods similar to those used in the preceding chapter [see (4.1.1) and (4.1.2)]. Expanding $\frac{1}{|\underline{r}_{ki}-\underline{r}_{\ell j}|} - \frac{1}{|\underline{r}_{ki}-\underline{r}'_{\ell j}|}$ in a Taylor series about $\underline{r}_k$ [see (4.2.9)], we write the correlation energy density, (5.0.3), in the form:

$$\rho U_\phi = \frac{1}{2}\sum_{n=0}^{\infty}\sum_{r=0}^{n}\frac{(-1)^{(n-r)}}{r!\,(n-r)!}\sum_{\substack{k=\ell\\ ij}}\left\langle\!\left\langle e_{ki}e_{\ell j}\left[\underline{\underline{R}}_{ki}^{(n-r)}\,\underline{\underline{R}}_{\ell j}^{(r)}\cdot^{(n)}\left(\frac{\partial}{\partial\underline{r}_\ell}\right)^{(n)}\frac{1}{|\underline{r}_k-\underline{r}_\ell|}\right.\right.\right.$$

$$\left.\left.\left.-\,\underline{\underline{R}}_{ki}^{(n-r)}\,\underline{\underline{R}}_{\ell j}^{\prime(r)}\cdot^{(n)}\left(\frac{\partial}{\partial\underline{r}'_\ell}\right)^{(n)}\frac{1}{|\underline{r}_k-\underline{r}'_\ell|}\right]\delta(\underline{r}_k-\underline{r})\right\rangle\!\right\rangle. \qquad (5.1.1)$$

In writing (5.1.1), we have ignored the term,

$$\frac{1}{2}\sum_{\substack{k\\ i\neq j}}\left\langle\!\left\langle e_{ki}e_{kj}\left[\frac{1}{|\underline{r}_{ki}-\underline{r}_{kj}|}-\frac{1}{|\underline{r}_{ki}-\underline{r}'_{kj}|}\right]\delta(\underline{r}_k-\underline{r})\right\rangle\!\right\rangle, \qquad (5.1.2)$$

because this term, which involves a sum over k only, is of order $\frac{1}{M}$ compared to the term included in (5.1.1), which involves a sum over both k and l. Since M is the number of molecules in the system, M is sufficiently large that the error introduced by ignoring (5.1.2) is negligible.

Using the general equation of change, (1.5.16), we obtain for the time derivative of the correlation energy density,

$$\frac{\partial \rho U_\phi}{\partial t} = \frac{1}{2}\sum_{n=0}^{\infty}\sum_{r=0}^{n}\frac{(-1)^{(n-r)}}{r!\,(n-r)!}\sum_{\substack{k\neq l\\ i\,j}}\left\langle\left\langle e_{ki}e_{lj}\left[\underline{\underline{R}}_{ki}^{(n-r)}\underline{\underline{R}}_{lj}^{(r)}(\underline{u}_l-\underline{u}_k)\right.\right.\right.$$

$$\left.\left.\left.\cdot^{(n+1)}\left(\frac{\partial}{\partial \underline{r}_l}\right)^{(n+1)}\frac{1}{|\underline{r}_k-\underline{r}_l|}-\underline{\underline{R}}_{ki}^{(n-r)}\underline{\underline{R}}_{lj}^{\prime(r)}(\underline{u}_l^{\prime}-\underline{u}_k)\cdot\left(\frac{\partial}{\partial \underline{r}_l^{\prime}}\right)^{(n+1)}\frac{1}{|\underline{r}_k-\underline{r}_l^{\prime}|}\right]\delta(\underline{r}_k-\underline{r})\right\rangle\right\rangle$$

$$-\frac{1}{2}\frac{\partial}{\partial \underline{r}}\cdot\sum_{n=0}^{\infty}\sum_{r=0}^{n}\frac{(-1)^{(n-r)}}{r!\,(n-r)!}\sum_{\substack{k\neq l\\ i\,j}}\left\langle\left\langle e_{ki}e_{lj}\underline{u}_k\left[\underline{\underline{R}}_{ki}^{(n-r)}\underline{\underline{R}}_{lj}^{(r)}\right.\right.\right.$$

$$\left.\left.\left.\cdot^{(n)}\left(\frac{\partial}{\partial \underline{r}_l}\right)^{(n)}\frac{1}{|\underline{r}_k-\underline{r}_l|}-\underline{\underline{R}}_{ki}^{(n-r)}\underline{\underline{R}}_{lj}^{\prime(r)}\cdot^{(n)}\left(\frac{\partial}{\partial \underline{r}_l^{\prime}}\right)^{(n)}\frac{1}{|\underline{r}_k-\underline{r}_l^{\prime}|}\right]\delta(\underline{r}_k-\underline{r})\right\rangle\right\rangle$$

$$+\frac{1}{2}\sum_{n=0}^{\infty}\sum_{r=0}^{n}\frac{(-1)^{(n-r)}}{r!\,(n-r)!}\sum_{\substack{k\neq l\\ i\,j}}\left\langle\left\langle e_{ki}e_{lj}\left[\frac{d}{dt}\left(\underline{\underline{R}}_{ki}^{(n-r)}\underline{\underline{R}}_{lj}^{(r)}\right)\right.\right.\right.$$

$$\left.\left.\left.\cdot^{(n)}\left(\frac{\partial}{\partial \underline{r}_l}\right)^{(n)}\frac{1}{|\underline{r}_k-\underline{r}_l|}-\frac{d}{dt}\left(\underline{\underline{R}}_{ki}^{(n-r)}\underline{\underline{R}}_{lj}^{\prime(r)}\right)\cdot^{(n)}\left(\frac{\partial}{\partial \underline{r}_l^{\prime}}\right)^{(n)}\frac{1}{|\underline{r}_k-\underline{r}_l^{\prime}|}\right]\delta(\underline{r}_k-\underline{r})\right\rangle\right\rangle.$$

(5.1.3)

The general equation of change is also used to obtain the time derivative of the kinetic energy density

$$\frac{\partial \rho\left(U_K+\frac{1}{2}v^2\right)}{\partial t} = -\frac{1}{2}\frac{\partial}{\partial \underline{r}}\cdot\sum_k \langle m_k u_k^2 \underline{u}_k \delta(\underline{r}_k-\underline{r})\rangle \tag{5.1.4}$$

$$+\sum_{ki}\left\langle e_{ki}\left[\underline{\underline{E}}^{\mu}_{ki}(\underline{r}_{ki})+\frac{1}{c}\underline{u}_{ki}\times \underline{B}^{\mu}(\underline{r}_{ki})\right]\cdot\underline{u}_k\,\delta(\underline{r}_k-\underline{r})\right\rangle.$$

From the definitions of $\underline{v}$ and $\underline{v}_k$, we write the first term on the right of (5.1.4) as

$$-\frac{1}{2}\frac{\partial}{\partial \underline{r}}\cdot\sum_k\langle m_k u_k^2 \underline{u}_k\delta(\underline{r}_k-\underline{r})\rangle =$$

$$= -\frac{1}{2}\frac{\partial}{\partial \underline{r}}\cdot\left[\sum_k\langle m_k u_k^2\delta(\underline{r}_k-\underline{r})\rangle\underline{v}+\sum_k\langle m_k(\underline{v}+\underline{v}_k)\cdot(\underline{v}+\underline{v}_k)\underline{v}_k\delta(\underline{r}_k-\underline{r})\rangle\right]$$

$$= -\frac{\partial}{\partial \underline{r}}\cdot\left[\rho U_K\underline{v}+\rho v^2\underline{v}+\not{p}_K\cdot\underline{v}+\underline{q}_K\right]. \tag{5.1.5}$$

Here we make use of the definition of $\not{p}_K$, (4.1.5), and define

$$\underline{q}_K \equiv \frac{1}{2}\sum_k m_k\langle v_k^2\underline{v}_k\delta(\underline{r}_k-\underline{r})\rangle. \tag{5.1.6}$$

As we did in (4.1.7), we write the second term of (5.1.4) as the sum of two terms

$$\sum_{ki}\left\langle e_{ki}\left[\underline{E}^{\mu}_{ki}(\underline{r}_{ki})+\frac{1}{c}\,\underline{u}_{ki}\times\underline{B}^{\mu}(\underline{r}_{ki})\right]\cdot\underline{u}_k\,\delta(\underline{r}_k-\underline{r})\right\rangle$$

$$=\sum_{ki}\left\langle e_{ki}\left[\underline{E}(\underline{r}_{ki})+\frac{1}{c}\,\underline{U}_{ki}\times\underline{B}(\underline{r}_{ki})\right]\cdot\underline{u}_k\,\delta(\underline{r}_k-\underline{r})\right\rangle \qquad (5.1.7)$$

$$+\sum_{ki}\left\langle e_{ki}\left[\underline{E}^{\mu}_{ki}(\underline{r}_{ki})-\underline{E}_{ki}(\underline{r}_{ki})+\frac{1}{c}\,\underline{U}_{ki}\times\left(\underline{B}^{\mu}(\underline{r}_{ki})-\underline{B}(\underline{r}_{ki})\right)\right]\cdot\underline{u}_k\,\delta(\underline{r}_k-\underline{r})\right\rangle.$$

In the above equation $\underline{U}_{ki}\times\underline{B}$ appears in the terms on the right instead of $\underline{u}_{ki}\times\underline{B}$ since

$$(\underline{u}_k\times\underline{B})\cdot\underline{u}_k\equiv 0. \qquad (5.1.8)$$

Also $\underline{E}(\underline{r}_{ki})$ instead of $\underline{E}_{ki}(\underline{r}_{ki})$ appears in the first term on the right due to the neglect of the "self" electric field [see the discussion associated with (4.1.11) and (4.1.12)].

Finally combining (5.1.3), (5.1.4), (5.1.5), and (5.1.7), we write for the time derivative of the energy density

$$\frac{\partial\rho\left(U_K+\frac{1}{2}v^2+U_\phi\right)}{\partial t}=-\frac{\partial}{\partial\underline{r}}\cdot\left[\rho U_K\underline{v}+\rho v^2\underline{v}+\underline{p}_K\cdot\underline{v}+\underline{q}_K\right]+X+\Delta, \qquad (5.1.9)$$

where

$$X\equiv\sum_{ki}\left\langle e_{ki}\left[\underline{E}(\underline{r}_{ki})+\frac{1}{c}\,\underline{U}_{ki}\times\underline{B}(\underline{r}_{ki})\right]\cdot\underline{u}_k\,\delta(\underline{r}_k-\underline{r})\right\rangle \qquad (5.1.10)$$

and

$$\Delta \equiv \Delta^{(K)} + \Delta^{(c)}. \qquad (5.1.11)$$

The first term in (5.1.11),

$$\Delta^{(K)} \equiv \sum_{ki} \Big\langle e_{ki} \Big[\underline{E}^{\mu}_{ki}(\underline{r}_{ki}) - \underline{E}_{ki}(\underline{r}_{ki}) + \frac{1}{c} \underline{v}_{ki} \times \big(\underline{B}^{\mu}(\underline{r}_{ki}) - \underline{B}(\underline{r}_{ki}) \big) \Big] \cdot \underline{u}_k \, \delta(\underline{r}_k - \underline{r}) \Big\rangle, \qquad (5.1.12)$$

arises from the time derivative of the kinetic energy density [see (5.1.4) and (5.1.7)], while the second term,

$$\Delta^{(c)} \equiv \frac{\partial \rho U_{\phi}}{\partial t}, \qquad (5.1.13)$$

is the time derivative of the correlation energy density [see (5.1.3)].

