Journal of Statistical Physics, Vol. 1, No. 1, 1969

A Statistical Derivation of the Hydrodynamic Equations of Change for a System of Ionized Molecules.
I. General Equation of Change and the Maxwell Equations

R. J. Beshinske[1] and C. F. Curtiss[2]

Received January 24, 1969

Nonrelativistic, classical statistical mechanics is used to describe a dense fluid of molecules composed of nuclei and electrons with purely Coulomb interaction potentials. 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 are derived and expressed in terms of molecular properties, e.g., polarization and magnetization densities.

KEY WORDS: Maxwell equations; Hydrodynamic equation; Magnetohydrodynamic equations; Polarization; Magnetization; Ionized systems.

1. 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

---

This research was carried out in part under Grant NsG-275-62 from the National Aeronautics and Space Administration and in part under a grant from the National Science Foundation. This paper is based on a thesis submitted by R. J. B. to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree.

[1] Department of Chemistry, St. John's University, Jamaica, New York.

[2] Theoretical Chemistry Institute, University of Wisconsin, Madison, Wisconsin.

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. Of course, 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, where the interparticle forces are negligible, the hydrodynamic equations are well known.(1) Irving and Kirkwood(2) have studied the more general problem and have derived the equations of change for a dense fluid, where the interparticle forces must be taken into account. However, their work is restricted to systems for which the interparticle potential approaches zero faster than the inverse cube of the interparticle distance. Hence, the results are 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 basic to the study of magnetohydrodynamics, plasma physics, and any problem 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. Many of the derivations of the equations of change for a Coulomb system, however, are nonstatistical.(3,4) Although there is good agreement among these derivations when they are restricted to systems which can be described by a point particle model, conflicting results are obtained when attempts are made to introduce more realistic properties such as dipole and quadrupole moments into the model. Hence a statistical derivation of the equations of change for the Coulomb system is desirable.

In recent years several authors have in a limited way undertaken statistical derivations. Mazur(5) has derived an equation of momentum change by such an approach. He neglected magnetic effects, however, and treated only a system of neutral molecules. Brittin(6) included magnetic effects in his derivation of the mass and momentum equations for a Coulomb system but neglected molecular effects. Kaufman(7) derived an equation of change for the energy as well as for the mass and momentum, but he also neglected molecular effects.

It is the purpose of this work to derive the equations of change for a system of molecules, using nonrelativistic, classical statistical mechanics. Restricting this study to nonrelativistic phenomena does not place an excessive limitation on its application since relativistic effects are important only in systems at extremely high temperatures. 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.

In this first paper, we develop a general equation for the rate of change of a macroscopic quantity and use this equation to derive Maxwell's equations for our system. In a later paper, we will derive the particular equations of change.

2. THE GENERAL EQUATION OF CHANGE

The development of the general equation of change for molecules in this section closely parallels a similar development by Brittin(6) for a system of structureless particles. We include the development to introduce notation and certain basic relations which are useful in the remainder of this paper.

We consider a system composed of N charged point particles, the nuclei and electrons in a real system. For convenience in the remainder of this work, we make use of a double subscript notation suggesting that the particles are clustered into groups representing molecules and ions. Each particle i of molecule k is described by a position vector $\mathbf{r}_{ki}$, a velocity vector $\mathbf{u}_{ki}$, an electric charge e_{ki}, and a mass m_{ki}.

The microscopic magnetic and electric fields of the system are expressed as

$$\mathbf{B}^{\mu} = \sum_{\lambda} q_{\lambda} \frac{\partial}{\partial \mathbf{r}} \times \mathbf{A}_{\lambda}(\mathbf{r}) + \mathbf{B}^{(e)}(\mathbf{r}) \tag{1}$$

and

$$\mathbf{E}^{\mu} = \sum_{ki} e_{ki} \frac{\mathbf{r} - \mathbf{r}_{ki}}{|\mathbf{r} - \mathbf{r}_{ki}|^3} - \frac{1}{c} \sum_{\lambda} p_{\lambda} \mathbf{A}_{\lambda}(\mathbf{r}) + \mathbf{E}^{(e)}(\mathbf{r}) \tag{2}$$

