QUANTUM HYDRODYNAMICS

A STATISTICAL MECHANICAL THEORY OF LIGHT SCATTERING FROM SIMPLE NON-POLAR FLUIDS

Thesis by

Robert Walter Zwanzig

In Partial Fulfillment
for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1952

ACKNOWLEDGMENTS

I am deeply indebted to Professor John G. Kirkwood for many reasons. He introduced to me the beauties of modern statistical mechanics, and he instilled in me a proper respect for accuracy and rigor in theoretical research. He was patient with my faults and helpful in my difficulties, both of which were numerous. This work was performed under contract n6-onr-244 with the Office of Naval Research, under Professor Kirkwood's direction, and I am indeed grateful for the financial assistance that this offered me. Finally, I must acknowledge my debt to the other members of our theoretical chemistry group, and to the California Institute of Technology for providing the intellectual atmosphere necessary for this kind of work.

ABSTRACT

The first part of this thesis is concerned with certain extensions of a formal technique devised by Wigner for handling problems in quantum statistical mechanics, especially to problems in quantum mechanical transport processes. The approach is to find the closest possible analogy between classical and quantum statistical mechanics, so that the extensive work in classical statistical mechanics can be utilized. This analogy is attained with the Wigner distribution function, with which averages of dynamical variables in quantum mechanics may be calculated by integrations in phase space. We will first state some basic properties of distribution functions in classical statistical mechanics, and then state the corresponding properties of the density matrix in quantum mechanics. We will define and discuss the Wigner distribution function, show that it has the desired averaging properties, and obtain the analogue of the Liouville equation satisfied by this function. We will derive the analogue of the Liouville equation in reduced phase space, and then obtain the equations of hydrodynamics from quantum statistical mechanics. This will lead to expressions for the stress tensor and heat current density in terms of singlet and pair distribution functions.

In the second part of this thesis, the statistical mechanical theory of light scattering from fluids is developed. The model used consists of a collection of spherically symmetric, optically isotropic particles, which are capable of interacting both mechanically and electromagnetically. The effects of these interactions are included rigorously. This is done by using the radial distribution function for the spatial configuration of the particles, and the pair moment distribution function, which gives the dipole moment of a particle when it and another particle are fixed at specified positions, and the rest are averaged out. A chain of integral equations is set up, which is capable of giving the local field within the fluid. The index of refraction is then derived, with corrections to the Clausius-Mosotti formula. Finally, the light scattering cross section is obtained. This reduces to the result obtained with the Einstein-Smoluchowski theory in the proper limit, but contains corrections when the wavelength of the light is of the order of interparticle distances.

TABLE OF CONTENTS

QUANTUM HYDRODYNAMICS

QUANTUM HYDRODYNAMICS

I Distribution Functions in Classical Statistical Mechanics

Gibbsian statistical mechanics is based on the concept of a distribution of systems in phase space. His "density-in-phase" is now usually called the distribution function. (Hereafter, we will abbreviate this to d.f.) When normalized over the entire volume accessible to the system, it becomes the probability d.f, and gives the probability that the coordinates and momenta of a system of N particles will have the values $\vec{R}_1$, $\vec{R}_2$, ... $\vec{R}_N$, and $\vec{p}_1$, $\vec{p}_2$, ... $\vec{p}_N$. (When no confusion will result, we will refer to the sets of coordinates and momenta with single symbols $\vec{R}$, $\vec{p}$.) In equilibrium, for a canonical ensemble, the probability d.f has the form

$$f^{(N)}(\vec{R}, \vec{p}) = e^{\beta(A - H^{(N)})} \tag{1.1}$$

where A is the free energy of the system, and $H^{(N)}$ is the Hamiltonian function

$$H^{(N)} = \sum_{K=1}^{N} \frac{p_K^2}{2m_K} + U(\vec{R}_1, \ldots, \vec{R}_N) \tag{1.2}$$

In a nonequilibrium state, the time behavior of the d.f is given by Liouville's equation,

$$\frac{\partial f^{(N)}}{\partial t} + \sum_{K=1}^{N} \frac{\vec{p}_K}{m_K} \cdot \nabla_{R_K} f^{(N)} + \sum_{K=1}^{N} (\nabla_{R_K} U) \cdot \nabla_{p_K} f^{(N)} = 0 \tag{1.3}$$

Usually the potential is simplified to a sum of terms which refer to interactions between single particles and an external field, and other terms which refer to interactions between pairs of particles:

$$U(\vec{R}) = \sum_{K=1}^{N} \phi_K(\vec{R}_K) + \frac{1}{2}\sum_{j \neq K}^{N}\sum^{N} V_{jK}(\vec{R}_j, \vec{R}_K) \tag{1.4}$$

When this is done, reduced d.f's, and in particular the singlet and pair d.f become useful. The reduced d.f's are defined by

$$f^{(m)}(\vec{R}_1, .. \vec{R}_m, \vec{p}_1, .. \vec{p}_m ; t) = \int \cdots \int f^{(N)} \prod_{m+1}^{N} d^3\vec{R}_K \, d^3\vec{p}_K \tag{1.5}$$

and are called specific d.f's because they refer to the precise specification of each particle. Also used are the generic d.f's, which refer to the probability of finding any particle of the required type at a point in phase space. With the assumption of pair potentials many thermodynamic and transport properties of fluids can be expressed in terms of the singlet and pair d.f alone. An excellent discussion on the use of these d.f's in equilibrium statistical mechanics may be found in an article by DeBoer(1).

II Transition to Quantum Mechanics

It is not immediately clear how one should go about setting up the quantum mechanical analogue of classical Gibbsian statistical mechanics. The difficulty lies in the fact that the uncertainty principle prohibits the precise specification of the location of a system in phase space. Several approaches are possible in defining quantum mechanical d.f's. One of them is to use instead of the phase space technique, the matrix formulation of quantum mechanics, in which the analogue of the d.f is the density matrix. A second possibility is to construct a d.f which has no simple interpretation in terms of probability concepts, but which can be used for calculating averages over phase space in a way which is formally identical with the classical one. This is the procedure that was followed by Wigner(2) and which will be utilized later in this paper.*

The density matrix method can be developed in a very general way(3); however, it is usually used in the "coordinate" representation. This has been studied in great detail by Husimi(4) and by Born and Green(5). The density matrix is defined for a pure state as

$$\rho(\vec{R}, \vec{R}'; t) = \Psi^*(\vec{R}'; t)\, \Psi(\vec{R}; t) \tag{2.1}$$

where $\Psi(\vec{R}; t)$ is the wave function for the state of the system. When we deal with an ensemble of systems, or a mixed state, the density matrix has the form

$$\rho(\vec{R}, \vec{R}'; t) = \sum_j A_j\, \Psi_j^*(\vec{R}', t)\, \Psi_j(\vec{R}; t) \tag{2.2}$$

---

* Another possibility may be to use some kind of coarse-graining in phase space, so that one may talk about the probability of finding a system in a certain cell, possibly of volume h^{3N}, in phase space. This approach has not yet been used successfully.

where Ψ_j is the wave function and A_j is the statistical weight of the j'th state in the ensemble. The space d.f is given by $\rho(\vec{R}, \vec{R}; t)$ and reduced d.f's are defined in the usual way. Averages of dynamical variables are calculated as traces of matrix products: if $\alpha(\vec{R},\vec{R}')$ is the matrix associated with the variable α, then the average value of α is the trace of the matrix product of α and ρ,

$$\langle\alpha\rangle_{AV} = \iint \alpha(\vec{R}, \vec{R}')\rho(\vec{R}', \vec{R})\, d^3\vec{R}'\, d^3\vec{R} . \qquad (2.3)$$

This is the average over a state, if the system is in a pure state; or it is the ensemble average of the pure state averages, if the system is in a mixed state. Matrices are assigned to the basic variables in the following way -

coordinates:

$$\alpha(\vec{R}_1, \dots \vec{R}_N) \longrightarrow \alpha(\vec{R}_1, \dots \vec{R}_N) \prod_K \delta(\vec{R}_K - \vec{R}_K') \qquad (2.4)$$

momenta: $\vec{p}_j \longrightarrow -i\hbar \nabla_{R_j} \prod_K \delta(\vec{R}_K - \vec{R}_K')$.

For example, the Hamiltonian operator is

$$H^{(N)}(\vec{R}, \vec{R}') = \left\{ -\sum_j \frac{\hbar^2}{2m_j} \nabla^2_{R_j} + U(\vec{R}) \right\} \prod_K \delta(\vec{R}_K - \vec{R}_K') \qquad (2.5)$$

and Schrödinger's time dependent equation is

$$\frac{\partial\rho^{(N)}}{\partial t} = -\frac{i}{\hbar}\left\{ -\sum_K \frac{\hbar^2}{2m_K} \nabla^2_{R_K} \rho^{(N)} + \sum_K \frac{\hbar^2}{2m_K} \nabla^2_{R_K'} \rho^{(N)} + U(\vec{R})\rho^{(N)} - U(\vec{R}')\rho^{(N)} \right\}. \qquad (2.6)$$

(The superscript on ρ refers to the number of particles in the system.) This equation is the quantum mechanical analogue of the classical Liouville equation in the density matrix formalism. Born and Green$^{(5)}$ have made use of this in their method for setting up a quantum mechanical theory of transport processes.

In 1932, Wigner$^{(2)}$ showed how a phase space d.f could be constructed and used for simple evaluations of averages. This function is defined most conveniently in terms of the density matrix

$$f^{(N)}(\vec{R}, \vec{p}; t) = \left(\frac{1}{\hbar\pi}\right)^{3N} \int_{-\infty}^{+\infty} \cdots \int e^{\frac{2i}{\hbar}\vec{p}\cdot\vec{Y}} \rho^{(N)}(\vec{R}-\vec{Y}, \vec{R}+\vec{Y}; t)\, d^3\vec{Y} \qquad (2.7)$$

Some of the more important properties of the Wigner d.f are:

1) $f^{(N)}$ is everywhere real, though not necessarily positive.

2)
$$\int f^{(N)} d^3\vec{p} = \rho^{(N)}(\vec{R}, \vec{R}; t) \qquad (2.8)$$

so that the integral of the d.f over momentum space <u>does</u> give the probability density in configuration space.

3)
$$\int f^{(N)} d^2 \vec{R} = \sigma^{(N)}(p, p; t) \qquad (2.9)$$

where $\sigma^{(N)}(\vec{p}, \vec{p}'; t)$ is the momentum representation of the density matrix.* Therefore, the integral of the d.f over configuration space gives the probability density in momentum space.

4) $$\int \frac{\vec{p}_j}{m_j} f^{(N)} d^3\vec{p} = \frac{\hbar}{2i}\left\{\Psi^* \nabla_{R_j} \Psi - \Psi \nabla_{R_j} \Psi^*\right\} \qquad (2.10)$$

when $f^{(N)}$ represents the pure state Ψ . The right side is recognized as the standard expression for the probability current density in configuration space.

$$f^{(N)}(\vec{R}, \vec{p}; t) =$$

5) $$\left(\frac{1}{\pi\hbar}\right)^{3N} \int_{-\infty}^{+\infty}\!\!\cdots\!\int e^{-\frac{2i}{\hbar}\vec{R}\cdot\vec{p}\,'} \sigma^{(N)}(\vec{p}-\vec{p}\,', \vec{p}+\vec{p}\,'; t)\, d^3\vec{p}\,' \qquad (2.11)$$

which is an expression for $f^{(N)}$ dual to equation (2.7) where the roles of coordinates and momenta are changed, and i is replaced by -i.

6) Since the Wigner d.f is a bilinear form in Ψ , it is symmetric for both symmetric and anti-symmetric wave functions. However, it is possible to determine whether any particular d.f corresponds to a Bose-Einstein or a Fermi-Dirac system in this way: take the inverse Fourier transform of $f^{(N)}$ to obtain $\rho^{(N)}(\vec{R},\vec{R}')$ and then examine the symmetry of this function by interchanging either the primed or the unprimed quantities, but not both.

---

* $\sigma^{(N)}$ is not independent of $\rho^{(N)}$ because of the Fourier transform relation between coordinate and momentum representations of the wave function. This is a point of major difference between quantum mechanics and classical mechanics, where the probability densities in configuration and momentum space may be specified independently. This independence permits, for example, a factorization of the classical d.f for a canonical ensemble.