Equation (5.1.9) has the form of a conservation equation, i.e. the time derivative of a scalar (the energy density) is equal to the divergence of a vector (the energy flux) plus a scalar (the energy source term). Hence, X and Δ may be interpreted as the rate at which the electromagnetic fields do work on a small region of fluid about a point, $\underline{r}$. These quantities may, thus, be called the power density terms. Referring to the discussion in section 4.1, we interpret X as the long range power density due to the macroscopic fields. This is analogous to the interpretation of the long range force, $\underline{X}$, in (4.1.14). Similarly, analogous to the treatment of the short range force, $\underline{\Delta}$, in (4.1.14), Δ is interpreted as the short range power density due to the effects of correlation.

5.2 The Short Range Term

We consider the short range power, Δ, in greater detail. In comparing the forms of the two parts of Δ, $\Delta^{(c)}$ and $\Delta^{(\kappa)}$, [see (5.1.12) and (5.1.13)] with the Δ of section 4.1 [see (4.1.9)], we see that the form of $\Delta^{(\kappa)}$ is very similar to that of Δ. Therefore, we first treat $\Delta^{(\kappa)}$ in a manner paralleling our treatment of $\underline{\Delta}$ in section 4.2. In the latter part of this section, we return to $\Delta^{(c)}$ and show that it cancels some of the terms in the resulting expression for $\Delta^{(\kappa)}$.

Using the double average notation introduced in (4.2.1), we separate $\Delta^{(\kappa)}$ into two terms

$$\Delta^{(\kappa)} \equiv \Delta_c^{(\kappa)} + \Delta_M^{(\kappa)} . \qquad (5.2.1)$$

The first term,

$$\Delta_c^{(\kappa)} \equiv \sum_{ki \neq \ell j} \left\langle\!\left\langle e_{ki} e_{\ell j} \left[\frac{\underline{r}_{ki} - \underline{r}_{\ell j}}{|\underline{r}_{ki} - \underline{r}_{\ell j}|^3} - \frac{\underline{r}_{ki} - \underline{r}'_{\ell j}}{|\underline{r}_{ki} - \underline{r}'_{\ell j}|^3} \right] \cdot \underline{u}_k \, \delta(\underline{r}_k - \underline{r}) \right\rangle\!\right\rangle , \qquad (5.2.2)$$

is the coulombic interaction term analogous to $\underline{\Delta}_c$ [see (4.2.4)] in section 4.2. The second term,

$$\begin{aligned} \Delta_M^{(\kappa)} \equiv -\frac{1}{c} \sum_{ki} \Big\langle\!\Big\langle e_{ki} \Big[& \underline{E}^T(\underline{r}_{ki}) - \underline{E}^{T\prime}(\underline{r}_{ki}) \\ & - \frac{1}{c} \underline{U}_{ki} \times \left(\underline{B}(\underline{r}_{ki}) - \underline{B}'(\underline{r}_{ki}) \right) \Big] \cdot \underline{u}_k \, \delta(\underline{r}_k - \underline{r}) \Big\rangle\!\Big\rangle , \end{aligned} \qquad (5.2.3)$$

where $\underline{\underline{E}}^{T}(\underline{r}_{ki})$ is defined by (4.2.6), is the retardation correction to the coulombic interaction plus the short range magnetic interaction term. This term is analogous to $\underline{\Delta}_{M}$ $\left[\text{see } (4.2.5)\right]$ and, as is pointed out in section 4.2, is probably small.

Expanding $\dfrac{\underline{r}_{ki}-\underline{r}_{lj}}{|\underline{r}_{ki}-\underline{r}_{lj}|^{3}}$ in a Taylor series $\left[\text{see } (4.2.9)\right]$ we write

$$\Delta_{c}^{(K)} = \sum_{n=0}^{\infty}\sum_{r=0}^{n}\frac{(-1)^{(n-r)}}{r!\,(n-r)!}\sum_{\substack{k\neq l\\ ij}}\Big\langle\!\Big\langle e_{ki}e_{lj}\Big[\underline{\underline{R}}_{ki}^{(n-r)}\underline{\underline{R}}_{lj}^{(r)}\cdot^{(n)}\left(\frac{\partial}{\partial\underline{r}_{l}}\right)^{(n+1)}\frac{1}{|\underline{r}_{k}-\underline{r}_{l}|}$$
$$-\underline{\underline{R}}_{ki}^{(n-r)}\underline{\underline{R}}_{lj}^{\prime(r)}\cdot^{(n)}\left(\frac{\partial}{\partial\underline{r}_{l}'}\right)^{(n+1)}\frac{1}{|\underline{r}_{k}-\underline{r}_{l}'|}\Big]\cdot\underline{u}_{k}\,\delta(\underline{r}_{k}-\underline{r})\Big\rangle\!\Big\rangle. \tag{5.2.4}$$

On the right side of (5.2.4), we have not included the term,

$$\sum_{\substack{k\\ i\neq j}}\Big\langle\!\Big\langle e_{ki}e_{kj}\Big[\frac{\underline{r}_{ki}-\underline{r}_{kj}}{|\underline{r}_{ki}-\underline{r}_{kj}|^{3}}-\frac{\underline{r}_{ki}-\underline{r}_{kj}'}{|\underline{r}_{ki}-\underline{r}_{kj}'|^{3}}\Big]\cdot\underline{u}_{k}\,\delta(\underline{r}_{k}-\underline{r})\Big\rangle\!\Big\rangle, \tag{5.2.5}$$

since it is negligible compared to the term we have included. This point is discussed further following (4.2.10).

We now introduce a function

$$\underline{\underline{G}}^{(n)}(\underline{r}',\underline{r}'',\underline{u}',\underline{u}'')\equiv$$

$$\sum_{r=0}^{n}\frac{(-1)^{(n-r)}}{r!\,(n-r)!}\sum_{\substack{k\neq l\\ ij}}\Big\langle\!\Big\langle e_{ki}e_{lj}\Big[\underline{\underline{R}}_{ki}^{(n-r)}\underline{\underline{R}}_{lj}^{(r)}\delta(\underline{r}_{k}-\underline{r}')\delta(\underline{r}_{l}-\underline{r}'')\delta(\underline{u}_{k}-\underline{u}')\delta(\underline{u}_{l}-\underline{u}'')$$
$$-\underline{\underline{R}}_{ki}^{(n-r)}\underline{\underline{R}}_{lj}^{\prime(r)}\delta(\underline{r}_{k}-\underline{r}')\delta(\underline{r}_{l}'-\underline{r}'')\delta(\underline{u}_{k}-\underline{u}')\delta(\underline{u}_{l}'-\underline{u}'')\Big]\Big\rangle\!\Big\rangle, \tag{5.2.6}$$

similar to the $\underline{\underline{N}}^{(m)}(\underline{r}',\underline{r}'')$ [see (4.2.12)] of section 4.2 except that $\underline{\underline{G}}^{(m)}$ involves the velocity as well as the position. The zeroth order term of (5.2.6), is

$$\underline{\underline{G}}^{(0)}(\underline{r}',\underline{r}'';\underline{u}',\underline{u}'') \equiv \sum_{k\neq l} e_k e_l \Big\langle\Big\langle \delta(\underline{r}_k-\underline{r}')\,\delta(\underline{r}_l-\underline{r}'')\,\delta(\underline{u}_k-\underline{u}')\,\delta(\underline{u}_l-\underline{u}'')$$

$$-\,\delta(\underline{r}_k-\underline{r}')\,\delta(\underline{r}_l'-\underline{r}'')\,\delta(\underline{u}_k-\underline{u}')\,\delta(\underline{u}_l'-\underline{u}'')\Big\rangle\Big\rangle. \qquad (5.2.7)$$

This function is closely related to the difference between the pair distribution function and the product of single particle distribution functions. The higher order terms in the expression for $\underline{\underline{G}}^{(m)}$ describe the effects of molecular structure. In the absence of pair correlation with respect to either position or velocity, $\underline{\underline{G}}^{(m)}$ vanishes, hence $\underline{\underline{G}}^{(m)}$ is a correlation function.

In terms of $\underline{\underline{G}}^{(m)}$, (5.2.4) may be written

$$\Delta_c^{(K)} = \int \sum_{m=0}^{\infty} \underline{\underline{G}}^{(m)}(\underline{r}',\underline{r}'';\underline{u}',\underline{u}'')\,\underline{u}'\,\delta(\underline{r}'-\underline{r}) \cdot^{(m+1)} \left(\frac{\partial}{\partial \underline{r}''}\right)^{(m+1)} \frac{1}{|\underline{r}'-\underline{r}''|}\, d\underline{r}'\, d\underline{r}''\, d\underline{u}'\, d\underline{u}''$$

$$(5.2.8)$$

$$= -\int \sum_{m=0}^{\infty} \underline{\underline{G}}^{(m)}(\underline{r}',\underline{r}'';\underline{u}',\underline{u}'')\,\underline{u}''\,\delta(\underline{r}''-\underline{r}) \cdot^{(m+1)} \left(\frac{\partial}{\partial \underline{r}''}\right)^{(m+1)} \frac{1}{|\underline{r}'-\underline{r}''|}\, d\underline{r}'\, d\underline{r}''\, d\underline{u}'\, d\underline{u}''.$$

The last line in (5.2.8) is obtained by interchanging variables in a manner similar to that used in developing (4.2.16) and by using the relation

$$\underline{\underline{G}}^{(m)}(\underline{r}',\underline{r}'';\underline{u}',\underline{u}'') \cdot^{(m)} \underline{\underline{T}}^{(m)} \equiv (-1)^{(m)}\,\underline{\underline{G}}^{(m)}(\underline{r}'',\underline{r}';\underline{u}'',\underline{u}') \cdot^{(m)} \underline{\underline{T}}^{(m)}, \qquad (5.2.9)$$

where $\underline{\underline{T}}^{(n)}$ is an arbitrary tensor of order n. The derivation of (5.2.9) follows lines similar to those used in deriving the corresponding relation involving $\underline{\underline{N}}^{(n)}(\underline{r}', \underline{r}'')$ [see (4.2.14)]. Combining the first and second lines of (5.2.8), we write

$$\Delta_c^{(K)} = \frac{1}{2} \int \sum_{n=0}^{\infty} \underline{\underline{G}}^{(n)}(\underline{r}', \underline{r}'', \underline{u}', \underline{u}'') \left[\underline{u}' \delta(\underline{r}' - \underline{r}) - \underline{u}'' \delta(\underline{r}'' - \underline{r}) \right]$$

$$\cdot^{(n+1)} \left(\frac{\partial}{\partial \underline{r}''} \right)^{(n+1)} \frac{1}{|\underline{r}' - \underline{r}''|} \, d\underline{r}' d\underline{r}'' d\underline{u}' d\underline{u}''. \qquad (5.2.10)$$