where c is the speed of light in a vacuum. In Eqs. (1) and (2), $\mathbf{E}^{(e)}(\mathbf{r})$ and $\mathbf{B}^{(e)}(\mathbf{r})$ are the contributions to the electric and magnetic fields due to be external sources. The $\mathbf{A}_{\lambda}(\mathbf{r})$ are a set of orthogonal time-independent functions forming a basis set for the familiar oscillator expansion of the vector potential.(8) The $\mathbf{A}_{\lambda}$ are constrained to obey the prescribed boundary conditions of the system and the set of equations

$$\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{A}_{\lambda} = 0 \tag{3}$$

$$\frac{\partial^2 \mathbf{A}_{\lambda}}{\partial \mathbf{r}^2} + \frac{{\omega_{\lambda}}^2}{c^2} \mathbf{A}_{\lambda} = 0 \tag{4}$$

and

$$\int_V \mathbf{A}_{\lambda} \cdot \mathbf{A}_{\mu} \, d\mathbf{r} = 4\pi c^2 V \, \delta_{\lambda\mu} \tag{5}$$

where $\delta_{\lambda\mu}$ is the Kronecker delta, V is the volume of the system, and ω_{λ} is a parameter depending on the boundary conditions. The q_{λ} are the coefficients of the $\mathbf{A}_{\lambda}$ in this expansion and form a set of canonical coordinates describing the state of the transverse electromagnetic fields. Finally, the

$$p_{\lambda} = \frac{dq_{\lambda}}{dt} \tag{6}$$

are the momenta conjugate to the q_{λ}.

In the usual way, an ensemble of systems is introduced and described by a distribution function, $f^{(N)}(\mathbf{r}_{ki}, \mathbf{u}_{ki}, q_\lambda, p_\lambda, t)$, in a multidimensional space in which the coordinates are the complete set of $\mathbf{r}_{ki}$, $\mathbf{u}_{ki}$, q_λ, and p_λ. This distribution function obeys the equation

$$\frac{\partial f^{(N)}}{\partial t} + \Lambda f^{(N)} = 0 \tag{7}$$

analogous to the Liouville equation. The operator Λ is given by

$$\begin{aligned}\Lambda = {} & \sum_{ki} \mathbf{u}_{ki} \cdot \frac{\partial}{\partial \mathbf{r}_{ki}} + \sum_{ki} \frac{e_{ki}}{m_{ki}} \left[\mathbf{E}^{\mu}_{ki}(\mathbf{r}_{ki}) + \frac{1}{c} \mathbf{u}_{ki} \times \mathbf{B}^{\mu}(\mathbf{r}_{ki})\right] \cdot \frac{\partial}{\partial \mathbf{u}_{ki}} \\ & + \sum_{\lambda} p_\lambda \frac{\partial}{\partial q_\lambda} + \sum_{\lambda} \left[\sum_{ki} \frac{e_{ki}}{c} \mathbf{u}_{ki} \cdot \mathbf{A}_\lambda(\mathbf{r}_{ki}) - \omega_\lambda{}^2 q_\lambda\right] \frac{\partial}{\partial p_\lambda}\end{aligned} \tag{8}$$

where

$$\mathbf{E}^{\mu}_{ki}(\mathbf{r}_{ki}) \equiv \sum_{\substack{lj \\ (lj \neq ki)}} e_{ki} \frac{\mathbf{r}_{ki} - \mathbf{r}_{lj}}{|\mathbf{r}_{ki} - \mathbf{r}_{lj}|^3} - \frac{1}{c} \sum_{\lambda} p_\lambda \mathbf{A}_\lambda(\mathbf{r}_{ki}) + \mathbf{E}^{(e)}(\mathbf{r}_{ki}) \tag{9}$$

is the electric field at $\mathbf{r}_{ki}$, excluding the effects of particle ki.