7) The great value of the Wigner d.f is that it is possible to calculate averages of dynamical variables by direct integration over phase space, without using operator technique. Although Wigner showed this only for some special kinds of variables, it gives the correct average for any function of coordinates and momenta, if the Weyl coorespondence(6,7) for quantum mechanical operators is used. This assignment of operators is made in the following way: if $g(\vec{p},\vec{q})$ is the classical variable whose operator is desired, we obtain its Fourier expansion ξ,

$$g(\vec{p},\vec{q})=\iint e^{i(\vec{\sigma}\cdot\vec{p}+\vec{\tau}\cdot\vec{q})}\,\xi(\vec{\sigma},\vec{\tau})\,d^3\vec{\sigma}\,d^3\vec{\tau} \qquad (2.12)$$

Then, the quantum mechanical operator is defined as

$$G(\vec{x},\vec{x}')=\iint e^{i(\vec{\sigma}\cdot\vec{P}+\vec{\tau}\cdot\vec{Q})}\,\xi(\vec{\sigma},\vec{\tau})\,d^3\vec{\sigma}\,d^3\tau \qquad (2.13)$$

where $\vec{P}\,(\vec{x},\vec{x}')$ and $\vec{Q}\,(\vec{x},\vec{x}')$ are the operators corresponding to momentum and position. We will now derive this averaging property of the Wigner d.f, using the coordinate representation of the density matrix. For simplicity in notation, only one dimension will be considered — the generalization is obvious. The operators P and Q are now

$$P=-i\hbar\frac{d}{dx}\,\delta(x-x') \quad ; \quad P^n=\left(-i\hbar\frac{d}{dx}\right)^n\delta(x-x')$$

$$Q=\quad x\,\delta(x-x') \quad ; \quad Q^n=\quad x^n\,\delta(x-x')$$

and the average value of g is

$$\langle g\rangle_{AV} = \iint\left\{\int G(x,x')\rho(x',x'')\,dx'\right\}\delta(x-x'')\,dx\,dx''$$

Substitute the expression for g into the integral, and use the following property(7) of the exponential operator

$$e^{i(\sigma P+\tau Q)} = e^{i\frac{\hbar\sigma\tau}{2}}e^{i\tau Q}e^{i\sigma P}$$

to get

$$\langle g\rangle_{AV} = \int\left[e^{i\frac{\hbar\sigma\tau}{2}}e^{i\tau Q}e^{i\sigma P}\rho(x',x'')\right]$$

$$\cdot\,\xi(\sigma,\tau)\,\delta(x-x'')\,dx'dx''dx\,d\sigma\,d\tau$$

then, the Taylor's series expansion property

$$e^{i\sigma P(x,x')}\rho(x',x'') = \rho(x'+\sigma\hbar,x'')\,\delta(x-x')$$

leads to

$$\langle g\rangle_{AV} = \int\left[e^{i\frac{\hbar\sigma\tau}{2}}e^{i\tau Q(x,x')}\rho(x'+\sigma\hbar,x'')\right]\xi(\sigma,\tau)$$

$$\cdot\,\delta(x-x')\,\delta(x-x'')\,dx\,dx'dx''\,d\sigma\,d\tau$$

and integration over x' and x" gives

$$\langle g\rangle_{AV} = \int e^{i\frac{\hbar\sigma\tau}{2}} e^{i\tau x}\rho(x+\sigma\hbar, x)\,\xi(\sigma,\tau)\,dx\,d\sigma\,d\tau.$$

Now replace $\xi(\sigma,\tau)$ by its expansion $g(p,q)$:

$$\langle g\rangle_{AV} = \left(\frac{1}{2\pi}\right)^2\int e^{i\frac{\hbar\sigma\tau}{2}} e^{i\tau x}\rho(x+\sigma\hbar, x) \cdot g(p,q)\,e^{-i(\sigma p+\tau q)}\,dx\,d\sigma\,d\tau\,dp\,dq.$$

Integrate over τ and then over x, using the Fourier theorem to get

$$\langle g\rangle_{AV} = \frac{1}{2\pi}\int e^{-i\sigma p}\,g(p,q)\,\rho\left(q+\frac{\hbar\sigma}{2}, q-\frac{\hbar\sigma}{2}\right)d\sigma\,dp\,dq.$$

Now, take $\frac{\hbar\sigma}{2} = -Y$, and

$$\langle g\rangle_{AV} = \frac{1}{\hbar\pi}\int e^{\frac{2i}{\hbar}pY}\,g(p,q)\,\rho(q-Y, q+Y)\,dp\,dq\,dY \tag{2.14}$$

or

$$\langle g\rangle_{AV} = \int g(p,q)\,f(p,q)\,dp\,dq$$

$$f(p,q) = \frac{1}{\hbar\pi}\int e^{\frac{2i}{\hbar}pY}\rho(q-Y, q+Y)\,dY \tag{2.15}$$

where f is the Wigner d.f for one dimension.

With this theorem, it should be possible to carry large parts of classical statistical mechanics into quantum mechanical language merely by changing the definition of the d.f.

This will be illustrated in this paper by deriving the equations of hydrodynamics.

The starting point for a statistical mechanical theory of transport processes in quantum mechanics is the analogue of the Liouville equation. The quantum mechanical equation of motion has already been given in the density matrix formalism, and can be used to get the equation of motion for Wigner's d.f. Although this is described in detail by Wigner$^{(2)}$ we will outline the derivation here. We replace $\vec{R}$ by $\vec{R}-\vec{Y}$ and $\vec{R}'$ by $\vec{R}+\vec{Y}$ in equation (2.6), multiply through by $\left(\frac{1}{\hbar\pi}\right)^{3N} \exp\left(\frac{2i\vec{p}\cdot\vec{Y}}{\hbar}\right)$ and integrate over $\vec{Y}$: This gives

$$\frac{\partial f^{(N)}}{\partial t} = -\frac{i}{\hbar}\left(\frac{1}{\pi\hbar}\right)^{3N} \sum_{K=1}^{N} \frac{\hbar^2}{2m_K} \int e^{\frac{2i\vec{p}\cdot\vec{Y}}{\hbar}} \Big[\nabla^2_{R_K+Y_K}\, \rho^{(N)}(\vec{R}-\vec{Y}, \vec{R}+\vec{Y})$$

$$- \nabla^2_{R_K-Y_K}\, \rho^{(N)}(\vec{R}-\vec{Y}, \vec{R}+\vec{Y})\Big]\, d^3\vec{Y}$$

$$-\frac{i}{\hbar}\left(\frac{1}{\hbar\pi}\right)^{3N} \int e^{\frac{2i\vec{p}\cdot\vec{Y}}{\hbar}} \left[U(\vec{R}-\vec{Y}) - U(\vec{R}+\vec{Y})\right] \rho^{(N)}(\vec{R}-\vec{Y}, \vec{R}+\vec{Y})\, d^3\vec{Y}.$$

The kinetic energy contributions can be integrated by parts,

$$\sum_{K=1}^{N} \frac{\hbar^2}{2m_K} \frac{i}{\hbar}\left(\frac{1}{\hbar\pi}\right)^{3N} \int e^{\frac{2i\vec{p}\cdot\vec{Y}}{\hbar}} \left[\nabla^2_{R_K+Y_K}\, \rho^{(N)} - \nabla^2_{R_K-Y_K}\, \rho^{(N)}\right] d^3\vec{Y}$$

$$= \sum_{K=1}^{N} \frac{\vec{p}_K}{m_K}\cdot\nabla_{R_K}\, f^{(N)}(\vec{R}, \vec{p}\,; t) \qquad (2.16)$$

which is identical in form with the classical result. The potential energy contribution is

$$\theta\cdot f^{(N)} = \frac{i}{\hbar}\left(\frac{1}{\hbar\pi}\right)^{3N}\int\left[U(\vec{R}-\vec{Y}) - U(\vec{R}+\vec{Y})\right] \cdot e^{\frac{2i}{\hbar}\vec{p}\cdot\vec{Y}}\rho^{(N)}(\vec{R}-\vec{Y},\ \vec{R}+\vec{Y};t)\,d^3\vec{Y} \tag{2.17}$$

and the equation of motion can be written

$$\frac{\partial f^{(N)}}{\partial t} + \sum_{K=1}^{N}\frac{\vec{p}_K}{m_K}\cdot\nabla_{R_K} f^{(N)} + \theta\cdot f^{(N)} = 0 \tag{2.18}$$

The potential dependent term can be put into several different forms, involving integral or differential operators. If we define the kernel

$$K(\vec{R},\vec{p}-\vec{p}\,') = \frac{i}{\hbar}\left(\frac{1}{\hbar\pi}\right)^{3N}\int_{-\infty}^{+\infty}\left[U(\vec{R}-\vec{X}) - U(\vec{R}+\vec{X})\right]e^{\frac{2i}{\hbar}\vec{p}\cdot\vec{Y}}\,d^3\vec{X} \tag{2.19}$$

then this term is

$$\theta\cdot f^{(N)} = \int_{-\infty}^{+\infty}K(\vec{R},\vec{p}-\vec{p}\,')\,f^{(N)}(\vec{R},\vec{p}\,';t)\,d^3\vec{p}\,' \tag{2.20}$$

Another possible form is

$$\theta\cdot f^{(N)} = \frac{i}{\hbar}\left(\frac{1}{\hbar\pi}\right)^{3N}\iint\left[f^{(N)}(\vec{R},\vec{p}-\vec{p}\,') - f^{(N)}(\vec{R},\vec{p}+\vec{p}\,')\right]e^{\frac{2i}{\hbar}\vec{p}\,'\cdot(\vec{R}-\vec{X})}\,U(\vec{X})\,d^3\vec{X}\,d^3\vec{p}\,' \tag{2.21}$$

The corresponding differential operator forms are

$$\theta\cdot f^{(N)} = \frac{i}{\hbar}\left[U\left(\vec{R}-\frac{\hbar}{2i}\nabla_p\right) - U\left(\vec{R}+\frac{\hbar}{2i}\nabla_p\right)\right]f^{(N)}(\vec{R},\vec{p};t) \tag{2.22}$$

$$\theta\cdot f^{(N)} = \frac{i}{\hbar}\left[f^{(N)}\left(\vec{R},\vec{p}-\frac{\hbar}{2i}\nabla_R\right) - f^{(N)}\left(\vec{R},\vec{p}+\frac{\hbar}{2i}\nabla_R\right)\right]U(\vec{R}) \tag{2.23}$$

and may be summarized in a convenient formal way:

$$\Theta \cdot f^{(N)} = -\frac{2}{\hbar} \sin\left[\frac{\hbar}{2} \nabla_R \nabla_p\right] U(\vec{R}) f^{(N)}(\vec{R}, \vec{p}) \qquad (2.24)$$

where ∇_R must operate on the potential only. The series expansion of this is the form that Wigner obtained originally. It shows that the quantum mechanical equation of motion differs from the classical one only in second and higher even powers of $\hbar$. For a system of harmonic oscillators the quantum mechanical and classical equations are identical.

If the potential can be expressed as a sum of pair potentials and an external part,

$$U = \sum_{i=1}^{N} \phi_i(\vec{R}_i) + \frac{1}{2} \sum_{i \neq j}^{N} \sum^{N} V_{ij}(\vec{R}_i, \vec{R}_j)$$

then the operator forms can be written in the same way,

$$\Theta \cdot f^{(N)} = \sum_{i=1}^{N} \Theta_i^{(e)} \cdot f^{(N)} + \frac{1}{2} \sum_{i \neq j}^{N} \sum^{N} \Theta_{ij} \cdot f^{(N)} \qquad (2.25)$$

where $\Theta_i^{(e)}$ is the operator corresponding to the i'th part of external potential and Θ_{ij} is the operator corresponding to the pair potential, V_{ij}.