Expanding $\delta(\underline{r}'' - \underline{r})$ in a Taylor series [see (4.2.18)], integrating over $\underline{r}'$, and dropping one of the primes on $\underline{r}''$, (5.2.10) becomes

$$\Delta_c^{(K)} = \frac{1}{2} \int \sum_{n=0}^{\infty} \underline{\underline{G}}^{(n)}(\underline{r}, \underline{r}', \underline{u}', \underline{u}'') (\underline{u}' - \underline{u}'') \cdot^{(n+1)} \left(\frac{\partial}{\partial \underline{r}'} \right)^{(n+1)} \frac{1}{|\underline{r} - \underline{r}'|} \, d\underline{r}' d\underline{u}' d\underline{u}''$$

$$(5.2.11)$$

$$- \frac{\partial}{\partial \underline{r}} \cdot \frac{1}{2} \int \sum_{s=0}^{\infty} \frac{1}{(s+1)!} \left(\frac{\partial}{\partial \underline{r}} \right)^{(s)} \cdot^{(s)} (\underline{r} - \underline{r}')^{(s+1)} \sum_{n=0}^{\infty} \underline{\underline{G}}^{(n)}(\underline{r}, \underline{r}', \underline{u}', \underline{u}'') \underline{u}'' \cdot^{(n+1)} \left(\frac{\partial}{\partial \underline{r}'} \right)^{(n+1)} \frac{1}{|\underline{r} - \underline{r}'|} \, d\underline{r}' d\underline{u}' d\underline{u}''.$$

If the above expression for $\Delta_c^{(K)}$ is added to the expression for $\Delta^{(c)}$, derived in the previous section [see (5.1.13) and (5.1.3)], a number of terms cancel. To carry out this addition, it is convenient to introduce the correlation function $\underline{\underline{G}}^{(n)}$ into the expression for $\Delta^{(c)}$. We first define a new correlation function,

$$\tilde{\underline{\underline{G}}}^{(n)}(\underline{r}', \underline{r}'', \underline{u}', \underline{u}'') \equiv \sum_{\alpha\beta} \frac{d \underline{R}_{\alpha\beta}}{dt} \cdot \frac{\partial \underline{\underline{G}}^{(n)}}{\partial \underline{R}_{\alpha\beta}}$$

$$\equiv \sum_{s=0}^{n} \frac{(-1)^{(n-s)}}{s!\,(n-s)!} \sum_{\substack{k=l \\ i\,j}} \left\langle\!\left\langle e_{ki} e_{lj} \left[\frac{d}{dt} \left(\underline{\underline{R}}_{ki}^{(n-s)} \underline{\underline{R}}_{lj}^{(s)} \right) \delta(\underline{r}_k - \underline{r}') \delta(\underline{r}_l - \underline{r}'') \delta(\underline{u}_k - \underline{u}') \delta(\underline{u}_l - \underline{u}'') \right.\right.\right.$$

$$\left.\left.\left. - \frac{d}{dt} \left(\underline{\underline{R}}_{ki}^{(n-s)} \underline{\underline{R}}_{lj}'^{(s)} \right) \delta(\underline{r}_k - \underline{r}') \delta(\underline{r}_l' - \underline{r}'') \delta(\underline{u}_k - \underline{u}') \delta(\underline{u}_l' - \underline{u}'') \right] \right\rangle\!\right\rangle \qquad (5.2.12)$$

which is a partial time derivative of $\underline{\underline{G}}^{(m)}$ taken over the intraparticle coordinates $\underline{R}_{ki}$. The zeroth order term of $\underline{\underline{\tilde{G}}}^{(m)}$ is, of course,

$$\underline{\underline{\tilde{G}}}^{(0)} \equiv 0. \tag{5.2.13}$$

The higher order terms of $\underline{\underline{\tilde{G}}}^{(m)}$, which involve time derivatives of $\underline{R}_{ki}$, are related to the magnetic effects of motion within a molecule.

Substituting $\underline{\underline{\tilde{G}}}^{(m)}(\underline{r},\underline{r}',\underline{u}',\underline{u}'')$ and $\underline{\underline{G}}^{(m)}(\underline{r},\underline{r}',\underline{u}',\underline{u}'')$ into (5.1.13) and (5.1.3), we obtain

$$\begin{aligned}\Delta^{(c)} = &-\frac{1}{2}\int \sum_{m=0}^{\infty} \underline{\underline{G}}^{(m)}(\underline{r},\underline{r}',\underline{u}',\underline{u}'')\,(\underline{u}'-\underline{u}'')\cdot^{(m+1)}\left(\frac{\partial}{\partial \underline{r}'}\right)^{(m+1)}\frac{1}{|\underline{r}-\underline{r}'|}\,d\underline{r}'\,d\underline{u}'\,d\underline{u}''\\ &-\frac{\partial}{\partial \underline{r}}\cdot\frac{1}{2}\int \sum_{m=0}^{\infty} \underline{u}'\,\underline{\underline{G}}^{(m)}(\underline{r},\underline{r}',\underline{u}',\underline{u}'')\cdot^{(m)}\left(\frac{\partial}{\partial \underline{r}'}\right)^{(m)}\frac{1}{|\underline{r}-\underline{r}'|}\,d\underline{r}'\,d\underline{u}'\,d\underline{u}''\\ &+\frac{1}{2}\int \sum_{m=0}^{\infty} \underline{\underline{\tilde{G}}}^{(m+1)}(\underline{r},\underline{r}',\underline{u}',\underline{u}'')\cdot^{(m+1)}\left(\frac{\partial}{\partial \underline{r}'}\right)^{(m+1)}\frac{1}{|\underline{r}-\underline{r}'|}\,d\underline{r}'\,d\underline{u}'\,d\underline{u}''.\end{aligned} \tag{5.2.14}$$

Adding the above equation to (5.2.17), and making use of (5.2.1) and (5.1.11) results in

$$\Delta = -\frac{\partial}{\partial \underline{r}} \cdot \frac{1}{2}\int \underline{u}' \sum_{n=0}^{\infty} \left[\left(\frac{\partial}{\partial \underline{r}'}\right)^{(n)} \frac{1}{|\underline{r}-\underline{r}'|}\right] \cdot^{(n)} \underline{\underline{G}}^{(n)}(\underline{r},\underline{r}',\underline{u}',\underline{u}'')\, d\underline{r}'\, d\underline{u}'\, d\underline{u}''$$

$$-\frac{\partial}{\partial \underline{r}} \cdot \frac{1}{2}\int \sum_{\substack{n=0\\ s=0}}^{\infty} \frac{1}{(s+1)!}\left(\frac{\partial}{\partial \underline{r}}\right)^{(s)} \cdot^{(s)} (\underline{r}-\underline{r}')^{(s+1)}\, \underline{u}'' \cdot \left[\left(\frac{\partial}{\partial \underline{r}'}\right)^{(n+1)} \frac{1}{|\underline{r}-\underline{r}'|}\right] \cdot^{(n)} \underline{\underline{G}}^{(n)}(\underline{r},\underline{r}',\underline{u}',\underline{u}'')\, d\underline{r}'\, d\underline{u}'\, d\underline{u}''$$

$$+\frac{1}{2}\int \sum_{n=0}^{\infty} \underline{\underline{G}}^{(n+1)}(\underline{r},\underline{r}',\underline{u}',\underline{u}'') \cdot^{(n+1)} \left(\frac{\partial}{\partial \underline{r}'}\right)^{(n+1)} \frac{1}{|\underline{r}-\underline{r}'|}\, d\underline{r}'\, d\underline{u}'\, d\underline{u}''. \qquad (5.2.15)$$

By substituting $\underline{\underline{G}}^{(n)}(\underline{r},\underline{r}',\underline{u}',\underline{u}'')$ into the expression for $\underline{\underline{p}}_\phi$, (4.2.20), and ρU_ϕ, (5.1.1), we obtain

$$\underline{\underline{p}}_\phi = \frac{1}{2}\int \sum_{\substack{n=0\\ s=0}}^{\infty} \frac{1}{(s+1)!}\left(\frac{\partial}{\partial \underline{r}}\right)^{(s)} \cdot^{(s)} (\underline{r}-\underline{r}')^{(s+1)} \left[\left(\frac{\partial}{\partial \underline{r}'}\right)^{(n+1)} \frac{1}{|\underline{r}-\underline{r}'|}\right] \cdot^{(n)} \underline{\underline{G}}^{(n)}(\underline{r},\underline{r}',\underline{u}',\underline{u}'')\, d\underline{r}'\, d\underline{u}'\, d\underline{u}'' \qquad (5.2.16)$$

and

$$\rho U_\phi = \frac{1}{2}\int \sum_{n=0}^{\infty} \left[\left(\frac{\partial}{\partial \underline{r}'}\right)^{(n)} \frac{1}{|\underline{r}-\underline{r}'|}\right] \cdot^{(n)} \underline{\underline{G}}^{(n)}(\underline{r},\underline{r}',\underline{u}',\underline{u}'')\, d\underline{r}'\, d\underline{u}'\, d\underline{u}''. \qquad (5.2.17)$$

Using (5.2.16) and (5.2.17), (5.2.15) is written as

$$\Delta = -\frac{\partial}{\partial \underline{r}} \cdot \left(\underline{\underline{p}}_\phi \cdot \underline{u} + \rho U_\phi \underline{u} + \underline{q}_\phi\right) + \Delta', \qquad (5.2.18)$$

where

$$\Delta' \equiv \frac{1}{2}\int \sum_{n=0}^{\infty} \tilde{\underline{\underline{G}}}^{(n+1)}(\underline{r},\underline{r}',\underline{u}',\underline{u}'') \cdot^{(n+1)} \left(\frac{\partial}{\partial \underline{r}'}\right)^{(n+1)} \frac{1}{|\underline{r}-\underline{r}'|}\, d\underline{r}'\, d\underline{u}'\, d\underline{u}'' + \Delta_M^{(K)} \tag{5.2.19}$$

is that part of Δ which apparently cannot be written as a divergence. The term q_ϕ is defined by

$$q_\phi \equiv \frac{1}{2}\int \underline{v}' \sum_{n=0}^{\infty} \left[\left(\frac{\partial}{\partial \underline{r}'}\right)^{(n)} \frac{1}{|\underline{r}-\underline{r}'|}\right] \cdot^{(n)} \underline{\underline{G}}_v^{(n)}(\underline{r},\underline{r}',\underline{v}',\underline{v}'')\, d\underline{r}'\, d\underline{v}'\, d\underline{v}''$$

$$+\frac{1}{2}\int \sum_{\substack{n=0\\ s=0}}^{\infty} \frac{1}{(s+1)!} \left(\frac{\partial}{\partial \underline{r}}\right)^{(s)} \cdot^{(s)} (\underline{r}-\underline{r}')^{(s+1)}\, \underline{v}'' \cdot \left[\left(\frac{\partial}{\partial \underline{r}'}\right)^{(n+1)} \frac{1}{|\underline{r}-\underline{r}'|}\right] \cdot^{(n)} \underline{\underline{G}}_v^{(n)}(\underline{r},\underline{r}',\underline{v}',\underline{v}'')\, d\underline{r}'\, d\underline{v}'\, d\underline{v}'', \tag{5.2.20}$$

where

$$\underline{v}' \equiv \underline{u}' - \underline{v}, \tag{5.2.21}$$

$$\underline{v}'' = \underline{u}'' - \underline{v}, \tag{5.2.22}$$

and

$$\underline{\underline{G}}_v^{(n)}(\underline{r},\underline{r}',\underline{v}',\underline{v}'') \equiv$$

$$\sum_{r=0}^{n} \frac{(-1)^{(n-r)}}{r!\,(n-r)!} \sum_{\substack{k\neq l\\ i\,j}} \Big\langle\!\Big\langle e_k e_l \Big[\underline{\underline{R}}_{ki}^{(n-r)} \underline{\underline{R}}_{lj}^{(r)}\, \delta(\underline{r}_k-\underline{r})\, \delta(\underline{r}_l-\underline{r}')\, \delta(\underline{v}_k-\underline{v}')\, \delta(\underline{v}_l-\underline{v}'') \tag{5.2.23}$$

$$- \underline{\underline{R}}_{ki}^{(n-r)} \underline{\underline{R}}_{lj}'^{(r)}\, \delta(\underline{r}_k-\underline{r})\, \delta(\underline{r}_l'-\underline{r}')\, \delta(\underline{v}_k-\underline{v}')\, \delta(\underline{v}_l'-\underline{v}'')\Big]\Big\rangle\!\Big\rangle$$