The macroscopic value or ensemble average of any dynamical variable, $g(\mathbf{r}_{ki}, \mathbf{u}_{ki}, q_\lambda, p_\lambda)$, is given by

$$\langle g \rangle = \int g f^{(N)} \prod_{\substack{ki \\ \lambda}} d\mathbf{r}_{ki}\, d\mathbf{u}_{ki}\, dq_\lambda\, dp_\lambda \tag{10}$$

where $f^{(N)}$ is assumed to be normalized so that

$$\langle 1 \rangle = 1 \tag{11}$$

The time rate of change of $\langle g \rangle$ is the general equation of change and is given by

$$\frac{\partial \langle g \rangle}{\partial t} = \langle \Lambda g \rangle \tag{12}$$

where g is assumed to have no explicit time dependence.

Equation (12) is used in Section 3 to derive the set of Maxwell's equations for the macroscopic electric and magnetic field densities, and in later papers will be used to derive the equations of change for the mass density, momentum density, and energy density.

3. THE MAXWELL EQUATIONS IN A MATERIAL MEDIUM

In the previous section, we defined the microscopic electric and magnetic fields $\mathbf{E}^{\mu}$ and $\mathbf{B}^{\mu}$ [see Eqs. (1) and (2)]. These fields fluctuate rapidly with time; the measurable quantities, however, are the macroscopic fields, $\mathbf{E}$ and $\mathbf{B}$, obtained by averaging $\mathbf{E}^{\mu}$

and $\mathbf{B}^\mu$ over a statistical ensemble. The fields $\mathbf{E}^\mu$ and $\mathbf{B}^\mu$ obey the microscopic Maxwell equations

$$\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{B}^\mu = 0 \tag{13}$$

$$\frac{\partial \mathbf{B}^\mu}{\partial t} = -c \frac{\partial}{\partial \mathbf{r}} \times \mathbf{E}^\mu \tag{14}$$

$$\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{E}^\mu = 4\pi \sum_{ki} e_{ki}\, \delta(\mathbf{r}_{ki} - \mathbf{r}) \tag{15}$$

and

$$\frac{\partial \mathbf{E}^\mu}{\partial t} = -4\pi \sum_{ki} e_{ki}\mathbf{u}_{ki}\, \delta(\mathbf{r}_{ki} - \mathbf{r}) + c \frac{\partial}{\partial \mathbf{r}} \times \mathbf{B}^\mu \tag{16}$$

where $\delta(\mathbf{r})$ is the Dirac delta function. Similarly, the fields $\mathbf{E}$ and $\mathbf{B}$ obey a set of macroscopic Maxwell equations which may be derived by evaluating the quantities

$$\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{E}, \qquad \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{B}, \qquad \frac{\partial \mathbf{E}}{\partial t}, \qquad \text{and} \qquad \frac{\partial \mathbf{B}}{\partial t}$$

3.1. The First Maxwell Equation

The derivation of the first Maxwell equation for the macroscopic fields is trivial. Starting with the definition of $\mathbf{B}$,

$$\mathbf{B} \equiv \langle \mathbf{B}^\mu \rangle \tag{17}$$

we take the divergence of both sides to obtain

$$\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{B} = \left\langle \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{B}^\mu \right\rangle \tag{18}$$

or, since the divergence of $\mathbf{B}^\mu$ is zero,

$$\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{B} = 0 \tag{19}$$

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

3.2. The Second Maxwell Equation

We next consider $\partial \mathbf{B}/\partial t$. From the definition of $\mathbf{B}^\mu$, Eq. (1), and the general equation of change, Eq. (12), we have

$$\frac{\partial \mathbf{B}}{\partial t} = \left\langle \Lambda \sum_\lambda q_\lambda \frac{\partial}{\partial \mathbf{r}} \times \mathbf{A}_\lambda \right\rangle + \frac{\partial \mathbf{B}^{(e)}}{\partial t} \tag{20}$$

Applying the microscopic Maxwell equations to the second term on the right of Eq. (20) and carrying out the Λ operation in the first term, we obtain

$$\frac{\partial \mathbf{B}}{\partial t} = \sum_{\lambda} \left\langle p_{\lambda} \frac{\partial}{\partial \mathbf{r}} \times \mathbf{A}_{\lambda} \right\rangle - c \frac{\partial}{\partial \mathbf{r}} \times \mathbf{E}^{(e)} \tag{21}$$