The reduced equations of motion are analogous to the classical ones, with the correspondence of Θ_i in quantum mechanics to $-(\nabla_R U) \cdot \nabla_p$ in the classical case. The equation of motion for the set of particles $\underline{n}$ is obtained by integrating the equation of motion for the entire set $\underline{N}$ over the coordinates and momenta of the set $\underline{N-n}$. We restrict the discussion to the distributions for which the surface integrals of the currents vanish on the boundary of the phase space accessible to the system, so that Green's theorem may be used:

$$f^{(n)}(\vec{r},\vec{p}) = \iint f^{(N)}(\vec{r},\vec{p};\vec{R},\vec{P})\,d^3\vec{R}\,d^3\vec{P}$$

$$\frac{\partial f^{(n)}}{\partial t} + \sum_{i=1}^{n} \frac{\vec{p}_i}{m_i}\cdot\nabla_{R_i} f^{(n)} + \sum_{i=1}^{n} \theta_i^{(e)}\cdot f^{(n)} = -X^{(n)} \tag{2.26}$$

$$X^{(n)} = \iint \Big\{ \sum_{i=n+1}^{N} \theta_i^{(e)}\cdot f^{(N)} + \frac{1}{2}\sum_{i\neq j=1}^{N}\sum^{N} \theta_{ij}\cdot f^{(N)} \Big\}\,d^3\vec{R}\,d^3\vec{P}$$

where $\vec{r}$, $\vec{p}$ refer to the set *n* and $\vec{R}$, $\vec{P}$ refer to the set *N-n*. The first part of the integral vanishes by integration over $\vec{P}$. The second part can be split up into three groups of terms, one containing terms referring to pair interactions for which both particles are in the set *n*, another in which one particle is in set *n* and the other is in set *N-n*, and the third in which both particles are in set *N-n*:

$$X^{(n)} = \frac{1}{2}\sum_{i\neq j=1}^{n}\sum^{n}\iint \theta_{ij}\cdot f^{(N)}\,d^3\vec{R}\,d^3\vec{P} + \sum_{i=1}^{n}\sum_{j=n+1}^{N}\iint \theta_{ij}\cdot f^{(N)}\,d^3\vec{R}\,d^3\vec{P}$$

$$+\ \frac{1}{2}\sum_{i\neq j=n+1}^{N}\sum^{N}\iint \theta_{ij}\cdot f^{(N)}\,d^3\vec{R}\,d^3\vec{P}$$

The third group of terms vanish by integration over $\vec{P}$, the first group integrates obviously, and the second group leads to integrals involving $f^{(n+1)}$:

$$X^{(n)} = \frac{1}{2}\sum_{i\neq j=1}^{n}\sum^{n} \theta_{ij}\cdot f^{(n)} + \sum_{i=1}^{n}\sum_{j=n+1}^{N} X_{ij}^{(n)} \tag{2.27}$$

$$X_{ij}^{(n)} = \iint \theta_{ij} \cdot f^{(n+1)}(\vec{r}, \vec{p}\,;\, \vec{R}_j, \vec{P}_j\,;\, t)\, d^3\vec{R}_j\, d^3\vec{P}_j$$

Equations (2.26) and (2.27) contain the reduced Liouville equation in quantum statistical mechanics. The specialization to the equation for the singlet d.f is given here as an illustration:

$$\frac{\partial f^{(1)}}{\partial t} + \frac{\vec{p}_1}{m_1} \cdot \nabla_{R_1} f^{(1)} + \theta_1^{(e)} \cdot f^{(1)}$$

$$= -\sum_{j=2}^{N} \iint \theta_{ij} \cdot f^{(2)}(\vec{R}_1, \vec{R}_j, \vec{p}_1, \vec{p}_j\,;\, t)\, d^3\vec{R}_j\, d^3\vec{p}_j \tag{2.28}$$

III The Equations of Hydrodynamics

In this section, we will show how the equations of hydrodynamics can be derived in quantum statistical mechanics. In particular, we will show that the derivations and results are formally identical with those obtained by Irving and Kirkwood$^{(8)}$. Their derivations have been given in great detail, and there is no need to duplicate them here. The goal of the following discussion is a statement of the equations of hydrodynamics in a form which involves all N particles in the system. The remainder of the derivation consists in reducing these equations to a form which involves singlet and pair d.f's, and may be found in the paper of Irving and Kirkwood. The notation used here will be the same as their's.

The equations of hydrodynamics are obtained by calculating the time derivatives at a point of the fluid of the mass density, the momentum density, and the energy density. For this purpose, the following results are useful. If $\alpha(\vec{R},\vec{p})$ is a dynamical variable, the average of α is

$$\begin{aligned}\langle\alpha\rangle_{AV} &\equiv \left\langle \alpha(\vec{R},\vec{p})\,;\, f^{(N)}(\vec{R},\vec{p};t)\right\rangle \\ &= \int \alpha(\vec{R},\vec{p})\, f^{(N)}(\vec{R},\vec{p};t)\, d^3\vec{R}\, d^3\vec{p}\end{aligned} \tag{3.1}$$

and if α is not an explicit function of the time,

$$\frac{\partial\langle\alpha\rangle_{AV}}{\partial t} = \left\langle \alpha(\vec{R},\vec{p})\,;\, \frac{\partial}{\partial t} f^{(N)}(\vec{R},\vec{p};t)\right\rangle \tag{3.2}$$

When we use the analogue of Liouville's theorem in this expression, we get

$$\frac{\partial\langle\alpha\rangle_{AV}}{\partial t} = -\left\langle \alpha\,;\sum_{K=1}^{N} \frac{\vec{p}_K}{m_K}\cdot\nabla_{R_K} f^{(N)}\right\rangle - \left\langle \alpha\,;\,\theta\cdot f^{(N)}\right\rangle \tag{3.3}$$

The first term is identical with the classical one, and can be transformed with Green's theorem to

$$\left\langle \alpha\,;-\sum_{k=1}^{N} \frac{\vec{p}_K}{m_K}\cdot\nabla_{R_K} f^{(N)}\right\rangle = \left\langle \sum_{K=1}^{N} \frac{\vec{p}_K}{m_K}\cdot\nabla_{R_K}\alpha\,;\, f^{(N)}\right\rangle \tag{3.4}$$

The other term is (using equation (2.21))

$$\left\langle \alpha\,;\,\theta\cdot f^{(N)}\right\rangle = \frac{i}{\hbar}\left(\frac{1}{\hbar\pi}\right)^{3N}\iint \alpha(\vec{R},\vec{p})\left\{ f^{(N)}(\vec{R},\vec{p}-\vec{p}\,') - f^{(N)}(\vec{R},\vec{p}+\vec{p}\,')\right\} e^{\frac{2i}{\hbar}\vec{p}\,'\cdot(\vec{R}-\vec{R}\,')}\, U(\vec{R}\,')\, d^3\vec{R}\, d^3\vec{p}\, d^3\vec{R}\,'\, d^3\vec{p}\,'$$

and when $\vec{p}-\vec{p}'$ is replaced by $\vec{p}$ in the first term of the integral, and $\vec{p}+\vec{p}'$ is replaced by $\vec{p}$ in the second term (the limits remaining from minus infinity to plus infinity), we get

$$\langle \alpha ; \theta \cdot f^{(N)} \rangle = \langle A ; f^{(N)} \rangle$$

$$A = \frac{i}{\hbar}\left(\frac{1}{\hbar\pi}\right)^{3N} \iint \left\{ \alpha(\vec{R}, \vec{p}+\vec{p}') - \alpha(\vec{R}, \vec{p}-\vec{p}') \right\} \tag{3.5}$$

$$\cdot\, e^{\frac{2i}{\hbar}\vec{p}'\cdot(\vec{R}-\vec{R}')}\, U(\vec{R}')\ d^3\vec{R}'\, d^3\vec{p}'$$

This can also be put into operator form,

$$A = \frac{i}{\hbar}\left\{ \alpha\left(\vec{R}, \vec{p}+\frac{\hbar}{2i}\nabla_R\right) - \alpha\left(\vec{R}, \vec{p}-\frac{\hbar}{2i}\nabla_R\right) \right\} U(\vec{R}) \tag{3.6}$$

If we expand this as a series in $\hbar$ and take the limit as $\hbar$ approaches zero, the classical result is obtained. A more useful result is this: if α is of the form

$$\alpha = \alpha_1(\vec{R}) + \sum_{k=1}^{N} \alpha_{2k}(\vec{R})\, \vec{p}_k + \sum_{j=1}^{N}\sum_{k=1}^{N} \alpha_{3jk}(\vec{R})\, \vec{p}_j \cdot \vec{p}_k \tag{3.7}$$

this leads by a simple substitution to the equation for the rate of change of the average value of this special α :

$$\frac{\partial \langle \alpha \rangle_{AV}}{\partial t} = \sum_{k=1}^{N} \left\langle \frac{\vec{p}_k}{m_k} \cdot \nabla_{R_k} \alpha_1 ; f^{(N)} \right\rangle$$

$$+ \sum_{k=1}^{N}\sum_{j=1}^{N} \left\langle \frac{\vec{p}_j\, \vec{p}_k}{m_k} \cdot \nabla_{R_k} \alpha_{2j} ; f^{(N)} \right\rangle \tag{3.8}$$

$$+ \sum_{k=1}^{N} \left\langle \alpha_{2k} (\nabla_{R_k} U) ; f^{(N)} \right\rangle +$$

$$+\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{K=1}^{N}\left\langle \vec{p}_i\cdot\vec{p}_j\,\frac{\vec{p}_K}{m_K}\cdot\nabla_{R_K}\,\alpha_{3ij}\;;\;f^{(N)}\right\rangle$$

$$+\sum_{j=1}^{N}\sum_{K=1}^{N}\left\langle \alpha_{3jK}\left(\vec{p}_j\cdot\nabla_{R_K}U+\vec{p}_K\cdot\nabla_{R_j}U\right);\;f^{(N)}\right\rangle$$

which differs from the corresponding classical equation only in the definition of the d.f. It can also be shown that higher terms in the expansion of α in powers of $\vec{p}$ will lead to expressions differing in form from the classical ones.

As a special case of this theorem, take the following values of -

$$\alpha_d=\sum_{K=1}^{N} m_K\,\delta(\vec{R}_K-\vec{r})$$

$$\vec{\alpha}_m=\sum_{K=1}^{N}\vec{p}_K\,\delta(\vec{R}_K-\vec{r})$$

$$\alpha_E=\sum_{K=1}^{N}\left\{\frac{p_K^2}{2m_K}+\phi_K(\vec{R}_K)+\frac{1}{2}\sum_{\substack{i=1\\ \neq j}}^{N}V_{iK}(\vec{R}_i,\vec{R}_K)\right\}\delta(\vec{R}_K-\vec{r}) \tag{3.9}$$

These quantities define the mass density, the momentum density, and the energy density:

$$\rho(\vec{r};t)=\left\langle \alpha_d\;;\;f^{(N)}\right\rangle \tag{3.10}$$

$$\rho(\vec{r};t)\,\vec{u}(\vec{r};t)=\left\langle \vec{\alpha}_m\;;\;f^{(N)}\right\rangle \tag{3.11}$$

$$E(\vec{r};t)=\left\langle \alpha_E\;;\;f^{(N)}\right\rangle \tag{3.12}$$

and lead to the equations of continuity, momentum transport, and energy transport respectively:

$$\frac{\partial \rho(\vec{r};t)}{\partial t} = -\nabla_r \cdot \left[\rho(\vec{r};t)\,\vec{u}(\vec{r};t)\right], \tag{3.13}$$

$$\begin{aligned}\frac{\partial}{\partial t}\left[\rho(\vec{r};t)\,\vec{u}(\vec{r};t)\right] = &-\nabla_r \cdot \sum_{K=1}^{N} \left\langle \frac{\vec{p}_K \vec{p}_K}{m_K}\,\delta(\vec{R}_K-\vec{r})\,;\, f^{(N)} \right\rangle \\ &- \sum_{j\neq K=1}^{N}\sum^{N} \left\langle \left(\nabla_{R_K} V_{jK}\right) \delta(\vec{R}_K-\vec{r})\,;\, f^{(N)} \right\rangle \\ &- \sum_{K=1}^{N} \left[\nabla_r\, \phi_K(\vec{r})\right] \left\langle \delta(\vec{R}_K-\vec{r})\,;\, f^{(N)} \right\rangle,\end{aligned} \tag{3.14}$$

$$\begin{aligned}\frac{\partial E(\vec{r};t)}{\partial t} = -\nabla_r \cdot \Bigg[&\sum_{K=1}^{N} \left\langle \frac{p_K^2}{2m_K}\,\frac{\vec{p}_K}{m_K}\,\delta(\vec{R}_K-\vec{r})\,;\, f^{(N)} \right\rangle \\ &+ \sum_{K=1}^{N} \phi_K(\vec{r}) \left\langle \frac{\vec{p}_K}{m_K}\,\delta(\vec{R}_K-\vec{r})\,;\, f^{(N)} \right\rangle \\ &+ \frac{1}{2}\sum_{j\neq K=1}^{N}\sum^{N} \left\langle V_{jK}\,\frac{\vec{p}_K}{m_K}\,\delta(\vec{R}_K-\vec{r})\,;\, f^{(N)} \right\rangle \Bigg] \\ &+ \frac{1}{2}\sum_{j\neq K=1}^{N}\sum^{N} \left\langle \left(\nabla_{R_K} V_{jK}\right)\cdot \frac{\vec{p}_K}{m_K} \left[\delta(\vec{R}_j-\vec{r}) - \delta(\vec{R}_K-\vec{r})\right]; f^{(N)} \right\rangle.\end{aligned} \tag{3.15}$$