In the above definitions, the $\underline{\nu}'$ and $\underline{\nu}''$ are analogous to the $\underline{\nu}_k$ and may be thought of as random velocities relative to the stream velocity $\underline{\nu}$. The $\underline{\underline{G}}^{(m)}_{\nu}$ is analogous to $\underline{\underline{G}}^{(m)}$, but is a correlation function over the random velocity instead of the total velocity.

From (5.2.16), (5.2.17), and (5.2.20), we see that $\underline{\underline{P}}_{\phi}$, ρU_{ϕ}, and $\underline{q}_{\phi}$ are correlation quantities since they all involve some version of the correlation function. Since the first term in the expression for Δ', (5.2.19) involves a version of $\underline{\underline{G}}^{(m)}$, it, also, is a correlation term. Finally by comparing $\Delta^{(k)}_{M}$ [see (5.2.3)] with $\underline{\Delta}_{M}$ [see (4.2.5)] both are seen to have similar forms; hence by an argument analogous to that used to show that $\underline{\Delta}_{M}$ is a correlation term [see the discussion following (4.2.24)], it can be shown that $\Delta^{(k)}_{M}$ is also correlation dependent. Thus Δ' and Δ are correlation quantities. As was pointed out in the discussion at the end of section 4.2, correlation implies a short range collisional interaction. It is in this sense that we regard the term, Δ, as a short range term.

5.3 The Long Range Term

We now return to the term X which represents the long range macroscopic effects of the electromagnetic fields. The discussion in this section closely parallels the discussion of $\underline{X}$ in section 4.3.

Expanding (5.1.10) in a Taylor series, we write

$$X=\sum_{n=0}^{\infty}\frac{1}{n!}\sum_{ki}\left\langle e_{ki}\underline{u}_k\,\underline{\underline{R}}_{ki}^{(n)}\delta(\underline{r}_k-\underline{r})\right\rangle\cdot^{(n+1)}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n)}\underline{E}$$

$$+\frac{1}{c}\sum_{n=0}^{\infty}\frac{1}{n!}\sum_{ki}\left\langle e_{ki}\left(\underline{u}_k\times\underline{U}_{ki}\right)\underline{\underline{R}}_{ki}^{(n)}\delta(\underline{r}_k-\underline{r})\right\rangle\cdot^{(n+1)}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n)}\underline{B}. \quad (5.3.1)$$

Applying (4.3.5), the order of differentiation in (5.3.1) is interchanged to give

$$X=\sum_{n=0}^{\infty}\sum_{l=0}^{n}\frac{(-1)^l}{l!(n-l)!}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n-l)}\cdot^{(n-l)}\left[\left(\frac{\partial}{\partial\underline{r}}\right)^{(l)}\cdot^{(l)}\sum_{ki}\left\langle e_{ki}\,\underline{\underline{R}}_{ki}^{(n)}\underline{u}_k\,\delta(\underline{r}_k-\underline{r})\right\rangle\right]\cdot\underline{E}$$

$$+\frac{1}{c}\sum_{n=0}^{\infty}\sum_{l=0}^{n}\frac{(-1)^l}{l!(n-l)!}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n-l)}\cdot^{(n-l)}\left[\left(\frac{\partial}{\partial\underline{r}}\right)^{(l)}\cdot^{(l)}\sum_{ki}\left\langle e_{ki}\,\underline{\underline{R}}_{ki}^{(n)}\left(\underline{u}_k\times\underline{U}_{ki}\right)\delta(\underline{r}_k-\underline{r})\right\rangle\right]\cdot\underline{B}$$

$$=\sum_{n=0}^{\infty}\sum_{l=0}^{n}\frac{(-1)^l}{l!(n-l)!}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n-l)}\cdot^{(n-l)}\left[\left(\frac{\partial}{\partial\underline{r}}\right)^{(l)}\cdot^{(l)}\sum_{ki}\left\langle e_{ki}\left(\underline{\underline{R}}_{ki}^{(n)}\underline{u}_k-\underline{u}_k\underline{\underline{R}}_{ki}^{(n)}\right)\delta(\underline{r}_k-\underline{r})\right\rangle\right]\cdot\underline{E}$$

$$-\frac{1}{c}\sum_{n=0}^{\infty}\sum_{l=0}^{n}\frac{(-1)^l}{l!(n-l)!}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n-l)}\cdot^{(n-l)}\left[\left(\frac{\partial}{\partial\underline{r}}\right)^{(l)}\cdot^{(l)}\sum_{ki}\left\langle e_{ki}\,\underline{\underline{R}}_{ki}^{(n)}\underline{U}_{ki}\times\underline{u}_k\,\delta(\underline{r}_k-\underline{r})\right\rangle\right]\cdot\underline{B}$$

$$+\sum_{n=0}^{\infty}\sum_{l=0}^{n}\frac{(-1)^l n!}{l!(n-l)!}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n-l)}\cdot^{(n-l)}\left[\left(\frac{\partial}{\partial\underline{r}}\right)^{(l)}\cdot^{(l)}\sum_{ki}\left\langle e_{ki}\underline{u}_k\,\underline{\underline{R}}_{ki}^{(n)}\delta(\underline{r}_k-\underline{r})\right\rangle\right]\cdot\underline{E}$$

$$(5.3.2)$$

Using standard vector identities, the above is rewritten as

$$X = \underline{J}\cdot\underline{E} - \sum_{n=0}^{\infty}\sum_{r=0}^{n+1}\frac{(-1)^{r}}{r!\,(n+1-r)!}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n+1-r)}_{\cdot(n+1-r)}\left[\left(\frac{\partial}{\partial\underline{r}}\right)^{(r)}_{\cdot(r)}\sum_{ki}\left\langle e_{ki}\left(\underline{\underline{R}}^{(n+1)}_{ki}\times\underline{u}_{k}\right)\delta(\underline{r}_{k}-\underline{r})\right\rangle\right]\times\underline{E}$$

$$+\sum_{n=0}^{\infty}\sum_{r=0}^{n}\frac{(-1)^{r}}{r!\,(n+1-r)!}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n+1-r)}_{\cdot(n+1-r)}\left[\left(\frac{\partial}{\partial\underline{r}}\right)^{(r)}_{\cdot(r)}\sum_{ki}\left\langle e_{ki}\,\underline{u}_{k}\,\underline{\underline{R}}^{(n+1)}_{ki}\,\delta(\underline{r}_{k}-\underline{r})\right\rangle\right]\cdot\underline{E}$$

$$+\sum_{n=0}^{\infty}\frac{(-1)^{(n+1)}}{(n+1)!}\left[\left(\frac{\partial}{\partial\underline{r}}\right)^{(n+1)}_{\cdot(n+1)}\sum_{ki}\left\langle e_{ki}\,\underline{u}_{k}\,\underline{\underline{R}}^{(n+1)}_{ki}\,\delta(\underline{r}_{k}-\underline{r})\right\rangle\right]\cdot\underline{E}$$

$$-\frac{1}{c}\sum_{n=0}^{\infty}\sum_{r=0}^{n}\frac{(-1)^{r}}{r!\,(n-r)!}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n-r)}_{\cdot(n-r)}\left[\left(\frac{\partial}{\partial\underline{r}}\right)^{(r)}_{\cdot(r)}\sum_{ki}\left\langle e_{ki}\,\underline{\underline{R}}^{(n)}_{ki}\,\underline{U}_{ki}\times\underline{u}_{k}\,\delta(\underline{r}_{k}-\underline{r})\right\rangle\right]\cdot\underline{B}$$

$$=\underline{J}\cdot\underline{E}+c\left(\frac{\partial}{\partial\underline{r}}\times\underline{M}\right)\cdot\underline{E}-c\left(\frac{\partial}{\partial\underline{r}}\times\underline{M}_{U}\right)\cdot\underline{E}-c\frac{\partial}{\partial\underline{r}}\cdot\left(\underline{\mathfrak{M}}_{u}\times\underline{E}\right)$$

$$+\frac{\partial}{\partial\underline{r}}\cdot\underline{\underline{\Phi}}_{P_1}\cdot\underline{E}+\frac{\partial\underline{P}}{\partial t}\cdot\underline{E}-\tilde{\underline{P}}\cdot\underline{E}-\tilde{\underline{\mathfrak{M}}}_{u}\cdot\underline{B}. \qquad (5.3.3)$$

To simplify the notation in the final form of (5.3.3), three new quantities are introduced. The first quantity,

$$\underline{M}_{U}\equiv\frac{1}{c}\sum_{n=0}^{\infty}(-1)^{n}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n)}_{\cdot(n)}\underline{\underline{M}}^{(n+1)}_{U}, \qquad (5.3.4)$$

is that part of $\underline{M}$ which is dependent upon $\underline{U}_{ki}$. The second, quantity

$$\underline{\mathfrak{M}}_{u}\equiv\frac{1}{c}\sum_{n=0}^{\infty}\sum_{r=0}^{n}\frac{(-1)^{r}(n+1)!}{r!\,(n+1-r)!}\left(\frac{\partial}{\partial\underline{r}}\right)^{(n-r)}_{\cdot(n-r)}\left[\left(\frac{\partial}{\partial\underline{r}}\right)^{(r)}_{\cdot(r)}\underline{\underline{M}}^{(n+1)}_{u}\right] \qquad (5.3.5)$$

is an operator in the sense of the magnetic moment operator, $\underline{\mathfrak{m}}$ [see (4.3.15)], and is, in fact, that part of $\underline{\mathfrak{m}}$ which is dependent on $\underline{u}_k$. The final quantity,

$$\underline{\widetilde{\mathfrak{m}}}_u \equiv \frac{1}{c}\sum_{n=0}^{\infty}\sum_{\ell=0}^{n}\frac{(-1)^{\ell}}{\ell!\,(n-\ell)!}\left(\frac{\partial}{\partial \underline{r}}\right)^{(n-\ell)}$$

$$\cdot^{(n-\ell)}\left[\left(\frac{\partial}{\partial \underline{r}}\right)^{(\ell)}\cdot^{(\ell)}\sum_{ki}\left\langle e_{ki}\,\underline{\underline{R}}_{ki}^{(n)}\,\underline{V}_{ki}\times\underline{u}_k\,\delta(\underline{r}_k-\underline{r})\right\rangle\right], \tag{5.3.6}$$

is related to $\underline{\mathfrak{m}}_u$ in a manner similar to that in which $\underline{\widetilde{P}}$ [see (2.5.9)] is related to $\underline{P}$. To further simplify (5.3.3), the previously defined current density, $\underline{J}$, magnetic moment density, $\underline{M}$, and polarization current operator, $\underline{\mathcal{J}}_{P_1}$, [see (2.4.21), (2.4.22), and (4.3.17)] are introduced. The sixth and seventh terms of the last form of (5.3.3) result from the application of the conservation equation for $\underline{P}$, (2.5.9), to the fourth term of the initial form of (5.3.3).