Since the macroscopic electric field is defined as $\mathbf{E} \equiv \langle \mathbf{E}^{\mu} \rangle$, the definition of $\mathbf{E}^{\mu}$, Eq. (2), may be used to write Eq. (21) in the form

$$\frac{\partial \mathbf{B}}{\partial t} = -c \frac{\partial}{\partial \mathbf{r}} \times \mathbf{E} \tag{22}$$

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

3.3. The Third Maxwell Equation

From Eq. (2), we write

$$\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{E} = -\frac{\partial^2}{\partial \mathbf{r}^2} \sum_{ki} \left\langle \frac{e_{ki}}{|\mathbf{r}_{ki} - \mathbf{r}|} \right\rangle + \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{E}^{(e)} \tag{23}$$

The second term on the right is zero because there are no sources of the external field in the system. By carrying out the differentiation in the first term on the right, we obtain

$$\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{E} = 4\pi \sum_{ki} \langle e_{ki}\, \delta(\mathbf{r}_{ki} - \mathbf{r}) \rangle \tag{24}$$

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

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

$$\mathbf{r}_k \equiv \sum_{i} \frac{m_{ki} \mathbf{r}_{ki}}{m_k} \tag{25}$$

and m_k is the mass of molecule k,

$$m_k = \sum_{i} m_{ki} \tag{26}$$

To do this we expand each k-subscripted term on the right of Eq. (24) in a Taylor series about $\mathbf{r}_k$:

$$\sum_{ki} \langle e_{ki}\, \delta(\mathbf{r}_{ki} - \mathbf{r}) \rangle = \sum_{n=0}^{\infty} \frac{1}{n!} \sum_{ki} \left\langle e_{ki} \mathbf{R}_{ki}^{(n)} \cdot^{(n)} \left(\frac{\partial}{\partial \mathbf{r}_k} \right)^{(n)} \delta(\mathbf{r}_k - \mathbf{r}) \right\rangle \tag{27}$$

The superscript n has the obvious meaning, e.g.,

$$\mathbf{R}_{ki}^{(3)} \cdot^{(3)} \left(\frac{\partial}{\partial \mathbf{r}_k} \right)^{(3)} \equiv \mathbf{R}_{ki} \mathbf{R}_{ki} \mathbf{R}_{ki} \,\vdots\, \frac{\partial}{\partial \mathbf{r}_k} \frac{\partial}{\partial \mathbf{r}_k} \frac{\partial}{\partial \mathbf{r}_k} \tag{28}$$

where

$$\mathbf{R}_{ki} = \mathbf{r}_{ki} - \mathbf{r}_k \tag{29}$$

is the vector from the center of mass of molecule k to particle i of molecule k. Now, using the symmetry of the delta function,

$$\frac{\partial}{\partial \mathbf{r}_k}\,\delta(\mathbf{r}_k - \mathbf{r}) = -\frac{\partial}{\partial \mathbf{r}}\,\delta(\mathbf{r}_k - \mathbf{r}) \tag{30}$$

we write Eq. (27) as

$$\sum_{ki} \langle e_{ki}\delta(\mathbf{r}_{ki} - \mathbf{r})\rangle = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!}\left(\frac{\partial}{\partial \mathbf{r}}\right)^{(n)} \cdot^{(n)} \sum_{ki} \langle e_{ki}\mathbf{R}_{ki}^{(n)}\,\delta(\mathbf{r}_k - \mathbf{r})\rangle \tag{31}$$

We now define a tensor of rank n

$$\mathbf{Q}^{(n)} \equiv \frac{1}{n!}\sum_{ki} \langle e_{ki}\mathbf{R}_{ki}^{(n)}\,\delta(\mathbf{r}_k - \mathbf{r})\rangle \tag{32}$$

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

Utilizing Eqs. (31) and (32), we may write (24) as

$$\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{E} = 4\pi\mathbf{Q}^{(0)} + 4\pi \sum_{n=0}^{\infty} (-1)^{n+1}\left(\frac{\partial}{\partial \mathbf{r}}\right)^{(n+1)} \cdot^{(n+1)} \mathbf{Q}^{(n+1)} \tag{33}$$