These results have the same form as the classical ones, as obtained by Irving and Kirkwood(8), although the d.f is of course determined by the laws of quantum mechanics. The remainder of their derivation consists in transforming these equations into the form in which the stress tensor and heat current density are given in terms of singlet and pair d.f's and the potential of intermolecular force. Since these transformations are identical with those of the classical case, they will not be repeated here. We will now state the results of these calculations. The microscopically correct hydrodynamical equations are the continuity equation:

$$\frac{\partial \rho}{\partial t} = - \nabla_r \cdot [\rho \vec{u}] \tag{3.13'}$$

the equation of motion (momentum transport equation):

$$\frac{\partial}{\partial t}(\rho \vec{u}) = - \nabla_r \cdot [\rho \vec{u} \vec{u}] + \vec{X} + \nabla_r \cdot \underset{\sim}{\sigma} \tag{3.14'}$$

and the energy transport equation

$$\frac{\partial E}{\partial t} = - \nabla_r \cdot \left[E \vec{u} + \vec{q} - \vec{u} \cdot \underset{\sim}{\sigma} \right] \tag{3.15'}$$

The quantities appearing in the above equations are defined as follows:

$$\rho(\vec{r};t) = \sum_{k=1}^{N} \left\langle m_k \, \delta(\vec{R}_k - \vec{r}) ; f^{(N)} \right\rangle \tag{3.10}$$

is the mass density at $\vec{r}$.

$$\vec{u}(\vec{r};t) = \frac{1}{\rho}\sum_{K=1}^{N}\left\langle \vec{p}_K\,\delta(\vec{R}_K-\vec{r})\,;\, f^{(N)}\right\rangle \tag{3.11}$$

is the mean molecular velocity (fluid velocity) at $\vec{r}$.

$$\vec{X}(\vec{r};t) = -\sum_{K=1}^{N}\left[\nabla_r\,\phi_K(\vec{r})\right]\left\langle \delta(\vec{R}_K-\vec{r})\,;\, f^{(N)}\right\rangle \tag{3.16}$$

is the body force per unit volume due to external fields at $\vec{r}$.

$$E(\vec{r};t) = E_K + E_\phi + E_V \tag{3.17}$$

is the internal energy density at $\vec{r}$, where

$$E_K(\vec{r};t) = \sum_{K=1}^{N}\left\langle \frac{p_K^2}{2m_K}\,\delta(\vec{R}_K-\vec{r})\,;\, f^{(N)}\right\rangle \tag{3.18}$$

is the kinetic energy density,

$$E_\phi(\vec{r};t) = \sum_{K=1}^{N}\phi_K(\vec{r})\left\langle \delta(\vec{R}_K-\vec{r})\,;\, f^{(N)}\right\rangle \tag{3.19}$$

is the potential energy density associated with external fields, and

$$E_V(\vec{r};t) = \frac{1}{2}\sum_{\substack{j\neq K\\=1}}^{N}\sum^{N}\left\langle V_{jK}\,\delta(\vec{R}_K-\vec{r});\, f^{(N)}\right\rangle \tag{3.20}$$

is the potential energy density due to molecular interaction. (In defining E_V it is assumed that the potential energy of interaction between two molecules is localized half at each molecule.)

These definitions are completely general. The other quantities, however, appearing in the above hydrodynamical equations, $\underset{\sim}{\sigma}$ and $\vec{q}$, have been defined only for a single component, single phase system in which the intermolecular force is central, depending on range only. Their definitions follow.

$$\underset{\sim}{\sigma}(\vec{r};t) = \underset{\sim}{\sigma}_K + \underset{\sim}{\sigma}_V \qquad (3.21)$$

is the stress tensor at $\vec{r}$, where

$$\underset{\sim}{\sigma}_K = -\sum_{K=1}^{N} m \left\langle \left(\frac{\vec{p}_K}{m} - \vec{u}\right)\left(\frac{\vec{p}_K}{m} - \vec{u}\right)\delta(\vec{R}_K - \vec{r})\,;\, f^{(N)} \right\rangle \qquad (3.22)$$

is the kinetic contribution to the stress tensor, and

$$\underset{\sim}{\sigma}_V = \frac{1}{2}\int \frac{\vec{R}\,\vec{R}}{|R|} V'(R)\left\{1 - \frac{1}{2}\vec{R}\cdot\nabla_r + \cdots\right\} \times \rho^{(2)}(\vec{r}, \vec{r} + \vec{R}; t)\, d^3\vec{R} \qquad (3.23)$$

is the intermolecular force contribution to the stress tensor.

$$\vec{q}(\vec{r};t) = \vec{q}_K + \vec{q}_V \qquad (3.24)$$

is the heat current density at $\vec{r}$, where

$$\vec{q}_K = \sum_{K=1}^{N} \left\langle \frac{m}{2}\left|\frac{\vec{p}_K}{m}-\vec{u}\right|^2 \left(\frac{\vec{p}_K}{m}-\vec{u}\right) \delta(\vec{R}_K-\vec{r})\,;\, f^{(N)} \right\rangle \tag{3.25}$$

is the heat current due to transport of thermal kinetic energy, and

$$\begin{aligned} \vec{q}_V = &-\frac{1}{2}\,\vec{u}\cdot\int\left[V(R)\vec{1} - \frac{\vec{R}\vec{R}}{R}V'(R)\left\{1-\frac{1}{2}\vec{R}\cdot\nabla_r+\cdots\right\}\right] \\ &\qquad \times\rho^{(2)}(\vec{r},\vec{r}+\vec{R};t)\,d^3\vec{R} \\ &+\frac{1}{2}\int\left[V(R)\vec{1} - \frac{\vec{R}\vec{R}}{R}V'(R)\left\{1-\frac{1}{2}R\cdot\nabla_r+\cdots\right\}\right] \\ &\qquad \cdot\,\vec{j}_1^{(2)}(\vec{r},\vec{r}+\vec{R},t)\,d^3\vec{R} \end{aligned} \tag{3.26}$$

is the contribution to the heat current density by molecular interaction.

In the definitions of $\underset{\sim}{\sigma}_V$ and $\vec{q}_V$ the following quantities appear:

$$\rho^{(2)}(\vec{r},\vec{r}\,';t) = \sum_{j\neq K}^{N}\sum^{N} \left\langle \delta(\vec{R}_j-\vec{r})\,\delta(\vec{R}_K-\vec{r}\,')\,;\, f^{(N)}\right\rangle \tag{3.27}$$

is the pair density at $\vec{r}$ and $\vec{r}\,'$, the probability per (unit volume)^2 that one particle (any particle) will be at $\vec{r}$ and another at $\vec{r}\,'$.

$$\vec{j}_1^{(2)} = \sum_{j\neq K}^{N}\sum^{N} \left\langle \frac{\vec{p}_K}{m_K}\,\delta(\vec{R}_K-\vec{r})\,\delta(\vec{R}_j-\vec{r}\,')\,;\, f^{(N)}\right\rangle \tag{3.28}$$

is the projection onto the space of $\vec{r}$ of the particle current density at $\vec{r}$, $\vec{r}\,'$ in pair space, and is the particle current density at $\vec{r}$ if another particle is at $\vec{r}\,'$ multiplied by the particle density at $\vec{r}\,'$.

The differential operator, ∇_r , occurring in the definitions of $\underset{\sim}{\sigma}_V$ and $\vec{q}_V$ operates on $\rho^{(2)}(\vec{r},\vec{r}+\vec{R};t)$ and $\vec{j}_1^{(2)}(\vec{r},\vec{r}+\vec{R};t)$ with $\vec{R}$ held fixed. Since in the interior of a fluid $\rho^{(2)}$ and $\vec{j}_1^{(2)}$ are slow functions of $\vec{r}$ (holding $\vec{R}$ fixed), changing negligibly for $\vec{r}$ varying by a displacement whose length is of the order of the "range" of intermolecular forces, all terms beyond the first may be neglected in the brace appearing in the definitions of $\underset{\sim}{\sigma}_V$ and $\vec{q}_V$. This yields the simplified expressions:

$$\underset{\sim}{\sigma}_V(\vec{r};t)=\frac{1}{2m^2}\Big[\rho(\vec{r};t)\Big]^2\int\frac{\vec{R}\vec{R}}{R}V'(R)\,g^{(2)}(\vec{r},\vec{R};t)\,d^3\vec{R} \tag{3.29}$$

$$\vec{q}_V(\vec{r};t)=\frac{1}{2}\int\Big[V(R)\vec{1}-\frac{\vec{R}\vec{R}}{R}V'(R)\Big]\cdot\Big[\vec{j}_1^{(2)}(\vec{r},\vec{r}+\vec{R};t)$$

$$-\vec{u}(\vec{r};t)\rho^{(2)}(\vec{r},\vec{r}+\vec{R};t)\,d^3\vec{R} \tag{3.30}$$

where the correlation function $g^{(2)}$ is defined by

$$\rho^{(2)}(\vec{r},\vec{r}+\vec{R};t)=\frac{1}{m^2}\rho(\vec{r};t)\rho(\vec{r}+\vec{R};t)\,g^{(2)}(\vec{r},\vec{R};t) \tag{3.31}$$

The pressure is defined by

$$P(\vec{r};t)=-\frac{1}{3}\,\mathrm{Tr}\Big\{\underset{\sim}{\sigma}(\vec{r};t)\Big\} \tag{3.32}$$

In an ensemble which is in equilibrium, the pressure is

$$P = \frac{2}{3}\sum_{k=1}^{N}\left\langle \frac{p_k^2}{2m}\,\delta(\vec{R}_k-\vec{r})\,;\,f^{(N)}\right\rangle$$

$$-\frac{2\pi}{3}\left(\frac{\rho}{m}\right)^2\int_0^\infty R^3\,V'(R)\,g^{(2)}(R)\,dR \tag{3.33}$$

(In deriving the stress tensor, it is assumed that $\vec{R}\cdot\nabla_r\,\rho^{(2)}$ is negligible. In the absence of external forces, and with the neglect of surface effects, this assumption is justified.) We cannot replace the average kinetic energy by 3kT/2, because this is now a quantum mechanical system. Thus, the temperature enters into the equation in an implicit way. This is the quantum mechanical equation of state that has been obtained by Born and Green(5) using the virial theorem and by DeBoer(1) using statistical thermodynamics. There is some ambiguity in the derivation presented here, for the following reason: the stress tensor obtained by this method is undetermined up to an arbitrary tensor of vanishing divergence. This arbitrary tensor may not necessarily have a vanishing trace, and may therefore contribute to the pressure. In the classical case, Irving and Kirkwood(8) showed that the definition used here in terms of the d.f is consistent with the physical picture involving the force "acting across" a unit area. This definition may be used in the quantum mechanical case, but is still arbitrary.

IV Conclusions

The equations of hydrodynamics have been derived from quantum statistical mechanics, and contain microscopically correct expressions for the stress tensor and heat current density of a quantum fluid. These expressions are identical with the classical ones, except in the specification of the distribution function, which must be obtained using some quantum mechanical theory. Born and Green(5) have obtained similar expressions in the density matrix formalism. Their efforts to apply these expressions to the problem of liquid helium II have not been entirely successful. What is needed is a logical procedure for terminating the chain of reduced equations of motion, so that $f^{(2)}$ can be evaluated with fair accuracy. This may take the form of a quantum mechanical analogue of the theory of Brownian motion developed by Kirkwood(9), or some other way of introducing the irreversibility of hydrodynamic effects. When such a theory is available, it should be possible to construct a rigorous molecular theory of quantum superfluids.