It is also possible to write X in another form. Coupling the Maxwell equations, (2.2.7) and (2.4.24), we obtain

$$\frac{\partial \underline{D}}{\partial t}\cdot\underline{E}+\frac{\partial \underline{B}}{\partial t}\cdot\underline{B} = -4\pi\,\underline{J}\cdot\underline{E} + c\left(\frac{\partial}{\partial \underline{r}}\times\underline{H}\right)\cdot\underline{E} - c\left(\frac{\partial}{\partial \underline{r}}\times\underline{E}\right)\cdot\underline{B}. \tag{5.3.7}$$

Using the definition of $\underline{D}$, (2.3.16), and $\underline{H}$, (2.4.23), and rearranging terms, we write (5.3.7) as

$$\underline{J}\cdot\underline{E}+\frac{\partial \underline{P}}{\partial t}\cdot\underline{E}+c\left(\frac{\partial}{\partial \underline{r}}\times\underline{M}\right)\cdot\underline{E} = -\frac{1}{8\pi}\frac{\partial}{\partial t}\left(E^2+B^2\right)-\frac{c}{4\pi}\frac{\partial}{\partial \underline{r}}\cdot\left(\underline{E}\times\underline{B}\right). \tag{5.3.8}$$

Substituting (5.3.8) into (5.3.3) gives

$$X = -\frac{\partial}{\partial t}\frac{1}{8\pi}\left(E^2+B^2\right) + \frac{\partial}{\partial \underline{r}}\cdot\left[\frac{c}{4\pi}\left(\underline{\mathcal{H}}_u \times \underline{E}\right) + \underline{\mathcal{J}}_{P_1}\cdot\underline{E}\right] + X', \tag{5.3.9}$$

where $\underline{\mathcal{H}}_u$ is an operator defined by

$$\underline{\mathcal{H}}_u \equiv \underline{B} - 4\pi\,\underline{\mathcal{M}}_u, \tag{5.3.10}$$

and

$$X' \equiv -c\left(\frac{\partial}{\partial \underline{r}} \times \underline{\mathcal{M}}_u\right) \text{[illegible]}\ \underline{\mathcal{M}}_u \cdot \underline{B} \tag{5.3.11}$$

is the part of X which apparently cannot be written as a time derivative or divergence.

Finally defining

$$U_L \equiv \frac{1}{8\pi}\left(E^2+B^2\right) \tag{5.3.12}$$

and

$$\underline{q}_L \equiv -\frac{c}{4\pi}\left(\underline{\mathcal{H}}_u \times \underline{E}\right) - \underline{\mathcal{J}}_{P_1}\cdot\underline{E}, \tag{5.3.13}$$

we write

$$X = -\frac{\partial U_L}{\partial t} - \frac{\partial}{\partial \underline{r}}\cdot\underline{q}_L + X'. \tag{5.3.14}$$

In (5.3.14), then, the long range electromagnetic contribution to the equation of energy change has been expressed as the sum of three terms. The first term is the time derivative of a quantity, U_L , which may be interpreted as the electromagnetic contribution to the energy density. The second term is the divergence of a quantity, $\mathbf{q}_L$, which may be interpreted as the electromagnetic contribution to the energy flux. The final term, X' , is not so easily interpreted. From (5.3.11), it is clear that every term of X' contains the time derivative of $\underline{R}_{ki}$, i.e., $\underline{U}_{ki}$, the velocity of a particle within a molecule with respect to the center of mass of the molecule. These intramolecular motions give rise to the magnetic properties of the individual molecules; hence X' is related to the magnetic effects.

5.4 Two Forms of the Energy Equation of Change

For a gas in which the molecules interact according to a short range potential, the energy equation of change is[18]

$$\frac{\partial \rho\left(U_K + U'_\phi + \frac{1}{2}v^2\right)}{\partial t} = -\frac{\partial}{\partial \underline{r}}\cdot\left[\rho\left(U_K + U'_\phi + \frac{1}{2}v^2\right)\underline{v} + \left(\mathbf{p}_K + \mathbf{p}'_\phi\right)\underline{v} + \mathbf{q}_K + \mathbf{q}'_\phi\right], \tag{5.4.1}$$

where U'_ϕ , $\mathbf{p}'_\phi$, and $\mathbf{q}'_\phi$ are similar to, but not identical with our correlation energy density, U_ϕ , correlation pressure, $\mathbf{p}_\phi$, and correlation energy flux, $\mathbf{q}_\phi$. This point is amplified in the next section.

From (5.1.9) and (5.2.18), our energy equation of change may be written

$$\frac{\partial \rho\left(U+\frac{1}{2}v^2\right)}{\partial t} = -\frac{\partial}{\partial \underline{r}}\cdot\left[\rho\left(U+\frac{1}{2}v^2\right)\underline{v} + \underline{\underline{p}}\cdot\underline{v} + \underline{q}\right] + X + \Delta', \qquad (5.4.2)$$

where

$$U = U_K + U_\phi , \qquad (5.4.3)$$

$$\underline{\underline{p}} = \underline{\underline{p}}_K + \underline{\underline{p}}_\phi , \qquad (4.4.3)$$

and

$$\underline{q} = \underline{q}_K + \underline{q}_\phi . \qquad (5.4.4)$$

In the form of the equation of change given in (5.4.2), the effects of the long range electromagnetic fields are contained in the long range electromagnetic power term, X $\left[\text{see (5.3.3)}\right]$.

Substituting the expression for X given by (5.3.14) into (5.4.2), we arrive at an alternate form of the equation of energy change:

$$\frac{\partial}{\partial t}\left[\rho\left(U+\frac{1}{2}v^2\right) + U_L\right] = \qquad (5.4.5)$$

$$-\frac{\partial}{\partial \underline{r}}\cdot\left[\rho\left(U+\frac{1}{2}v^2\right)\underline{v} + \underline{\underline{p}}\cdot\underline{v} + \underline{q} + \underline{q}_L\right] + X' + \Delta'.$$

In this form the long range electromagnetic effects are contained in the long range electromagnetic energy density, U_L , and the long range electromagnetic energy flux, $\underline{q}_L$, plus an "extraneous" power, X' .

Both (5.4.2) and (5.4.5) should be useful in dealing with practical problems involving the energy equation of change.

5.5 Limiting Forms of the Electromagnetic Terms

As an indication of the interpretation of the electromagnetic terms in the energy equation of change, we consider the detailed expressions for X , U_L , $\underline{q}_L$, U_ϕ, and $\underline{q}_\phi$, keeping only terms of first order in $\underline{R}_{ki}$ and $\underline{U}_{ki}$.

In the limit just outlined, we write the long range electromagnetic power [see (5.3.3)] as

$$X = \underline{J}\cdot\underline{E} + c\left(\frac{\partial}{\partial\underline{r}} \times \underline{M}\right)\cdot\underline{E} - c\,\frac{\partial}{\partial\underline{r}}\cdot\left(\underline{M}\times\underline{E}\right)$$

$$+\frac{\partial}{\partial\underline{r}}\cdot\underline{\underline{J}}_p\cdot\underline{E} + \frac{\partial\underline{P}}{\partial t}\cdot\underline{E} - \underline{\widetilde{P}}\cdot\underline{E} - \underline{\widetilde{M}}\cdot\underline{B}, \qquad (5.5.1)$$

where we retain only the dipole terms in the expressions for $\underline{P}$, $\underline{M}$, $\underline{\underline{J}}_p$, and $\underline{\widetilde{P}}$. In other words (4.5.2), (4.5.3), and (4.5.4) hold for $\underline{P}$, $\underline{M}$, and $\underline{\underline{J}}_p$, and $\underline{\widetilde{P}}$ [see (2.5.8)] is expressed as

$$\underline{\widetilde{P}} = \sum_{ki} \left\langle e_{ki}\, \underline{U}_{ki}\, \delta\left(\underline{r}_k - \underline{r}\right)\right\rangle. \qquad (5.5.2)$$

In this limit, the operator, $\widetilde{\underline{m}}$, in (5.3.3) is written in (5.5.1) as the function,

$$\widetilde{\underline{M}} \equiv \frac{1}{c}\sum_{ki}\langle e_{ki}\,\underline{U}_{ki}\times\underline{u}_k\,\delta(\underline{r}_k-\underline{r})\rangle$$

$$= \frac{1}{c}\,\widetilde{\underline{P}}\times\underline{\nu}. \tag{5.5.3}$$

In the last line of (5.5.3) the stream velocity, $\underline{v}$ [see (2.4.25)] is introduced, neglecting the effects of the Brownian motion velocity, $\underline{\nu}_k$ [see (2.4.26)]. Comparing (5.5.3) with the limiting forms for $\widetilde{\underline{P}}$ and $\underline{M}$ given by (5.5.2) and (4.5.3) makes it reasonable in the limit of this section to interpret $\widetilde{\underline{M}}$ as a source term of the magnetization, $\underline{M}$, in the sense that $\widetilde{\underline{P}}$ is interpreted as a source term of the polarization, $\underline{P}$.

Applying Maxwell's second equation, (2.2.7), to the second and third terms of (5.5.1) and applying the polarization conservation equation, (2.5.9), to the fourth, fifth, and sixth terms, we obtain

$$X = \underline{J}\cdot\underline{E} + \underline{\underline{J}}_p : \frac{\partial\underline{E}}{\partial\underline{r}} - \underline{M}\cdot\frac{\partial\underline{B}}{\partial t} - \widetilde{\underline{M}}\cdot\underline{B}. \tag{5.5.4}$$

The first term of (5.5.6) is the usual Joule heat term. The second term represents the rate that work is done by the interaction of the polarization current and the electric field, while the third and fourth terms represent the rate that work is done by the interaction of the magnetization and the magnetic field.

Considering the electromagnetic energy density next, we see that the simplifying assumptions introduced at the beginning of this section produce no changes; hence

$$U_L = \frac{1}{8\pi}\left(E^2 + B^2\right). \tag{5.3.12}$$

This equation differs from the usual macroscopically derived expression for the electromagnetic energy density[19] which is

$$U_L' = \frac{1}{8\pi}\left(\underline{E}\cdot\underline{D} + \underline{B}\cdot\underline{H}\right). \tag{5.5.5}$$

Both (5.3.12) and (5.5.5) reduce to the same form for a system of isolated point charges in a vacuum. However, when the point charges are grouped into molecules and the effects of multipole moments are introduced, a difference exists which we now examine in greater detail.