It is convenient to define the molecular charge density by

$$\rho_e \equiv \mathbf{Q}^{(0)} = \sum_k \langle e_k\,\delta(\mathbf{r}_k - \mathbf{r})\rangle \tag{34}$$

where

$$e_k \equiv \sum_i e_{ki} \tag{35}$$

is the charge of molecule k. It is also convenient to define the electric polarization, **P**, by

$$\mathbf{P} \equiv \sum_{n=0}^{\infty} (-1)^n\left(\frac{\partial}{\partial \mathbf{r}}\right)^{(n)} \cdot^{(n)} \mathbf{Q}^{(n+1)} \tag{36}$$

and the electric displacement, **D**, as

$$\mathbf{D} \equiv \mathbf{E} + 4\pi\mathbf{P} \tag{37}$$

In terms of these quantities, Eq. (33) becomes

$$\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{D} = 4\pi\rho_e \tag{38}$$

In form, this is a usual macroscopic Maxwell equation but the definition of **P** in this work is a generalization of that usually given since moments of higher order than the dipole are included. From Eq. (38), it is clear that **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 **D**, it is seen from Eq. (24) that the field **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 **D** is that quantity which **E** approaches as the average intermolecular distance increases. In dilute systems, therefore, **D** is a close approximation to **E**, and **P** in Eq. (37) is negligible. As the density of the system increases, **P** has a greater effect, and more terms must be retained in its series representation, Eq. (36), to obtain accurate results.

3.4. The Fourth Maxwell Equation

To obtain the final Maxwell equation, we evaluate

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

$$+ \sum_{\lambda} \left\langle \frac{\omega_\lambda^2}{c} q_\lambda \mathbf{A}_\lambda(\mathbf{r}) \right\rangle + \frac{\partial \mathbf{E}^{(e)}}{\partial t} \tag{39}$$

The first term in Eq. (39) is simplified by use of the identity

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

$$= 4\pi \sum_{ki} e_{ki}\mathbf{u}_{ki}\, \delta(\mathbf{r}_{ki} - \mathbf{r}) \tag{40}$$

derived from the microscopic Maxwell equations. If Eq. (40) is substituted into the first term of Eq. (39), and the defining equation for $\mathbf{A}_\lambda$, Eq. (4), is substituted into the second term, the result is

$$\frac{\partial \mathbf{E}}{\partial t} = -4\pi \sum_{ki} \langle e_{ki}\mathbf{u}_{ki}\, \delta(\mathbf{r}_{ki} - \mathbf{r})\rangle + c \frac{\partial}{\partial \mathbf{r}} \times \mathbf{B} \tag{41}$$

The term $\sum_{ki} \langle e_{ki}\mathbf{u}_{ki}\delta(\mathbf{r}_{ki} - \mathbf{r})\rangle$ is the total macroscopic current density analogous to the total macroscopic charge density, $\sum_{ki} \langle e_{ki}\delta(\mathbf{r}_{ki} - \mathbf{r})\rangle$. Equation (41) is the particle-centered equation analogous to Eq. (24).

Again, as we did for the divergence in Section 3.3, we transform this equation to a molecule-centered expression. Expanding $\sum_{ki} \langle e_{ki}\mathbf{u}_{ki}\delta(\mathbf{r}_{ki} - \mathbf{r})\rangle$ in a Taylor series similar to Eq. (31), we obtain

$$\sum_{ki} \langle e_{ki}\mathbf{u}_{ki}\, \delta(\mathbf{r}_{ki} - \mathbf{r})\rangle = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \left(\frac{\partial}{\partial \mathbf{r}}\right)^{(n)} \cdot^{(n)} \sum_{ki} \langle e_{ki}\mathbf{R}_{ki}^{(n)}\mathbf{u}_{ki}\, \delta(\mathbf{r}_k - \mathbf{r})\rangle \tag{42}$$

When this expression is substituted into Eq. (41) and the result into the definition of **D**, it is seen that

$$\frac{\partial \mathbf{D}}{\partial t} = -4\pi \sum_{ki} \langle e_{ki}\mathbf{u}_{ki}\, \delta(\mathbf{r}_{ki} - \mathbf{r})\rangle + c\,\frac{\partial}{\partial \mathbf{r}} \times \mathbf{B} + 4\pi \frac{\partial \mathbf{P}}{\partial t} \tag{43}$$