REFERENCES

1. J. DeBoer, Reports on Progress in Physics XII, pp. 305-374 (1948-9).
2. E. P. Wigner, Phys. Rev. 40, 749 (1932).
3. J. Von Neumann, Mathematische Grundlage der Quantenmechanik, Dover
4. K. Husimi, Proc. Phys. - Math. Soc. Japan, 22, 264 (1940).
5. M. Born and H. S. Green, A General Kinetic Theory of Liquids, Cambridge Press (1949).
6. H. Weyl, The Theory of Groups and Quantum Mechanics, London, p. 274.
7. N. H. McCoy, Proc. Nat. Acad. Sci. 18, 674 (1932).
8. J. H. Irving and J. G. Kirkwood, J. Chem. Phys. 18, 817 (1950).
9. J. G. Kirkwood, J. Chem. Phys., 14, 180 (1946).

A STATISTICAL MECHANICAL THEORY OF LIGHT SCATTERING FROM SIMPLE NON-POLAR FLUIDS

A STATISTICAL MECHANICAL THEORY OF LIGHT SCATTERING FROM SIMPLE NON-POLAR FLUIDS

I Introduction

In the last few years, the technique of light scattering has become a valuable tool for the study of the size and shape of macromolecules. The theory of light scattering is a strange intermingling of statistical and phenonemonological, discrete and continuum ideas. In this thesis, a completely statistical mechanical theory of a very simple model is discussed. The purpose is not so much to produce experimentally meaningful results as it is to clarify various aspects of the existing theory and to develop methods for extending the statistical theory to more useful cases.

When a beam of light (which will be used hereafter to refer to electromagnetic radiation of any wavelength, visible or otherwise) propagates through matter, some of the light is scattered away from the direction of propagation. This scattering arises in a quantum mechanical theory in the following way: the time-dependent perturbation due to the electromagnetic field causes transitions between quantum states of the system, from states of lower to states of higher energy, and reverse transitions occur, releasing the extra energy as light. In a cruder theory, the field induces dipole and higher moments in the distribution of electrons in the atoms and molecules, and these oscillating moments re-radiate light. The intensity, angular distribution, polarization, and possible fine structure of the scattered light are determined by the properties of the incident light and by the properties and distribution of the atoms and molecules in the system. The reverse of this statement is true, within certain limits. Some of the atomic and molecular properties, and some information about the distribution of the atoms and molecules can be obtained from a study of the properties of the scattered light.

A complete quantum mechanical theory is impractically complicated for systems of interest to chemists. The approximations that must be made are dictated by what kind of information one wants. The experimental situations which are most common, and to which the theory must pay special attention are these:

1) The system consists of a small number of components, each of which is a relatively simple molecule, in a solid or fluid phase. The properties of the individual atoms are assumed to be known. X-rays are used, and the distribution of the atoms in each molecule, and of the molecules in the solid or liquid is desired. This situation, with solid phases, has been of interest for many years; with liquid phases, it has become of importance only recently.

2) The system consists of a liquid solution, one of whose components is a solvent of simple and known structure. The other components are usually large complicated molecules, about which little is known. Visible light is used, and the size and shape of these molecules is desired. This problem

is more complicated than that of situation (1), but less information is desired.

The theory of the diffraction of x-rays from liquids and solids (situation (1)) has been worked out in fairly great detail. The approximations which are necessary here are usually quite satisfactory, and the theory works rather well. Perhaps the biggest stumbling block at present in the theory of x-ray scattering from liquids is the lack of detailed knowledge about the scattering from individual atoms. The existing theory of light scattering from solutions of macromolecules (situation (2)) is different. It works well enough to encourage experimentalists to use it, but the validity of some of the approximations used in the derivation of this theory is doubtful. Unfortunately, these approximations are made at the very beginning of the derivations, and cannot be amended in a convenient way. For this reason, an investigation of the theory of light scattering was undertaken for the simplest possible physically meaningful case, a single component liquid composed of spherically symmetric, optically isotropic particles. Every effort was made to keep the development of this theory as rigorous as possible. The interest in the theory lies not only in the actual results, but also in the methods. Methods were developed with an eye toward possible extensions to multicomponent solutions, optically anisotropic molecules, and so on.

In the course of this research, it was necessary to work out a theory of the dielectric constant or index of refraction of a liquid of spherically symmetric, optically isotropic molecules. This is also capable of extension to more complicated cases.

II Historical Background

Theoretical discussions of light scattering may be classed into several groups. These are

1) scattering by a single particle,
2) scattering by a collection of independent particles,
3) scattering by a collection of dependent particles.

The third group is of greatest interest here. The existing theories of scattering are based largely on a result obtained for group two, which in turn rests directly upon several results in group one. Most of the material in this survey of the literature of light scattering was obtained from a review article by Oster(1), which contains a gratifying amount of detail. For this reason, no attempt will be made to carry out a thorough study of the literature here.

The scattering of light by a simple atom or molecule may be studied quantum mechanically. Except in the theory of x-ray scattering, no one ever does this, and even in this case a classical approximation is made. For complicated molecules, the quantum mechanical problem becomes prohibitively difficult. Therefore it is customary to use some simple model for a particle, and to treat the scattering with classical electromagnetic field theory. The models which have been used are a point dipole, a spherical dielectric or conductor, and an ellipsoidal dielectric or conductor. If the particle is small compared with the wave length of the incident light, the scattered light is obtained from the equation for the intensity of radiation from an oscillating point dipole. This calculation was first performed by Rayleigh; the details are now available in almost any text on electromagnetic theory, e.g. Stratton(2). The result is

$$\frac{i}{I} = \frac{8\pi^4 \alpha^2}{\lambda^4 r^2}\left(1 + \cos^2\theta\right) \tag{2.1}$$

where i is the intensity of scattered light, I is the intensity of the incident beam, r is the distance from the particle to the observer, θ is the angle between the line of observation and the direction of propagation of the incident beam, λ is the wavelength of the light, and α is the polarizibility of the particle. This equation applies for the case where the incident beam is unpolarized. The case with polarization is derived first, and the result is then averaged over all directions of polarization to give this equation.

If the particle is not small compared with the wavelength of the light, the mathematical treatment is much more complicated, and has been performed even for ellipsoidal particles only in an approximate way(3,4). For spherical particles, either transparent with a given index of refraction or else metallic, the scattering problem has been solved by Mie(5). Several important contributions have also been made by Debye(6). The details of this calculation also are given by Stratton(2). There is no need to state the results of these calculations here. In the limit of small size, the result given above is naturally obtained. For very large particles, the problem reduces to one in geometrical optics. For intermediate sizes, the scattering intensity is hard to calculate. Atoms are fortunately small compared with the wavelength of visible light, so that they may be treated as point dipoles with a certain polarizability. (This cannot be done for x-ray scattering.) The scattering of visible light by a molecule may in principle be calculated with a knowledge of the structure of the molecule, using point dipole scattering from its constituent atoms. This method requires more information, but on the other hand is capable of yielding more information than the simple picture in which the molecule is a sphere with a certain dielectric constant. This method is actually used, for example by Debye(7) and by Zimm, Stein, and Doty(8).

The scattering by a collection of independent particles is obtained by adding the scattering intensities of the single particles. "Independence" here implies that the scattering is incoherent, so that the intensities are additive. This seems to be taken as the definition of independence in light scattering theory. In this case, the scattering from a collection of small isotropic particles is

$$\frac{i}{I} = \frac{8\pi^4 \alpha^2 \rho^{(1)}}{\lambda^4 R^2}(1+\cos^2\theta) \qquad (2.2)$$

in which $\rho^{(1)}$ is the density of particles, i is the intensity of scattered light per unit volume of particles, and the other symbols have the same meaning as before. A quantity which is often used is the turbidity, τ, of the system. This is the logarithm of the fractional decrease in the transmitted intensity,

$$I = I_0 e^{-\tau l} \qquad (2.3)$$

and l is the length of the optical path along the direction of propagation. For this simple system, the turbidity is

$$\tau = \frac{128\pi^5 \alpha^2}{3\lambda^4}\rho^{(1)} \qquad (2.4)$$

This indicates that Beer's law is satisfied by this system. When this expression is used, the polarizibility seldom is available, but the index of refraction usually is available. Further, the system usually considered consists of the scattering particles immersed in a transparent, non-scattering medium of dielectric constant ϵ_0. In this case, the dielectric constant of the mixture, ϵ, (which is the square of the refractive index) and the dielectric constant of the solvent are related to the polarizibility

$$4\pi\alpha\rho = \frac{\epsilon-\epsilon_0}{\epsilon_0} \tag{2.5}$$

Using this, the turbidity of the mixture is

$$\tau = \frac{8\pi^3(\epsilon-\epsilon_0)^2}{3\lambda^4\rho} \tag{2.6}$$

This is the prototype of the expressions which are used in the theory of scattering from collections of dependent particles.

When one talks about dependent particles, there are two kinds of dependence which must be kept in mind. One of these is the dependence which arises from mechanical interactions between particles, giving rise to a distribution of particles differing from that of an ideal gas. The other kind of dependence comes from the electromagnetic interaction between particles, because each particle exists in the field not only of the external source but also of all the other particles. With the exception of the work of Yvon, to which later reference shall be made, all theoretical discussions have avoided an explicit consideration of the latter kind of dependence by using a semi-phenomenological model. This model and the treatment of it is due to Einstein(9) and Smoluchowski(10). The scattering element is a small volume of the liquid. Because of fluctuations in density, composition, and anything else that can fluctuate, the dielectric constant of this small volume will be instantaneously different from that of the liquid as a whole. If the volume is indeed small compared with the wavelength of the light, it may be treated as a small isotropic particle of dielectric constant ϵ immersed in a medium of dielectric constant ϵ_0 , and thereafter the theory of scattering from an independent set of such particles may be used. The average square of the polarizibility for the volume δv is given by

$$\left\langle (\Delta\epsilon)^2 \right\rangle \frac{(\delta v)^2}{16\pi^2 \epsilon_0^2} \qquad (2.7)$$

with $\Delta\epsilon = \epsilon - \epsilon_0$.

The intensity of scattering per unit volume of scatterer is

$$\frac{i}{I_0} = \frac{\pi^2}{2\lambda^4 r^2} (\delta v) \left\langle (\Delta\epsilon)^2 \right\rangle (1 + \cos^2\theta) \qquad (2.8)$$

and the turbidity is

$$\tau = \frac{8\pi^3}{3\lambda^4} \left\langle (\Delta\epsilon)^2 \right\rangle (\delta v)$$

The rest of the problem is to relate the mean square fluctuation of the dielectric constant to the equilibrium properties of the liquid. For a single component liquid, the only fluctuation of importance is the density. In this case, the scattering is

$$\frac{i}{I_0} = \frac{\pi^2}{2\lambda^4 r^2} \left(\rho \frac{\partial\epsilon}{\partial\rho} \right)^2 kT\beta \, (1 + \cos^2\theta) \qquad (2.9)$$

where β is the isothermal compressibility. To use this expression, the dependence of the dielectric constant on density is needed; to a good approximation the Clausius-Mosotti equation holds:

$$\frac{\epsilon+2}{\epsilon-1} = \left(\frac{4\pi}{3}\alpha\rho\right)^{-1} \tag{2.10}$$

Using this together with equation (2.9), fair agreement is obtained with experiment for scattering from argon and some other substances. For ethylene and similar compounds, corrections for depolarization are necessary because of the lack of symmetry of the molecules. These corrections will not be considered here.