The usual form, U_L' , may be shown macroscopically to be equal to the work done in assembling the true charges and currents of the system,[20] i.e. in assembling the charges and currents that contribute to ρ_e and $\underline{J}$. However, choosing this definition is arbitrary. It is possible, for instance, to choose instead the work done in assembling the total charges and currents, i.e. those that contribute to

$$\sum_{ki}\langle e_{ki}\,\delta(\underline{r}_{ki}-\underline{r})\rangle = \rho_e - \frac{\partial}{\partial \underline{r}}\cdot\underline{P} \tag{5.5.6}$$

and

$$\sum_{ki}\langle e_{ki}\,\underline{u}_{ki}\,\delta(\underline{r}_{ki}-\underline{r})\rangle = \underline{J} + c\,\frac{\partial}{\partial \underline{r}}\times\underline{M} + \frac{\partial \underline{P}}{\partial t}\,. \tag{5.5.7}$$

In fact, if we use this "total work" as a basis of the definition of the energy density, we obtain, using the macroscopic derivation cited above, our expression, $\frac{1}{8\pi}(E^2+B^2)$.

We do not, however, base our definition of the energy density on the above observation. Our definition is chosen because, when the energy equation of change is written in the form of (5.4.5), with as many terms as possible written as a time derivative plus a divergence, the term U_L is grouped with the energy terms. It is, consequently, quite natural and convenient to call U_L an energy density.

Turning now to the energy flux, and introducing the simplifying approximations discussed previously, we write from (5.3.13)

$$q_L = \frac{c}{4\pi}(\underline{E}\times\underline{H}) - \underline{\underline{J}}_p\cdot\underline{E}\,. \tag{5.5.8}$$

The first term in this equation is the usual expression for the Poynting vector. The second term represents the energy flow due to the polarization current.

We now consider the collisional terms U_ϕ and q_ϕ. Treating

U_ϕ first, we retain only the first two terms in its series expansion (5.2.17), to write

$$\rho U_\phi = \frac{1}{2}\int \frac{1}{|\underline{r}-\underline{r}'|}\,\underline{\underline{G}}^{(0)}(\underline{r},\underline{r}';\underline{u}',\underline{u}'')\,d\underline{r}'d\underline{u}'d\underline{u}'' + \frac{1}{2}\int \frac{\underline{r}-\underline{r}'}{|\underline{r}-\underline{r}'|^3}\cdot\underline{\underline{G}}^{(1)}(\underline{r},\underline{r}';\underline{u}',\underline{u}'')\,d\underline{r}'d\underline{u}'d\underline{u}''$$

$$= \frac{1}{2}\int \frac{1}{|\underline{r}-\underline{r}'|}\,\underline{\underline{N}}^{(0)}(\underline{r},\underline{r}')\,d\underline{r}' + \frac{1}{2}\int \frac{\underline{r}-\underline{r}'}{|\underline{r}-\underline{r}'|^3}\cdot\underline{\underline{N}}^{(1)}(\underline{r},\underline{r}')\,d\underline{r}'. \qquad (5.5.9)$$

The last line in the above equation is the result of carrying out the integrations over $\underline{u}'$ and $\underline{u}''$ in the first line. The explicit forms of $\underline{\underline{N}}^{(0)}$ and $\underline{\underline{N}}^{(1)}$ are given by (4.5.16) and (4.5.18). From these forms, as was pointed out in the discussion of $\pounds_\phi$ in section 4.5, we can interpret the first term in (5.5.9) as resulting from charge-charge interactions and the second term as being due to charge-dipole interactions.

Following the discussion of $\pounds_\phi$ still further, we consider the first term of (5.5.9) in greater detail. Introducing the radial distribution function $g_{\alpha\beta}(\underline{r},\underline{R})$ [see (4.5.19)] into the first term of (5.5.9) and discarding the second term, we obtain

$$\rho U_\phi = \frac{1}{2}\sum_{\alpha\beta}\int e_\alpha n_\alpha(\underline{r})\,e_\beta n_\beta(\underline{r}+\underline{R})\,\frac{1}{R}\left[g_{\alpha\beta}(\underline{r},\underline{R})-1\right]d\underline{R}, \qquad (5.5.10)$$

where $\underline{R}$ is given by (4.5.20) and n_α by (4.5.21). Introducing the low density limiting form for $g_{\alpha\beta}(\underline{r},\underline{R})$ given by (4.5.24), (5.5.10) becomes

$$\rho U_\phi = \frac{1}{2}\sum_{\alpha\beta}\frac{e_\alpha^2 e_\beta^2}{kT} n_\alpha(\underline{r})\, n_\beta(\underline{r}) \int \frac{1}{R^2} e^{-R/d\ell}\, d\underline{R}. \tag{5.5.11}$$

In the Irving and Kirkwood treatment of gases with a short range intermolecular potential, the collisional energy density in (5.4.1) is given by[20]

$$\rho U_\phi' = \frac{1}{2}\sum_{\alpha\beta} n_\alpha(\underline{r})\, n_\beta(\underline{r}) \int \phi_{\alpha\beta}(R)\, g_{\alpha\beta}(\underline{r},\underline{R})\, d\underline{R}. \tag{5.5.12}$$

For a coulombic potential to which the short range treatment does not apply, this becomes

$$\rho U_\phi' = \frac{1}{2}\sum_{\alpha\beta} e_\alpha n_\alpha(\underline{r})\, e_\beta n_\beta(\underline{r}) \left[\int \frac{1}{R} d\underline{R} - \frac{e_\alpha e_\beta}{kT}\int \frac{1}{R^2} e^{-R/d\ell}\, d\underline{R}\right]. \tag{5.5.13}$$

Comparing (5.5.11) and (5.5.13) ρU_ϕ is seen to involve only a convergent integral while $\rho U_\phi'$ contains a divergent integral as well. The convergence of ρU_ϕ is due to the presence of -1 in the integral in (5.5.10). The -1 is present because ρU_ϕ contains only the short range effects of the intermolecular potential. The long range effects of this potential which cause $\rho U_\phi'$ to be divergent are included in the long range power term, X , where they are expressed in terms of the macroscopic electromagnetic fields.

We now analyze $\mathfrak{q}_\phi$ in a similar fashion. Retaining only the first two terms (s = 0, n = 0,1) in the series expansion of $\mathfrak{q}_\phi$, (5.2.20), we obtain

$$\mathfrak{q}_\phi = \frac{1}{2}\int\left[\underline{v}'\frac{1}{|\underline{r}-\underline{r}'|} + \underline{v}''\cdot\frac{(\underline{r}-\underline{r}')(\underline{r}-\underline{r}')}{|\underline{r}-\underline{r}'|^3}\right]\underline{\underline{G}}_v^{(0)}(\underline{r},\underline{r}',\underline{v}',\underline{v}'')\,d\underline{r}'d\underline{v}'d\underline{v}''$$

$$+\frac{1}{2}\int\left[\underline{v}'\frac{\underline{r}-\underline{r}'}{|\underline{r}-\underline{r}'|^3} + 3\underline{v}''\cdot\frac{(\underline{r}-\underline{r}')(\underline{r}-\underline{r}')(\underline{r}-\underline{r}')}{|\underline{r}-\underline{r}'|^5} - \frac{\underline{r}-\underline{r}'}{|\underline{r}-\underline{r}'|^3}\underline{v}''\right]$$

$$\cdot\,\underline{\underline{G}}_v^{(1)}(\underline{r},\underline{r}',\underline{v}',\underline{v}'')\,d\underline{r}'d\underline{v}'d\underline{v}''. \qquad (5.5.14)$$

It may be shown by an analysis similar to that used in interpreting the lead terms of U_ϕ and $\mathfrak{q}_\phi$ [see (5.5.9) and (4.5.15)] that the first term in (5.5.14) is due to charge-current interactions and the second term to charge-dipole current interactions.

If, as a further approximation, we assume the position of the particles in our system are uncorrelated with the Brownian motion velocities, it is easily shown by techniques similar to those used in deriving (4.2.14) that

$$\underline{\underline{G}}_v^{(0)}(\underline{r},\underline{r}',\underline{v}',\underline{v}'') = \underline{\underline{G}}_v^{(0)}(\underline{r},\underline{r}',\underline{v}'',\underline{v}'). \qquad (5.5.15)$$

Therefore, eliminating the second term in (5.5.14) from further consideration we write after a bit of manipulation involving the dummy variables $\underline{v}'$ and $\underline{v}''$ in the first term,

$$q_\phi = \frac{1}{2}\iint\left[\underline{\underline{I}}\,\frac{1}{|\underline{r}-\underline{r}'|} + \frac{(\underline{r}-\underline{r}')(\underline{r}-\underline{r}')}{|\underline{r}-\underline{r}'|^3}\right]\cdot\underline{v}'\,\underline{\underline{G}}_v^{(0)}(\underline{r},\underline{r}',\underline{v}',\underline{v}'')\,d\underline{r}'d\underline{v}'d\underline{v}''$$

$$= \frac{1}{2}\iint\left[\underline{\underline{I}}\,\frac{1}{|\underline{r}-\underline{r}'|} + \frac{(\underline{r}-\underline{r}')(\underline{r}-\underline{r}')}{|\underline{r}-\underline{r}'|^3}\right]\cdot\underline{u}'\,\underline{\underline{G}}^{(0)}(\underline{r},\underline{r}',\underline{u}',\underline{u}'')\,d\underline{r}'d\underline{u}'d\underline{u}''$$

$$-\frac{1}{2}\underline{v}\cdot\iint\left[\underline{\underline{I}}\,\frac{1}{|\underline{r}-\underline{r}'|} + \frac{(\underline{r}-\underline{r}')(\underline{r}-\underline{r}')}{|\underline{r}-\underline{r}'|^3}\right.\,\underline{\underline{G}}^{(0)}(\underline{r},\underline{r}',\underline{u}',\underline{u}'')\,d\underline{r}'d\underline{u}'d\underline{u}''. \tag{5.5.16}$$

In proceeding from the initial to the final form of (5.5.16), we have made use of the expression relating the Brownian motion velocity, $\underline{v}'$, to the total velocity, $\underline{u}'$ $\left[\text{see (5.2.21)}\right]$.