In Section 3.5, we evaluate the time derivative of the polarization **P** [see Eq. (64)]. The result may be written as

$$\begin{aligned}\frac{\partial \mathbf{P}}{\partial t} &= \sum_{n=0}^{\infty} \sum_{m=0}^{n} \frac{(-1)^n}{(n+1)!} \left(\frac{\partial}{\partial \mathbf{r}}\right)^{(n)} \cdot {}^{(n)} \sum_{ki} \langle e_{ki}\mathbf{R}_{ki}^{(m)}\mathbf{U}_{ki}\mathbf{R}_{ki}^{(n-m)}\, \delta(\mathbf{r}_k - \mathbf{r})\rangle \\ &\quad - \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1)!} \left(\frac{\partial}{\partial \mathbf{r}}\right)^{(n+1)} \cdot {}^{(n+1)} \sum_{ki} \langle e_{ik}\mathbf{u}_k\mathbf{R}_{ki}^{(n+1)}\, \delta(\mathbf{r}_k - \mathbf{r})\rangle\end{aligned} \tag{44}$$

The quantity

$$\mathbf{u}_k = \frac{d\mathbf{r}_k}{dt} = \sum_{i} \frac{m_{ki}\mathbf{u}_{ki}}{m_k} \tag{45}$$

is the velocity of the center of mass of molecule *k*, and

$$\mathbf{U}_{ki} \equiv \frac{d\mathbf{R}_{ki}}{dt} = \mathbf{u}_{ki} - \mathbf{u}_k \tag{46}$$

is the velocity of particle *ki* about the center of mass of molecule *k*. Substituting Eqs. (42) and (44) into Eq. (43) allows (43) to be written after some rearrangement as

$$\begin{aligned}\frac{\partial \mathbf{D}}{\partial t} &= 4\pi \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+1)!} \left(\frac{\partial}{\partial \mathbf{r}}\right)^{(n+1)} \cdot {}^{(n+1)} \Bigg\{\sum_{ki} \langle e_{ki}[\mathbf{R}_{ki}^{(n+1)}\mathbf{u}_k - \mathbf{u}_k\mathbf{R}_{ki}^{(n+1)}]\, \delta(\mathbf{r}_k - \mathbf{r})\rangle \\ &\quad + \frac{1}{n+2} \sum_{m=0}^{n} \sum_{ki} \langle e_{ki}[\mathbf{R}_{ki}^{(n+1)}\mathbf{U}_{ki} - \mathbf{R}_{ki}^{(m)}\mathbf{U}_{ki}\mathbf{R}_{ki}^{(n+1-m)}]\, \delta(\mathbf{r}_k - \mathbf{r})\rangle\Bigg\} \\ &\quad - 4\pi \sum_{k} \langle e_k\mathbf{u}_k\, \delta(\mathbf{r}_k - \mathbf{r})\rangle + c\,\frac{\partial}{\partial \mathbf{r}} \times \mathbf{B}\end{aligned} \tag{47}$$

For convenience we define a "magnetic multipole density"

$$\mathbf{M}_U^{(n)} \equiv \frac{n}{(n+1)!}\,\frac{1}{c} \sum_{ki} \langle e_{ki}\mathbf{R}_{ki}^{(n)} \times \mathbf{U}_{ki}\, \delta(\mathbf{r}_k - \mathbf{r})\rangle \tag{48}$$

and an "equivalent magnetic multipole density"

$$\mathbf{M}_u^{(n)}\, \frac{1}{n!}\,\frac{1}{c} \sum_{ki} \langle e_{ki}\mathbf{R}_{ki}^{(n)} \times \mathbf{u}_k\, \delta(\mathbf{r}_k - \mathbf{r})\rangle \tag{49}$$

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

$$\mathbf{J} \equiv \mathbf{M}_u^{(0)} = \sum_k \langle e_k \mathbf{u}_k \, \delta(\mathbf{r}_k - \mathbf{r}) \rangle \tag{50}$$