When the system consists of a multicomponent solution, it is necessary to take into account not only the density fluctuations but also composition fluctuations. (Although the dielectric constant depends on temperature, in general, fluctuations in temperature seem to be too small to be considered.) The case of two components was treated by Smoluchowski$^{(10)}$ and by Einstein$^{(9)}$, and was extended by Debye to a form useful for practical calculation$^{(7)}$. The result of these treatments is the equation

$$H\frac{c}{\tau} = \frac{1}{M} + \frac{2Bc}{RT}$$

(2.11)

$$H = \frac{8\pi^3}{3N\lambda^4}\left(\frac{\partial\epsilon}{\partial c}\right)^2$$

in which c is the concentration of the scattering solute. The effect of the solvent is subtracted out. B is a measure of the deviation from ideality of the solution, and M is the molecular weight of the solute. This equation, or modifications of it, is most often used in the theoretical treatment of light scattering data. The theory of scattering from multi-component solutions has been worked out by Kirkwood and Goldberg(11), using this same fluctuation approach.

The theory of the scattering of x-rays by liquid elements was developed by Debye and Menke(12). The theory and experimental results have been reviewed by Gingrich(13). When x-rays are scattered by atoms, the classical dipole treatment is not valid, and "structure factors" are introduced instead. The kind of molecular dependence that is considered is the mechanical one, which gives rise to a spatial distrubiton of atoms. Interactions which might be described as multiple scattering are not considered. Since the dielectric constant for x-rays is very close to unity, the effect of electromagnetic interactions is negligible.

Zimm(14) has given a moderately rigorous treatment of light scattering. He made explicit use of distribution functions, but used for the average field at a particle the Lorentz-Lorenz field, which is derived with a continuum model.

The most successful attempt to place the theory of light scattering on a firm basis was made by Yvon(15). His work is relatively inaccessible, and deserves much wider attention than it has received. The model and procedure used by Yvon are quite similar to those used in this research. Some of his methods are not convenient for working out the theory in detail, and he has not done so. Since the ideas and notation used are rather involved, the similarities and differences between his work and the research reported here will be discussed after some notations and basic ideas have been established.

A corollary of a theory of light scattering is a theory of the dielectric constant or index of refraction of a liquid. This has been worked out to some extent by Kirkwood(16) and by Yvon(15). The case of the static dielectric constant was the subject of an excellent paper by W. F. Brown(17). In fact, the methods used here are a natural extension of those used by Brown.

III Physical Picture

The theory of the scattering of light by a liquid is in its statistical mechanical aspects quite complicated. So that the reader will not become lost in a maze of notations and equations, a brief verbal transcription of the theory will be given first. This will show what effects are to be considered, and approximately how they will be considered.

The physical situation is this: a liquid consisting of identical spherically symmetric particles, which interact electromagnetically as point dipoles, occupies a fixed volume. A plane polarized monochromatic light wave enters the liquid.

For convenience, the liquid will have at least one plane surface as a boundary, and the incident beam will have a direction of propagation normal to this plane surface. The problem is to determine the angular dependence, intensity, and polarization of the scattered light when the properties of the incident beam, the potential of interaction between the particles, and the polarizibility of the individual particles are given, and a certain temperature and density are specified.

What is a microscopic description of the scattering from this system? The incident beam will act on all the particles in the liquid, inducing a dipole moment in each. Since the incident wave is oscillating in time, the induced moments will also oscillate. Each induced dipole therefore radiates a field. The actual field which acts on a given particle is the sum of the external field and the radiation fields of all the other particles. From a photon point of view, this is a multiple scattering process. However, a slightly different description is more useful: the last particle to scatter a photon is called <u>the</u> scattering particle, and the motion of the photon up to this particle is described by an "average wave" propagating through the system. In any microscopic state of the system, the wave propagating from dipole to dipole through the liquid is a complicated affair. However, from a macroscopic point of view, this wave is a plane wave, whose nature is determined by the properties of the incident wave, the geometry of the system, and the dielectric constant of the system. To effect a correspondence between the microscopic and the macroscopic points of view, a statistical postulate is needed. The macroscopic field within the dielectric may be described in terms of the polarization or average dipole moment per unit volume (as a function of space and time). Then, the fundamental postulate is this: The macroscopic polarization is assumed to be the ensemble average of the actual dipole moment per unit volume. This average is calculated using the distribution function for the system, which is determined by the intermolecular potential, the density, and the temperature in canonical equilibrium. The propagation of the average wave is given by the propagation of the average polarization. This wave will travel with a velocity less than that of light in vacuo. The actual fields still propagate with the velocity of light in vacuo; however, the actual path traversed by a photon will be longer than the minimum one because of the multiple scattering effect. The velocity of the average wave is of course related to the index of refraction of the liquid. This is the way in which the index of refraction may be obtained.

The scattering intensity may be calculated in a rigorous way by determing the energy flux or Poynting vector of the actual electromagnetic field at the observer, due to all the oscillating dipoles. Again a statistical hypothesis is made: The macroscopic value of the intensity of scattered light from a system is assumed to be the ensemble average of the actual Poynting vector of each microscopic state. This leads in a first approximation to a theory similar to the theory of x-ray scattering from a liquid, but different in that the polarizability appears instead of the atomic structure factor. For the case of scattering of visible light, the first approximation is equivalent to the theory obtained using the Einstein-Smoluchowski fluctuation theory of light scattering.

IV Assumptions and Special Notations

One of the two basic dependences that will be considered in this theory is due to mechanical forces between particles, which give rise to distribution functions. These functions are used for evaluations of averages over a statistical ensemble. The particles that will be considered here are all identical and are spherically symmetric---there is no preferred orientation of one particle with respect to another. The force between any two particles is then a function only of the distance between the centers of the particles. It will not be necessary to specify further the form of this force, unless certain explicit calculations are to be made. These particles will also be interacting as electric dipoles, but the externally induced dipole-dipole force will be neglected as small compared with any other forces. Since the applied external field determines the magnitude of the induced dipoles, this approximation holds in the limit of low field strengths. A further approximation will be made in the neglect of the motion of these particles. It is assumed that the particle does not move appreciably during a period of the dipole oscillation. Without this assumption, there would be a "temperature broadening" of the scattered radiation. This approximation is made explicit by assuming that the particles are fixed in position. The distribution function which is important is

$$\rho^{(N)}(\vec{R}_1, \vec{R}_2, \ldots \vec{R}_N) \tag{4.1}$$

which is the probability density that the N particles of the system will be found at the positions R_1, $R_2, \ldots, R_N$. The reduced distribution functions, obtained by calculating the probability density that any n particles out of the set N will be found at the positions $r_1, r_2, \ldots, r_n$, are also necessary. The first two reduced distribution functions, the singlet and the pair, are defined in this way:

$$\rho^{(1)}(\vec{r}_1) = \underset{N\text{-FOLD}}{\int\cdots\int} \sum_{k=1}^{N} \delta(\vec{R}_k - \vec{r}_1)\,\rho^{(N)}\, d^3\vec{R}_1 \cdots d^3\vec{R}_N$$

$$\rho^{(2)}(\vec{r}_1, \vec{r}_2) = \underset{N\text{-FOLD}}{\int\cdots\int} \underset{\substack{j \neq k\\=1}}{\sum^{N}\sum^{N}} \delta(\vec{R}_k - \vec{r}_1)\,\delta(\vec{R}_j - \vec{r}_2)\,\rho^{(N)}\, d^3\vec{R}_1 \cdots d^3\vec{R}_N \tag{4.2}$$

and the higher ones are defined in an analogous way. (The Dirac delta function is used as a convenient way of singling out a particle and locating it at a specified point, and the summations are used because it is not essential to know which particle is located at that point.) There is a simple relationship between different order distribution functions:

$$\int \rho^{(n)}\, d^3\vec{r}_n = (N-n)\,\rho^{(n-1)} \tag{4.3}$$

If the system is in canonical equilibrium, the distribution function is given by

$$\rho^{(N)} = e^{-\frac{1}{kT} V_N}$$

where V_N is the potential energy of the entire system. For certain special potentials, the pair distribution function has been evaluated(18). An excellent discussion of some properties of these distribution functions is that of DeBoer(19).

The other basic dependence that is involved in this theory is due to electromagnetic interactions between induced dipoles. The dipole moment (always electric dipole) of the k'th particle, when the positions of all the particles in the system are fixed and known, is given the symbol $\vec{P}_k^{(N)}$. The average dipole moment of the first particle, when the positions of it and of the n-1 particles 2,3,...n are fixed and known, is $\vec{P}^{(n)}_{1;2,3,\dots n}$. When no confusion will arise, some of the subscripts will be omitted: then $\vec{P}_1^{(3)}$, $\vec{P}_2^{(3)}$, $\vec{P}_3^{(3)}$ will mean $\vec{P}^{(3)}_{1;2,3}$, $\vec{P}^{(3)}_{2;1,3}$, $\vec{P}^{(3)}_{3;1,2}$ respectively. There is a simple relationship between successive moment distribution functions--

$$\int_V \rho^{(n+1)} \vec{P}_1^{(n+1)} d^3\vec{R}_{n+1} = (N-n)\rho^{(n)} \vec{P}_1^{(n)} \qquad (4.4)$$

The macroscopic polarization is the average dipole moment per unit volume, and is therefore

$$\vec{P} = \rho^{(1)}(\vec{r}_1) \, \vec{P}_1^{(1)}(\vec{r}_1 ; t) \qquad (4.5)$$

This is in general still a function of position and time.

The electric field due to an oscillating dipole is given(2) by

$$\vec{E}(\vec{R}_1;t) = \nabla_{R_1} \times \nabla_{R_1} \times [\vec{\pi}(\vec{R}_2;t)] \tag{4.6}$$

where $[\vec{\pi}]$ is the retarded Hertz vector, defined by

$$[\vec{\pi}] = \frac{1}{R_{12}} \vec{P}\left(\vec{R}_2; t - \frac{R_{12}}{c}\right) \tag{4.7}$$

If the dipole oscillates harmonically with the time dependence $e^{-i\omega t}$, the retardation produces a factor on which the differential operators act. This differentiation may be performed explicitly, and the result may be written in a dyadic operator form(2)

$$\vec{E}(\vec{R}_1;t) = \mathbb{A}_{12} \cdot \vec{P}(\vec{R}_2;t)$$

$$\mathbb{A}_{12} = \frac{e^{iK_0 R_{12}}}{R_{12}^3}\left\{(3\vec{e}_{12}\vec{e}_{12} - \underset{\sim}{1}) - iK_0R_{12}(3\vec{e}_{12}\vec{e}_{12} - \underset{\sim}{1}) - (K_0R_{12})^2(\vec{e}_{12}\vec{e}_{12} - \underset{\sim}{1})\right\} \tag{4.8}$$

$$\vec{e}_{12} = \frac{\vec{R}_{12}}{|R_{12}|} \; ; \; \vec{R}_{12} = \vec{R}_2 - \vec{R}_1 \; ; \; K_0 = \frac{\omega}{c} = \frac{2\pi}{\lambda_0}$$

and $\underset{\sim}{1}$ is the unit dyad. A similar expression may be obtained for the magnetic field produced by the oscillating dipole,

$$\vec{H}(\vec{R}_1;t) = \vec{\mu}_{12} \times \vec{P}(\vec{R}_2;t)$$

$$\vec{\mu}_{12} = -i\omega\, e^{iK_0R_{12}}\left(\frac{1}{R_{12}^2} - \frac{iK_0}{R_{12}}\right)\vec{e}_{12} \tag{4.9}$$

The expression for the electric field used by Brown(17) for this purpose is the limit of the one given here as the frequency vanishes, and therefore gives the electrostatic field due to a stationary dipole. The extra frequency dependent terms give rise to departures from Brown's theory of the static dielectric constant.

The remaining assumption about the nature of the particles is that they are non-polar, but can possess an induced dipole moment $\vec{P}$ under the action of an applied field $\vec{E}$, according to the equation

$$\vec{P} = \alpha\,\vec{E}. \tag{4.10}$$

The polarizibility α is assumed to be a scalar, independent of the positions of the other particles. A more general theory would require this to be a tensor or dyadic; this will not add to the basic theory, but will add complications of a mathematical sort, and will not be considered here. Using this equation it is possible to define an average electric field

$$\vec{E}^{(n)}_{1;2,\dots n} = \frac{1}{\alpha}\,\vec{P}^{(n)}_{1;2,\dots n}\;.$$

Of greatest importance are the electric field $\vec{E}^{(N)}$ and the magnetic field $\vec{H}^{(N)}$ when all particles are at fixed known positions.