A second distribution function, $j_{\alpha\beta}(\underline{r},\underline{R})$, is now defined as

$$n_\alpha(\underline{r})\underline{v}_\alpha(\underline{r})n_\beta(\underline{r}+\underline{R})\,j_{\alpha\beta}(\underline{r},\underline{R}) = \sum_{k_\alpha\neq l_\beta}\left\langle\left\langle \underline{u}_{k_\alpha}\delta(\underline{r}_{k_\alpha}-\underline{r})\,\delta(\underline{r}_{l_\beta}-\underline{r}')\right\rangle\right\rangle, \tag{5.5.17}$$

In the above equation, $\underline{v}_\alpha(\underline{r})$, defined by

$$n_\alpha(\underline{r})\underline{v}_\alpha(\underline{r}) \equiv \sum_{k_\alpha}\left\langle \underline{u}_{k_\alpha}\delta(\underline{r}_{k_\alpha}-\underline{r})\right\rangle, \tag{5.5.18}$$

is the stream velocity of particles of type α. Treating $\underline{\underline{G}}^{(0)}$ in a manner similar to the treatment of $\underline{\underline{N}}^{(0)}$ in (4.5.16) and making use of the above distribution function results in the expression,

$$\int \underline{u}'\,\underline{\underline{G}}^{(0)}(\underline{r},\underline{r}',\underline{u}',\underline{u}'')\,d\underline{u}'d\underline{u}'' = \tag{5.5.19}$$

$$\sum_{\alpha\beta} n_\beta(\underline{r}+\underline{R})\,n_\alpha(\underline{r})\,\underline{v}_\alpha(\underline{r})\left[j_{\alpha\beta}(\underline{r},\underline{R})-1\right].$$

When (5.5.19) is substituted into (5.5.16), the energy flux density may be written as

$$q_\phi = \frac{1}{2}\sum_{\alpha\beta} e_\alpha e_\beta \int \left[\underline{\underline{I}}\,\frac{1}{R} + \frac{\underline{R}\,\underline{R}}{R^3}\right] \cdot n_\beta(\underline{r}+\underline{R})\, n_\alpha(\underline{r})\, \underline{v}_\alpha(\underline{r}) \left[j_{\alpha\beta}(\underline{r},\underline{R}) - 1\right] d\underline{R}$$

$$- \frac{1}{2}\underline{v} \cdot \sum_{\alpha\beta} e_\alpha e_\beta \int \left[\underline{\underline{I}}\,\frac{1}{R} + \frac{\underline{R}\,\underline{R}}{R^3}\right] n_\alpha(\underline{r})\, n_\beta(\underline{r}+\underline{R}) \left[g_{\alpha\beta}(\underline{r},\underline{R}) - 1\right] d\underline{R}$$

$$= \frac{1}{2}\sum_{\alpha\beta} e_\alpha e_\beta \int \left[\underline{\underline{I}}\,\frac{1}{R} + \frac{\underline{R}\,\underline{R}}{R^3}\right]$$

$$\cdot \left\{ n_\beta(\underline{r})\, n_\alpha(\underline{r})\, \underline{v}_\alpha(\underline{r}) \left[j_{\alpha\beta}(\underline{r},\underline{R}) - 1\right] - n_\beta(\underline{r})\, n_\alpha(\underline{r})\, \underline{v} \left[g_{\alpha\beta}(\underline{r},\underline{R}) - 1\right] \right\} d\underline{R}. \tag{5.5.20}$$

In writing the last form of (5.5.20), use is made of the previously discussed approximation,

$$n_\beta(\underline{r}+\underline{R}) = n_\beta(\underline{r}). \tag{4.5.27}$$

The Irving and Kirkwood expression for the collisional energy flux of a gas composed of molecules with a short range interaction potential becomes

$$q'_\phi = \frac{1}{2}\sum_{\alpha\beta} e_\alpha e_\beta \int \left[\underline{\underline{I}}\,\frac{1}{R} + \frac{\underline{R}\,\underline{R}}{R^3}\right] \tag{5.5.21}$$

$$\cdot \left[n_\beta(\underline{r})\, n_\alpha(\underline{r})\, \underline{v}_\alpha(\underline{r})\, j_{\alpha\beta}(\underline{r},\underline{R}) - n_\beta(\underline{r})\, n_\alpha(\underline{r})\, \underline{v}\, g_{\alpha\beta}(\underline{r},\underline{R}) \right] d\underline{R},$$

when the short range potential is replaced by a coulomb potential. For large R both $j(\underline{r}, \underline{R}) \rightarrow 1$ and $g(\underline{r}, \underline{R}) \rightarrow 1$ to a first approximation. Hence, in this limit, q'_ϕ is a divergent integral while the q_ϕ of this work is a convergent integral. As in the case of U_ϕ, the integral in q_ϕ converges because it involves only the short range effects of the intermolecular potential. The long range effects that make q'_ϕ divergent are included in this treatment in the long-range power term, X, where they are expressed in terms of the macroscopic electromagnetic fields.

5.6 Comparisons with Previous Results

In this section, we compare the form of the energy equation of change derived in this work with those obtained in earlier developments.

First we compare our results with those of Kaufman.[7] Kaufman, as was pointed out in section 4.6, treated statistically a system of point particles without internal structure ignoring magnetic effects. If we introduce these approximations into our equation (5.4.5), we obtain

$$\frac{\partial}{\partial t}\left[\rho\left(U+\frac{1}{2}v^2\right)+U_L\right]=-\frac{\partial}{\partial \underline{r}}\cdot\left[\rho\left(U+\frac{1}{2}v^2\right)\underline{v}+\underline{\underline{p}}\cdot\underline{v}+\underline{q}\right], \quad (5.6.1)$$

where [see (5.3.12)]

$$U_L = \frac{1}{8\pi} E^2 . \tag{5.6.2}$$

The kinetic contribution, U_k, to U remains unchanged while the collisional contribution [see (5.5.9)] becomes

$$U_\phi = \frac{1}{\rho} \int \frac{1}{|\underline{r}-\underline{r}'|} \underline{\underline{N}}^{(0)}(\underline{r},\underline{r}') d\underline{r}' . \tag{5.6.3}$$

Similarly, the kinetic contribution to $\underline{\underline{p}} \cdot \underline{v} + \underline{q}$ remains unchanged while the collisional contribution [see (5.2.16) and (5.2.20)] becomes

$$\underline{\underline{p}}_\phi \cdot \underline{v} + \underline{q}_\phi = \frac{1}{2} \int \Bigg[\frac{\underline{u}'-\underline{v}}{|\underline{r}-\underline{r}'|} + \sum_{s=0}^{\infty} \frac{1}{(s+1)!} \left(\frac{\partial}{\partial \underline{r}}\right)^{(s)} \odot^{(s)} (\underline{r}-\underline{r}')^{(s+1)} \frac{\underline{r}-\underline{r}'}{|\underline{r}-\underline{r}'|^3} \cdot \underline{u}'' \Bigg] \underline{\underline{G}}^{(0)}(\underline{r},\underline{r}',\underline{u}',\underline{u}'') d\underline{r}' d\underline{u}' d\underline{u}'' . \tag{5.6.4}$$

In our notation Kaufman's energy equation of change is

$$\frac{\partial}{\partial t} \left[\rho\left(U + \tfrac{1}{2} v^2\right) + \frac{1}{8\pi} E^2 + E_{self} \right] = - \frac{\partial}{\partial \underline{r}} \cdot \left[\rho\left(U + \tfrac{1}{2} v^2\right) + \underline{\underline{p}} \cdot \underline{v} + \underline{q}_{self} + \left(\underline{J} + \frac{1}{4\pi} \frac{\partial \underline{E}}{\partial t} \right) \langle \phi \rangle \right] . \tag{5.6.5}$$

Comparing this equation with (5.6.1) we see that the only difference is that Kaufman includes the "self field" terms, $\underline{E}_{self}$ and q_{self}, and the term, $\left(\underline{J}+\frac{1}{4\pi}\frac{\partial \underline{E}}{\partial t}\right)\langle\phi\rangle$. The "self field" terms are the terms we neglected in developing (5.1.1) and (5.2.4). In dropping the "self field" terms, we point out that they are neglected for a large scale system. In keeping these same terms, Kaufman points out that they are important only for a small scale system. On this point, then, there seems to be no conflict. Furthermore, it seems to us that Kaufman was in error in including the term, $\left(\underline{J}+\frac{1}{4\pi}\frac{\partial \underline{E}}{\partial t}\right)\langle\phi\rangle$, in his equation, because when we apply Kaufman's approximations to Maxwell's fourth equation, (2.4.24), we obtain

$$\underline{J}+\frac{1}{4\pi}\frac{\partial \underline{E}}{\partial t}=0. \tag{5.6.6}$$

It is, thus, our conclusion that there is no basic disagreement between our work and that of Kaufman.

We now compare our statistical treatment with Chu's "thermodynamic" treatment.[4] Chu's equation of energy change may be written

$$\begin{aligned}\frac{\partial}{\partial t}\left[\rho\left(U_K+\tfrac{1}{2}v^2\right)+\frac{1}{8\pi}\left(\underline{D}\cdot\underline{E}+\underline{B}\cdot\underline{H}\right)+\frac{1}{8\pi}\left(\underline{D}\cdot\underline{E}\,\frac{T}{\epsilon}\frac{\partial\epsilon}{\partial T}+\underline{B}\cdot\underline{H}\,\frac{T}{\mu}\frac{\partial\mu}{\partial T}\right)\right]= \\ -\frac{\partial}{\partial\underline{r}}\cdot\Bigg\{\rho\left(U_K+\tfrac{1}{2}v^2\right)\underline{v}+\mathbb{P}_K\cdot\underline{v}+q_K+\frac{c}{4\pi}\underline{E}\times\underline{H} \\ +\frac{1}{2}\left[E^2\left(\frac{T}{\epsilon}\frac{\partial\epsilon}{\partial T}+\frac{\rho}{\epsilon}\frac{\partial\epsilon}{\partial\rho}\right)+H^2\left(\frac{T}{\mu}\frac{\partial\mu}{\partial T}+\frac{\rho}{\epsilon}\frac{\partial\epsilon}{\partial\rho}\right)\right]\underline{v}\Bigg\},\end{aligned} \tag{5.6.7}$$

where ϵ , μ , and ρ are, respectively, the dielectric constant, the magnetic permeability, and the mass density of the system. Comparing the above equation with the equation of change, (5.4.5), derived in this work, we observe that the long range energy density, U_L , and energy flux, $\underline{q}_L$, $\Big[$see (5.3.12) and (5.3.13)$\Big]$ are replaced in Chu's work by $\frac{1}{8\pi}\left(\underline{D}\cdot\underline{E}+\underline{B}\cdot\underline{H}\right)$ and $\frac{c}{4\pi}\,\underline{E}\times\underline{H}$, respectively. Chu, therefore, agrees with the usual macroscopically derived expressions for the energy density and energy flux $\Big[$see (5.5.5) and the discussion following (5.5.8)$\Big]$, but he does not agree with our results. Furthermore, in comparing (5.6.7) and (5.4.5), we observe that the correlation energy density, ρU_ϕ , obtained here $\Big[$ see (5.2.16)$\Big]$ is replaced in Chu's treatment by $\frac{1}{8\pi}\left(\underline{D}\cdot\underline{E}\,\frac{T}{\epsilon}\frac{\partial\epsilon}{\partial T}+\underline{B}\cdot\underline{H}\,\frac{T}{\mu}\frac{\partial\mu}{\partial T}\right)$. Also, Chu replaces the correlation energy flux, $\rho U_\phi \underline{v}+\underline{\underline{p}}_\phi\cdot\underline{v}+\underline{q}_\phi$ of this work $\Big[$see (5.2.16), (5.2.17), and (5.2.20)$\Big]$ by his $\frac{1}{2}\Big[E^2\left(\frac{T}{\epsilon}\frac{\partial\epsilon}{\partial T}+\frac{\rho}{\epsilon}\frac{\partial\epsilon}{\partial\rho}\right)+H^2\left(\frac{T}{\mu}\frac{\partial\mu}{\partial T}+\frac{\rho}{E}\frac{\partial E}{\partial\rho}\right)$. This last difference results from the difference between a statistical basis and a thermodynamic basis for the derivation of the energy equation. The thermodynamic basis Chu uses treats the short range forces between molecules in terms of gradients of ϵ and μ , while the statistical basis used here treats these same forces in terms of the correlation quantities, U_ϕ , $\underline{\underline{p}}_\phi$ and $\underline{q}_\phi$.