We further define a magnetization

$$\mathbf{M} \equiv \sum_{n=0}^{\infty} (-1)^n \left(\frac{\partial}{\partial \mathbf{r}}\right)^{(n)} \cdot {}^{(n)}[\mathbf{M}_u^{(n+1)} + \mathbf{M}_U^{(n+1)}] \tag{51}$$

and a magnetic intensity

$$\mathbf{H} \equiv \mathbf{B} - 4\pi \mathbf{M} \tag{52}$$

With these definitions, Eq. (47) may be written as

$$\frac{\partial \mathbf{D}}{\partial t} = -4\pi \mathbf{J} + c \frac{\partial}{\partial \mathbf{r}} \times \mathbf{H} \tag{53}$$

The last equation is a familiar macroscopic Maxwell equation, as are the equations derived in the previous sections. The quantity **H** is analogous to **D** in that it is the magnetic field produced by the molecules regarded as point charges. This can be seen from Eq. (53) since **J** 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 3.3, **B** is interpreted as being produced by the "true" point charges (the nuclei and electrons). Hence, **H** is a close approximation to **B** for dilute systems, but for more concentrated systems **H** should be corrected by adding to it the magnetization **M**, which depends on the motions of the intramolecular charges. These terms are $\mathbf{M}_U^{(n)}$ and $\mathbf{M}_u^{(n)}$.

To clarify the interpretation of **M**, we introduce the concept of a mass-weighted macroscopic molecular velocity, the familiar "stream velocity"

$$\mathbf{v} \equiv \frac{\sum_k \langle m_k \mathbf{u}_k \, \delta(\mathbf{r}_k - \mathbf{r}) \rangle}{\sum_k \langle m_k \, \delta(\mathbf{r}_k - \mathbf{r}) \rangle} \tag{54}$$

and a fluctuation velocity

$$\mathbf{v}_k \equiv \mathbf{u}_k - \mathbf{v} \tag{55}$$

If we write **M** including only the terms to the second order in $\mathbf{R}_{ki}$ and $\mathbf{U}_{ki}$, we obtain, by using the above definitions,

$$\begin{aligned} \mathbf{M} = \mathbf{M}_U^{(1)} &+ \frac{1}{c}\left[\mathbf{Q}^{(1)} \times \mathbf{v} - \frac{\partial}{\partial \mathbf{r}} \cdot (\mathbf{Q}^{(2)} \times \mathbf{v})\right] \\ &+ \frac{1}{c} \sum_{ki} \left\langle e_{ki} \left[\mathbf{R}_{ki} \times \mathbf{v}_k - \frac{\partial}{\partial \mathbf{r}} \cdot (\mathbf{R}_{ki}\mathbf{R}_{ki} \times \mathbf{v}_k)\right] \delta(\mathbf{r}_k - \mathbf{r}) \right\rangle \end{aligned} \tag{56}$$

where

$$\mathbf{M}_U^{(1)} = \frac{1}{2c}\sum_{ki}\langle e_{ki}\mathbf{R}_{ki} \times \mathbf{U}_{ki}\,\delta(\mathbf{r}_k - \mathbf{r})\rangle \tag{57}$$

If we assume that the fluctuation velocity is small compared to the stream velocity, and neglect the quadruple term, we may write Eq. (56) as

$$\mathbf{M} = \mathbf{M}_U^{(1)} + \frac{1}{c}\mathbf{Q}^{(1)} \times \mathbf{v} \tag{58}$$

a familiar result for "constant-velocity" systems.⁽⁹⁾ If we assume further that the system is stationary, Eq. (58) becomes

$$\mathbf{M} = \mathbf{M}_U^{(1)} \tag{59}$$

which is another familiar expression.⁽¹⁰⁾

3.5. The General Conservation Equation

We next derive an expression for $\partial\mathbf{Q}^{(n)}/\partial t$. For $n = 0$, the result is the familiar equation of charge conservation. The general result is used frequently in conjunction with Maxwell's equations. Use was made of this general result in deriving the fourth Maxwell equation in the previous section [see Eq. (44)].