V Fundamental Equations of Light Scattering

The quantity that is of interest in a light scattering measurement is the energy flux at the observer (e.g., a photocell) which results from the oscillations of the induced dipoles in the system. The energy flux in a radiation field is given by the Poynting vector of the field. If the electric and magnetic fields are assumed to oscillate harmonically, with the time factor $e^{-i\omega t}$, it is in general convenient to use complex quantities throughout. In this case, the time average of the Poynting vector over one period of oscillation is

$$\vec{S} = Re\left\{ \frac{1}{2}\, \vec{E} \times \vec{H}^* \right\} \tag{5.1}$$

where $\vec{E}$ and $\vec{H}$ are the electric and magnetic fields, and the asterisk means as usual the complex conjugate. This time averaged Poynting vector will be used throughout. It will be shown later that the radiation field at the observer does contain the proper time dependence.

The oscillations of the induced dipoles give rise to the radiation field. The external field which induces the dipoles does not in any standard experimental arrangement extend to the observer. The fields at the observer are therefore

$$\vec{E}_0^{(N)} = \sum_{K=1}^{N} \boldsymbol{\lambda}_{0K} \cdot \vec{P}_K^{(N)}$$

$$\vec{H}_0^{(N)} = \sum_{K=1}^{N} \vec{\mu}_{0K} \times \vec{P}_K^{(N)} \tag{5.2}$$

The notation has been explained in section IV. The subscript zero refers to the position $\vec{R}_0$ of the observer. The time average of the Poynting vector is then

$$\vec{S} = \frac{1}{2} \operatorname{Re}\left\{ \left(\sum_{K=1}^{N} \boldsymbol{\lambda}_{0K} \cdot \vec{P}_K^{(N)} \right) \times \left(\sum_{j=1}^{N} \vec{\mu}_{0j} \times \vec{P}_j^{(N)} \right)^{*} \right\} \tag{5.3}$$

when all N particles are at known positions. The experimentally important quantity is the ensemble average of this, and is obtained by multiplying by $\rho^{(N)}$ and integrating over all positions of the N particles in the volume V accessible to the particles.

$$\langle \vec{S} \rangle_{AV} = \frac{1}{2} \operatorname{Re}\{ \vec{S}_0 \}$$

$$\vec{S}_0 = \int \cdots \int \sum^{N}_{j \neq K} \sum^{N} \left(\boldsymbol{\lambda}_{0K} \cdot \vec{P}_K^{(N)} \right) \times \left(\vec{\mu}_{0j}^{*} \times \vec{P}_j^{(N)*} \right) \rho^{(N)} d^3\vec{R}_1 \cdots d^3\vec{R}_N \tag{5.4}$$

$$+ \int \cdots \int \sum_{K=1}^{N} \left(\boldsymbol{\lambda}_{0K} \cdot \vec{P}_K^{(N)} \right) \times \left(\vec{\mu}_{0K}^{*} \times \vec{P}_K^{(N)*} \right) \rho^{(N)} d^3\vec{R}_1 \cdots d^3\vec{R}_N$$

or

$$\vec{S}_0 = \int_V \int_V \rho^{(2)}(\vec{R}_1, \vec{R}_2) \left(\boldsymbol{\lambda}_{01} \cdot \vec{P}_1^{(2)} \right) \times \left(\vec{\mu}_{02}^{*} \times \vec{P}_2^{(2)*} \right) d^3\vec{R}_1\, d^3\vec{R}_2$$

$$+ \int_V \rho^{(1)}(\vec{R}_1) \left(\boldsymbol{\lambda}_{01} \cdot \vec{P}_1^{(1)} \right) \times \left(\vec{\mu}_{01}^{*} \times \vec{P}_1^{(1)*} \right) d^3\vec{R}_1\, d^3\vec{R}_2 \tag{5.4'}$$

The important feature of this equation is that the "pair" moment distribution function is needed in the first term. This has not appeared in any previous theory of light scattering. In order to successfully complete the theory, a method is needed for evaluating this function. Before this is done, certain simplifications can be made, during the course of which a first order approximation, taking $\vec{P}^{(2)}_{1;2} = \vec{P}^{(1)}_{1}$, will be obtained. After some simple algebraic manipulation, the vector $\langle \vec{S} \rangle_{AV}$ becomes

$$\langle \vec{S} \rangle_{AV} = \frac{1}{2}\vec{S}_{00} + \frac{1}{2}\Delta\vec{S}_{0} \tag{5.5}$$

where

$$\begin{aligned}\vec{S}_{00} &= \iint \rho^{(2)}(\vec{R}_1, \vec{R}_2)\left(\Lambda_{01} \cdot \vec{P}_1^{(1)}\right) \times \left(\vec{\mu}_{02}^{\,*} \times \vec{P}_2^{(1)*}\right) d^3\vec{R}_1\, d^3\vec{R}_2 \\ &+ \int \rho^{(1)}(\vec{R}_1)\left(\Lambda_{01} \cdot \vec{P}_1^{(1)}\right) \times \left(\vec{\mu}_{01}^{\,*} \times P_1^{(1)*}\right) d^3\vec{R}_1\end{aligned} \tag{5.6}$$

and

$$\begin{aligned}\Delta\vec{S}_0 &= \iint \rho^{(2)}(\vec{R}_1, \vec{R}_2)\left[\Lambda_{01} \cdot \vec{P}_1^{(1)}\right] \times \left[\vec{\mu}_{02}^{\,*} \times \left(\vec{P}_2^{(2)*} - \vec{P}_2^{(1)*}\right)\right] d^3\vec{R}_1\, d^3\vec{R}_2 \\ &+ \iint \rho^{(2)}(\vec{R}_1, \vec{R}_2)\left[\Lambda_{01} \cdot \left(\vec{P}_1^{(2)} - \vec{P}_1^{(1)}\right)\right] \times \left[\vec{\mu}_{02}^{\,*} \times \vec{P}_2^{(1)*}\right] d^3\vec{R}_1\, d^3\vec{R}_2 \\ &+ \iint \rho^{(2)}(\vec{R}_1, \vec{R}_2)\left[\Lambda_{01} \cdot \left(\vec{P}_1^{(2)} - \vec{P}_1^{(1)}\right)\right] \times \left[\vec{\mu}_{02}^{\,*} \times \left(\vec{P}_2^{(2)*} - \vec{P}_2^{(1)*}\right)\right] d^3\vec{R}_1\, d^3\vec{R}_2\end{aligned} \tag{5.7}$$

The latter terms will be expanded later in a power series in the polarizibility, and the first few terms of the expansion will be stated explicitly. This will require a solution of a chain of linear integral equations. For the remainder of this section, attention will be focussed on the first part, $\vec{S}_{oo}$.

The distance from the observer to any particle in the system is assumed to be very large in relation to the wavelength of the light and the distance between any two particles in the system. This is from an experimental point of view a well-justified assumption. Also, the scattering will be calculated for a volume v which is small compared with the dimensions of the system but large compared with intermolecular dimensions, so that many particles are in it. The scattering formulas that will be derived are therefore "differential scattering cross sections". In this case, the following approximations hold:

$$\lambda_{01} \cong -\frac{e^{iK_0 R_{01}}}{R_{01}} K_0^2 \left(\vec{e}_{01} \vec{e}_{01} - \underline{\underline{1}} \right)$$

$$\vec{\mu}_{02} \cong \frac{e^{iK_0 R_{02}}}{R_{02}} c K_0^2 \vec{e}_{02} \qquad (5.8)$$

$$\vec{e}_{01} \cong \vec{e}_{02} \quad ; \quad R_{01} \cong R_{02}$$

and by vector algebra, a useful equation may be obtained:

$$(\lambda_{01}\cdot\vec{A})\times(\mu_{02}^{*}\times\vec{B}^{*})\cong$$

$$-\frac{C_0 K_0^4}{R_{01}^2}\, e^{i(R_{01}-R_{02})K_0}\left[(\vec{e}_{01}\vec{e}_{01}-\underset{\sim}{1})\cdot\vec{A}\times(\vec{e}_{01}\times\vec{B}^{*})\right] \qquad (5.9)$$

$$= -\vec{e}_{01}\,\frac{C_0 K_0^4}{R_{01}^2}\, e^{iK_0(R_{01}-R_{02})}\left[(\vec{B}^{*}\cdot\vec{e}_{01})(\vec{A}\cdot\vec{e}_{01})-(\vec{B}^{*}\cdot\vec{A})\right]$$

Since $\vec{e}_{01}\cong\vec{e}_{02}$, the exponential factor can be rearranged in this way,

$$e^{iK_0(R_{01}-R_{02})} = e^{iK_0\vec{e}_{01}\cdot(\vec{R}_{01}-\vec{R}_{02})} = e^{iK_0\vec{e}_{10}\cdot\vec{R}_{12}}$$

Therefore, $(\lambda_{01}\cdot\vec{A})\times(\vec{\mu}_{02}^{*}\times\vec{B}^{*})\cong$

$$\vec{e}_{10}\,\frac{C_0 K_0^4}{R_{01}^2}\, e^{iK_0\vec{e}_{10}\cdot\vec{R}_{12}}\left[(\vec{B}^{*}\cdot\vec{e}_{10})(\vec{A}\cdot\vec{e}_{10})-(\vec{B}^{*}\cdot\vec{A})\right] \qquad (5.10)$$

In order to apply this, it is necessary to know what $\vec{P}_1^{(1)}$ is. Using one of the fundamental correspondences, $\vec{P}_1^{(1)}$ is the macroscopic polarization at $\vec{R}_1$. It is certainly possible to construct a system in which the average wave is plane:

$$\vec{P}_1^{(1)} = \vec{P}_0\; e^{i\vec{K}_1\cdot\vec{R}_1}\; e^{-i\omega t} \qquad (5.11)$$

In this, $\vec{k}_1$ is the propagation vector of the plane wave; its direction is the direction of propagation, and its magnitude is

$$K_1 = nK_0 = n\frac{2\pi}{\lambda_0} \qquad ; \qquad \vec{P}_0\cdot\vec{K}_1 = 0$$

where n is the index of refraction of the liquid.

When these simplifications are made in equation (5.6), and the chosen form of $\vec{P}^{(1)}$ is substituted,

$$\vec{S}_{00} = \vec{e}_{10} \frac{C_0 K_0^4}{R_{01}^2} (\vec{P}_0^* \cdot \vec{P}_0) \sin^2\theta \quad \{\,\}$$

$$\cos\theta = \frac{1}{|\vec{P}_0|} (\vec{P}_0 \cdot \vec{e}_{01}) \quad ; \quad \vec{K}_{10} = K_0 \vec{e}_{10} \qquad (5.12)$$

$$\{\,\} = \int_v \rho^{(1)} d^3R_1 + \iint_{v\,v} \rho^{(2)}(\vec{R}_1, \vec{R}_2)\, e^{i(\vec{K}_{10} - \vec{K}_1)\cdot \vec{R}_{12}}\, d^3\vec{R}_1\, d^3\vec{R}_2 \quad ;$$

the bracket may be put into a more familiar form by a simple rearrangement,

$$\iint_{v\,v} \rho^{(2)} e^{i(\vec{K}_{10} - \vec{K}_1)\cdot \vec{R}_{12}} d^3R_1\, d^3R_2 = \iint_{v\,v} \left[\rho^{(2)} - \rho_1^{(1)} \rho_2^{(1)}\right] e^{i(\vec{K}_{10} - \vec{K}_1)\cdot R_{12}} d^3\vec{R}_1\, d^3\vec{R}_2$$

$$+ \iint_{v\,v} \rho_1^{(1)} \rho_2^{(1)}\, e^{i(\vec{K}_{10} - \vec{K}_1)\cdot \vec{R}_{12}} d^3\vec{R}_1\, d^3\vec{R}_2 \,.$$

The second term on the right side may be integrated. The singlet densities are for a fluid independent of position, and may be taken outside the integral sign. If the volume of integration is large, this integral is

$$\int e^{i(\vec{K}_{10} - \vec{K}_1)\cdot \vec{R}_{12}} d^3R_{12} \cong (2\pi)^3\, \delta(\vec{K}_{10} - \vec{K}_1)$$