The final comparison that we make is with the work of Pai.[21] His treatment is also based on thermodynamic arguments. In the notation used here, Pai's energy equation of change (ignoring the effects of radiation) is

$$\frac{\partial}{\partial t}\left[\rho\left(U_K+\frac{1}{2}v^2\right)+\frac{1}{8\pi}\left(\underline{D}\cdot\underline{E}+\underline{B}\cdot\underline{H}\right)\right]=-\frac{\partial}{\partial \underline{r}}\cdot\left[\rho U_K\underline{v}+\underline{\underline{p}}_K\cdot\underline{v}+\underline{q}_K+\frac{c}{4\pi}\underline{E}\times\underline{H}\right] \tag{5.6.8}$$

Comparing this equation with (5.4.5), we see that, as in the previous case, the U_L and $\underline{q}_L$ of our work is replaced by $\frac{1}{8\pi}\left(\underline{D}\cdot\underline{E}+\underline{B}\cdot\underline{H}\right)$ and $\frac{c}{4\pi}\underline{E}\times\underline{H}$ in Pai's treatment. Hence Pai's long range terms agree with those of the usual macroscopic derivations rather than with ours. Unlike Chu, however, Pai has no terms comparable with our collisional terms to take into account the short range intermolecular potential.

The essential point in the development of this chapter, as in the development of Chapter IV is the separation of the effect of the electromagnetic force into long and short range terms. The coulomb portion of the short range term leads to the collisional contributions ρU_ϕ, $\underline{\underline{p}}_\phi$ and $\underline{q}_\phi$, to the energy density, pressure tensor, and energy flux, respectively. The portion describing the retardation and magnetic effects is left as a power term, Δ'. The long range term is written in two ways. Writing it as a power term, X, gives rise to one form, (5.4.2), of the energy equation of change. Writing it as an electromagnetic contribution, $\underline{q}_L$, to the energy flux plus an electromagnetic contribution, ρU_L, to the energy density, plus an "extraneous" power, X', gives rise to a second form, (5.4.4), of this equation.

The present statistical derivations of the electromagnetic energy density and energy flux help to clarify the nature of these quantities. As in the previous chapter, on comparing this work with that of other authors, agreement is found with those using statistical methods and disagreement with those using "thermodynamic" derivations.

SUMMARY

In this work we have used classical, non-relativistic mechanics to describe a system of molecules composed of nuclei and electrons with a purely coulomb potential of interaction. The primary aim has been to derive the equations describing the time evolution of certain fundamental macroscopic properties of the system, namely the electric and magnetic field densities and the mass, momentum, and energy densities.

In Chapter I, the time evolution of the microscopic properties of the system is described in terms of Maxwell's and Newton's equations [see (1.1.1) through (1.1.6)] and the Hamiltonian of the system is derived [see (1.4.1)] . The concept of a macroscopic property is defined in terms of a statistical ensemble average of the corresponding microscopic property [see (1.5.2)] . From this definition and the Hamiltonian, an equation of change,

$$\frac{\partial \langle g \rangle}{\partial t} = \langle \Lambda g \rangle, \tag{1.5.16}$$

is derived for any macroscopic dynamical variable. The operator Λ is analogous to the Liouville operator for the system [see (1.5.10)]

In Chapter II, this general equation of change is used to derive the Maxwell equations,

$$\frac{\partial}{\partial \underline{r}} \cdot \underline{B} = 0, \tag{2.1.3}$$

$$\frac{1}{c}\frac{\partial \underline{B}}{\partial t} = -\frac{\partial}{\partial \underline{r}} \times \underline{E}, \tag{2.2.7}$$

$$\frac{\partial}{\partial \underline{r}} \cdot \underline{D} = 4\pi \rho_e, \tag{2.3.17}$$

and

$$\frac{\partial \underline{D}}{\partial t} = c\frac{\partial}{\partial \underline{r}} \times \underline{H} - 4\pi \underline{J} \tag{2.4.24}$$

for the macroscopic electromagnetic fields. In the above equations $\underline{E}$ and $\underline{B}$ [see (2.2.4) and (2.1.1)] are the macroscopic electric and magnetic fields, the sources of which are the nuclei and electrons of the system [see the discussions at the ends of sections 2.3 and 2.4]. The quantity ρ_e is the charge density [see (2.3.13)] and $\underline{J}$ is the current density [see (2.4.21)]. The quantities

$$\underline{D} = \underline{E} + 4\pi \underline{P} \tag{2.3.16}$$

and

$$\underline{H} = \underline{B} - 4\pi \underline{M} \tag{2.4.23}$$

are, respectively, the electric displacement and the magnetic intensity, the sources of which are the molecules of the system.

The polarization, $\underline{P}$, and magnetization, $\underline{M}$, appearing in the above equations are further defined [see (2.3.15) and (2.4.22)] in terms of the molecular multipole densities $\underline{\underline{Q}}^{(m)}$, $\underline{\underline{M}}_{V}^{(m)}$, and $\underline{\underline{M}}_{u}^{(m)}$ [see (2.3.11), (2.4.19), and (2.4.20)] which result from the one-center multipole expansion of the intermolecular potential. The Maxwell equations given here for a molecular system are the familiar Maxwell equations in a material medium. The statistical derivation of these equations is new, however, and the explicit expressions obtained for the polarization and magnetization clarify the physical significance of these quantities.

In the final three chapters the hydrodynamic equations of change are derived. The equation of change for the mass density, ρ, [see (3.0.4)] , which is

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \underline{r}} \cdot \rho \underline{v} = 0, \tag{3.0.5}$$

is the same for a coulomb gas as for a non-ionized gas.
The quantity $\underline{v}$ in the above equation is the stream velocity [see (2.4.25)] .

The equation of change for the momentum density is written in two forms,

$$\frac{\partial \rho \underline{v}}{\partial t} + \frac{\partial}{\partial \underline{r}} \cdot \rho \underline{v}\, \underline{v} = -\frac{\partial}{\partial \underline{r}} \cdot \left(\underline{\underline{p}}_K + \underline{\underline{p}}_\phi\right) + \underline{\Delta}_M + \underline{X} \tag{4.4.2}$$

and

$$\frac{\partial}{\partial t}\left(\rho\underline{v}+\underline{N}\right)+\frac{\partial}{\partial \underline{r}}\cdot\rho\underline{v}\underline{v}=-\frac{\partial}{\partial \underline{r}}\cdot\left(\underline{\underline{p}}_K+\underline{\underline{p}}_\phi+\underline{\underline{p}}_L\right)+\underline{\Delta}_M. \tag{4.4.4}$$

These equations may be compared with the momentum equation of change for a non-ionized dilute gas,

$$\frac{\partial \rho\underline{v}}{\partial t}+\frac{\partial}{\partial \underline{r}}\cdot\rho\underline{v}\underline{v}=-\frac{\partial}{\partial \underline{r}}\cdot\underline{\underline{p}}_K, \tag{0.0.2}$$

where $\underline{\underline{p}}_K$ is the kinetic pressure tensor [see (4.1.5)] . The terms by which (4.4.2) and (4.4.4) differ from the above equation represent the effects of the coulomb potential. These effects are of two types. The short range or "collisional" effects discussed in detail in section 4.2 are represented by $\underline{\underline{p}}_\phi$ [see (4.2.20)], the "collisional" contribution to the pressure tensor, and $\underline{\Delta}_M$ [see (4.2.5)] . The long range effects discussed in section 4.3 are represented in (4.4.2) by the "pondermotive" force, $\underline{X}$ [see (4.3.20)] or in (4.4.4) by the long range electromagnetic contribution to the pressure tensor, $\underline{\underline{p}}_L$ [see (4.3.33)] , and the electromagnetic contribution to the momentum density, $\underline{N}$ [see (4.3.32)] . The low density limit of the momentum equation is discussed in section 4.5 and compared with previous results in section 4.6.

The equation of change for the energy density is derived in Chapter V. Again two forms,

$$\frac{\partial \rho\left(U_K + U_\phi + \frac{1}{2}v^2\right)}{\partial t} =$$

$$-\frac{\partial}{\partial \underline{r}} \cdot \left[\rho\left(U_K + U_\phi + \frac{1}{2}v^2\right)\underline{v} + \left(\mathbf{p}_K + \mathbf{p}_\phi\right)\cdot \underline{v} + \mathbf{q}_K + \mathbf{q}_\phi\right] + X + \Delta' \tag{5.4.2}$$

and

$$\frac{\partial}{\partial t}\left[\rho\left(U_K + U_\phi + \frac{1}{2}v^2\right) + U_L\right] =$$

$$-\frac{\partial}{\partial \underline{r}} \cdot \left[\rho\left(U_K + U_\phi + \frac{1}{2}v^2\right)\underline{v} + \left(\mathbf{p}_K + \mathbf{p}_\phi\right)\cdot \underline{v} + \mathbf{q}_K + \mathbf{q}_\phi + \mathbf{q}_L\right] \tag{5.4.5}$$

$$+ X' + \Delta',$$

are obtained. The energy equation for a non-ionized gas is

$$\frac{\partial \rho\left(U_K + \frac{1}{2}v^2\right)}{\partial t} = -\frac{\partial}{\partial \underline{r}} \cdot \left[\rho\left(U_K + \frac{1}{2}v^2\right)\underline{v} + \mathbf{p}_K \cdot \underline{v} + \mathbf{q}_K\right] \tag{0.0.3}$$

where ρU_K is the kinetic energy density [see (5.0.1)] and $\mathbf{q}_K$ is the kinetic energy flux [see (5.1.6)]. The terms by which (5.4.2) and (5.4.5) differ from the above equation represent the effects of the coulomb potential. The short range effects discussed in section 5.2 are represented by ρU_ϕ, the collisional contribution to the energy density [see (5.2.17)], by $\mathbf{q}_\phi$, the short range contribution to the energy flux [see (5.2.20)], by $\mathbf{p}_\phi$, and by Δ' [see (5.2.19)]. The long range coulomb effects are represented in (5.4.2) by X , the electromagnetic power [see (5.3.3)] . In (5.4.5), the long range effects are represented by U_L and q_L , the electromagnetic contributions to the energy density and energy flux [see (5.3.12) and (5.3.13)] and by X' [see (5.3.11)] . The low density limit of the energy equation is discussed in section 5.5. and compared with previous results in section 5.6.

The results obtained in this work for the equations of change for the momentum and energy densities agree quite well with previous results derived, statistically, for various special cases. The results, however, disagree with several earlier results obtained by other, "thermodynamic", methods.

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