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

$$\begin{aligned}\frac{\partial\sum_{ki}\langle e_{ki}\mathbf{R}_{ki}^{(n)}\,\delta(\mathbf{r}_k - \mathbf{r})\rangle}{\partial t} &+ \frac{\partial}{\partial\mathbf{r}}\cdot\sum_{ki}\langle e_{ki}\mathbf{u}_k\mathbf{R}_{ki}^{(n)}\,\delta(\mathbf{r}_k - \mathbf{r})\rangle\\ &= \sum_{ki}\left\langle e_{ki}\frac{d\mathbf{R}_{ki}^{(n)}}{dt}\,\delta(\mathbf{r}_k - \mathbf{r})\right\rangle\end{aligned} \tag{60}$$

With $n = 0$, the above equation reduces to the familiar equation of charge conservation,

$$\frac{\partial\rho_e}{\partial t} + \frac{\partial}{\partial\mathbf{r}}\cdot\mathbf{J} = 0 \tag{61}$$

where ρ_e is the molecular charge density and $\mathbf{J}$ is the molecular current density.

Furthermore, the form of Eq. (60) suggests the definition of the new quantities.

$$\mathbf{J}_p = \sum_{n=0}^{\infty}\frac{(-1)^n}{(n+1)!}\left(\frac{\partial}{\partial\mathbf{r}}\right)^{(n)}\cdot^{(n)}\sum_{ki}\langle e_{ki}\mathbf{u}_k\mathbf{R}_{ki}^{(n+1)}\,\delta(\mathbf{r}_k - \mathbf{r})\rangle \tag{62}$$

and

$$\tilde{\mathbf{P}} = \sum_{n=0}^{\infty}\frac{(-1)^n}{(n+1)!}\left(\frac{\partial}{\partial\mathbf{r}}\right)^{(n)}\cdot^{(n)}\sum_{ki}\left\langle e_{ki}\frac{d\mathbf{R}_{ki}^{(n+1)}}{dt}\,\delta(\mathbf{r}_k - \mathbf{r})\right\rangle \tag{63}$$

If Eqs. (60), (62), and (63) are combined with the definition of **P**, the resulting equation is

$$\frac{\partial \mathbf{P}}{\partial t} + \frac{\partial}{\partial \mathbf{r}} \cdot \mathsf{J}_p = \tilde{\mathbf{P}} \tag{64}$$

This has the form of a "conservation" equation for the polarization **P**. In this equation, J_p may be interpreted as a polarization current and $\tilde{\mathbf{P}}$ as a "source" of polarization.

4. CONCLUSION

In this paper we have derived a set of Maxwell equations for a system composed of molecules and ions. These equations, (19), (22), (38), and (53), have the same form as the Maxwell equations usually derived for the electric and magnetic fields in a material medium. The significance of this work lies, however, in a redefinition of some of the quantities appearing in the Maxwell equations. Instead of the usual ambiguous definitions, we define the electric displacement **D** and the magnetic intensity **H** [see Eqs. (37) and (52)] rigorously in terms of the molecular species within the medium.

REFERENCES

1. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, John Wiley and Sons, Inc., New York (1954, 1964), pp. 462–463.
2. J. H. Irving and J. G. Kirkwood, *J. Chem. Phys.* **18**:817 (1950).
3. W. K. Panofsky and M. Phillips, *Classical Electricity and Magnetism*, Addison-Wesley, Publishing Company, Inc., Reading, Massachusetts (1955), pp. 160–164.
4. B. Chu, *Phys. Fluids* **2**:473 (1959).
5. P. Mazur, *Advances in Chemical Physics*, Vol. I, Interscience Publishers, Inc., New York (1958), p. 309.
6. W. E. Brittin, *Phys. Rev.* **106**:843 (1957).
7. A. Kaufman, *Phys. Fluids* **6**:1574 (1963).
8. W. Heitler, *The Quantum Theory of Radiation*, Oxford University Press, London (1954), 3rd ed., pp. 38–53.
9. W. K. Panofsky and M. Phillips, *op. cit.*, p. 148.
10. W. K. Panofsky and M. Phillips, *op. cit.*, p. 119.