But if the refractive index of the medium differs from unity,

$$\vec{K}_{10} - \vec{K}_1 = K_0 \vec{e}_{10} - n K_0 \frac{\vec{K}_1}{|\vec{K}_1|} \neq 0$$

so that this term vanishes, or is anyhow negligibly small. Some further simplifications can be made: the vector may take on all orientations in space, and its magnitude only is of importance. The average of the integrand over directions is

$$\int_0^{4\pi} e^{i|\vec{K}_{10}-\vec{K}_1| R_{12}\cos\alpha}\, d\Omega \Big/ \int_0^{4\pi} d\Omega$$

$$= \int_0^{\pi} e^{i|\vec{K}_{10}-\vec{K}_1| R_{12}\cos\alpha}\, 2\pi \sin\alpha\, d\alpha \Big/ 4\pi$$

$$= \frac{\sin|\vec{K}_{10}-\vec{K}_1| R_{12}}{|\vec{K}_{10}-\vec{K}_1| R_{12}}$$

Using a more familiar notation,

$$s = |\vec{K}_{10}-\vec{K}_1| \qquad (5.13)$$

the result of these manipulations is that the scattered intensity in the first approximation is given by

$$\langle S\rangle_{AV} = \vec{e}_{10}\, \frac{8\pi^4 C_0}{\lambda_0^4} \sin^2\Theta\, (\vec{P}_0^{*}\cdot\vec{P}_0)\, n_v \{\,\}$$

(5.14)

$$\{\,\} = 1 + \rho^{(1)}\int_0^{\infty} [g^{(2)}(R) - 1]\, 4\pi R^2\, \frac{\sin sR}{sR}\, dR$$

where n_v is the average number of particles within the element of scattering volume v, and $g^{(2)}(R_{12})$ is the radial distribution function, defined by

$$g^{(2)}(R_{12}) = \frac{\rho^{(2)}(\vec{R}_1, \vec{R}_2)}{\rho^{(1)}(\vec{R}_1)\,\rho^{(1)}(\vec{R}_2)} \tag{5.15}$$

The quantity s contains an angular dependence also. When the index of refraction is sufficiently close to unity,

$$s = \frac{4\pi}{\lambda_0} \sin\frac{\psi}{2} \tag{5.16}$$

where ψ is the scattering angle. For visible light scattered from a monatomic liquid, the term containing s may be neglected, in which case

$$\{\,\} = 1 + \rho^{(1)}\int_0^\infty 4\pi R^2\left[g^{(2)}(R)-1\right]dR \tag{5.17}$$

This is directly related to the fluctuation in density which appears in the Einstein-Smoluchowski theory. The fluctuation in density is determined by the quantity $\langle (n_v - \langle n_v\rangle)^2\rangle$ which is the mean square deviation in the number n_V of particles in the volume v. This relation was shown in a very simple way be DeBoer$^{(19)}$. The result is

$$\frac{\langle n_v^2\rangle - \langle n_v\rangle^2}{\langle n_v\rangle} = 1 + \rho^{(1)}\int_0^\infty \left[g^{(2)}(R)-1\right]d^3\vec{R}$$

$$= -\frac{RT}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{5.18}$$

and leads to the well known expression for scattering from a one component monatomic system.

The scattering intensity given by equation (5.14) is only the first approximation. The deviations from this depend upon $\vec{P}_{1;2}^{(2)} - \vec{P}_1^{(1)}$ which is the subject of the next section. This quantity is obtained by solving a chain of integral equations. Another relationship which is needed is the one between the amplitude of the average wave $\vec{P}_0$ and the external field $\vec{E}_0$. This depends upon the index of refraction. In a later section, the theory of the index of refraction will be developed.

VI Integral Equations for the Moment Distribution Functions

The expressions worked out in the preceding section are only correct in a first approximation. To the quantity $\vec{S}_{00}$ must be added $\Delta\vec{S}_0$. This depends upon the difference between the moment of particle 1 when 2 is fixed and the moment of 1 when all others are averaged out. The calculation of this quantity could be performed in principle by solving a set of N simultaneous linear equations in the variables $\vec{P}_k^{(N)}$, followed by N-2 integrations. For N of the order of Avogadro's number, this program is highly impractical. Therefore a scheme was developed using integral equation methods, quite similar to the procedure for evaluating the radial distribution function of a liquid. The integral equations and the methods of solution are almost identical with those used by Brown(17) in his theory of the static dielectric constant.

Consider a system containing N particles, of the type already described. These particles are under the influence of an external field $\vec{E}^{(o)}(\vec{R};t)$, and are also acted on by the radiation fields of all the other particles. Therefore, the dipole moment of the k'th particle, when all N particles are fixed in position, is

$$\vec{P}_k^{(N)} = \alpha\left\{\vec{E}^{(0)}(\vec{R}_k;t) + \sum_{\substack{j=1\\ \neq k}}^{N} \lambda_{jk}\cdot\vec{P}_j^{(N)}(\vec{R}_j;t)\right\} \qquad (6.1)$$

This set of equations for k = 1,2,...N, determines each $\vec{P}_k^{(N)}$ as a function of α, $\vec{E}^{(o)}$, and the relative positions of all the particles, and in principle may be solved for $\vec{P}_k^{(N)}$. Instead of doing this, the equation is multiplied throughout by $\rho^{(N)}$, to obtain an ensemble average, and then integrated over a subset N-n of the N particles. The particle k is kept in the subset n. The result of this integration, after using the notations of reduced distribution functions and reduced moment distribution functions, is

$$\vec{P}_j^{(n)}(\vec{R}_j;t) = \alpha\left\{\vec{E}^{(0)}(\vec{R}_j;t) + \sum_{\substack{k=1\\ \neq j}}^{n} \lambda_{jk}\cdot\vec{P}_k^{(n)}(\vec{R}_k;t)\right.$$

$$\left. + \int_V \frac{\rho^{(n+1)}}{\rho^{(n)}}\lambda_{j,n+1}\cdot\vec{P}_{n+1}^{(n+1)}(\vec{R}_{n+1};t)\,d^3\vec{R}_{n+1}\right. \qquad (6.2)$$

In particular, the first two equations of this series are

$$\vec{P}_1^{(1)}(\vec{R}_1;t) = \alpha\left\{ \vec{E}^{(0)}(R_1;t) + \int_V{}' \frac{\rho_{12}^{(2)}}{\rho^{(1)}}\, \mathbb{A}_{12}\cdot \vec{P}_{2;1}^{(2)}(\vec{R}_2;t)\, d^3\vec{R}_2 \right\} \tag{6.3}$$

and

$$\vec{P}_{1;2}^{(2)}(\vec{R}_1;t) = \alpha\left\{ \vec{E}^{(0)}(R_1;t) + \mathbb{A}_{12}\cdot \vec{P}_{2;1}^{(2)}(R_2;t) + \int_V \frac{\rho_{123}^{(3)}}{\rho_{12}^{(2)}}\, \mathbb{A}_{13}\cdot \vec{P}_{3;12}^{(3)}(R_3;t)\, d^3\vec{R}_3 \right\} \tag{6.4}$$

It is obvious that each moment distribution function depends upon integrals over the higher order moment and spatial distribution functions. There are two relatively simple methods for solving the chain of linear integral equations. One involves a kind of "superposition approximation", and uses only the first two equations, (6.3) and (6.4). This will be discussed later. The other method depends upon the expansion of a moment distribution function as a power series in the polarizibility:

$$\vec{P}_j^{(n)} = \sum_{s=0}^{\infty} \vec{P}_j^{(n)(s)}\, \alpha^s \tag{6.5}$$

First, the equation for $\vec{P}_j^{(1)}$ is subtracted from the general equation (6.2), so that the external field may be eliminated.

In this way, the independent variable is $\vec{P}_1^{(1)}$ instead of $\vec{E}^{(0)}$, and ultimately some relation will have to be derived between these two quantities. The equation is now

$$\vec{P}_j^{(n)} - \vec{P}_j^{(1)} = \alpha \Big\{ \sum_{\substack{k=1\\ \neq j}}^{n} \lambda_{jk} \cdot \vec{P}_k^{(n)}$$

$$+ \int_V \lambda_{j,n+1} \cdot \left[\frac{\rho^{(n+1)}}{\rho^{(n)}} \vec{P}_{n+1}^{(n+1)} - \frac{\rho^{(2)}_{j,n+1}}{\rho^{(1)}} \vec{P}^{(2)}_{n+1;j} \right] d^3\vec{R}_{n+1} \qquad (6.6)$$

After the series expansion is substituted in this, and coefficients of powers of α are collected, the results are

$$\vec{P}_j^{(n)(1)} = \sum_{\substack{k=1\\ \neq j}}^{n} \lambda_{jk} \cdot \vec{P}_k^{(1)} + \int_V \lambda_{j,n+1} \cdot \left[\frac{\rho^{(n+1)}}{\rho^{(n)}} - \frac{\rho^{(2)}_{j,n+1}}{\rho^{(1)}} \right] \vec{P}_{n+1}^{(1)} \, d^3\vec{R}_{n+1}$$

$$\vec{P}_j^{(n)(s)} = \sum_{\substack{k=1\\ \neq j}}^{n} \lambda_{jk} \cdot \vec{P}_k^{(n)(s-1)} \qquad (6.7)$$

$$+ \int_V \lambda_{j,n+1} \cdot \left[\frac{\rho^{(n+1)}}{\rho^{(n)}} \vec{P}_{n+1}^{(n+1)(s-1)} - \frac{\rho^{(2)}_{j,n+1}}{\rho^{(1)}} \vec{P}_{n+1}^{(2)(s-1)} \right] d^3\vec{R}_{n+1}$$

If the spatial distribution functions $\rho^{(n)}$ are known, this permits the calculation, at least in principle, of all the coefficients in the expansion. The case which is of greatest interest is of course that of $\vec{P}^{(2)}$. The first two terms in the expansion are

$$\vec{P}^{(2)}_{1;2} = \vec{P}^{(1)}_{1} + \alpha\, \vec{P}^{(2)(1)}_{1;2} + O(\alpha^2) \tag{6.8}$$

The termsof order of α^2 are exceedingly complicated, but they can if desired by obtained simply by performing the substitutions in equations (6.7). The first correction is

$$\vec{P}^{(2)(1)}_{1;2} = \lambda_{12}\cdot\vec{P}^{(1)}_{2} + \int_V \lambda_{13}\cdot\left[\frac{\rho^{(3)}_{123}}{\rho^{(2)}_{12}} - \frac{\rho^{(2)}_{13}}{\rho^{(1)}}\right]\vec{P}^{(1)}_{3}\, d^3\vec{R}_3 \tag{6.9}$$

These terms may be analyzed verbally in the following way: the field at 1 when 2 is fixed is equal to the field at 1 when 2 is averaged, plus the radiation field from the fixed 2, plus the field from a 3 which is averaged keeping 1 and 2 fixed. The quantity which is needed both in the light scattering theory and the index of refraction theory is $\vec{P}^{(2)}_{1;2} - \vec{P}^{(1)}_{1} = \alpha\, \vec{P}^{(2)(1)}_{1;2}$.

The other method for solving these integral equations will now be discussed. This depends upon a "superposition approximation",

$$\vec{P}^{(3)}_{1;23} = \vec{P}^{(1)}_{1} + \left\{\vec{P}^{(2)}_{1;2} - \vec{P}^{(1)}_{1}\right\} + \left\{\vec{P}^{(2)}_{1;3} - \vec{P}^{(1)}_{1}\right\} \tag{6.10}$$

which states that the moment of 1 when 2 and 3 are fixed is equal to the moment of 1 when 2 and 3 are averaged out plus the corrections due to first having 2 fixed and 3 averaged out and then having 3 fixed and 2 averaged out. In this way, the effects of electromagnetic interactions are retained in the theory up to a point, and the chain of integral equations can be terminated at the second one, (6.4). The resulting integral equation can be handled more neatly if the new variable ΔP is defined:

$$\Delta \vec{P}_{1;2}^{(2)} = \vec{P}_{1;2}^{(2)} - \vec{P}_1^{(1)} \tag{6.11}$$

Then the integral equation becomes, after some algebraic manipulation,

$$\begin{aligned}\Delta \vec{P}_{1;2}^{(2)} = \alpha \Big\{ \Lambda_{12} \cdot \vec{P}_2^{(1)} &+ \int_V \left[\frac{\rho^{(3)}}{\rho^{(2)}} - \frac{\rho^{(2)}}{\rho^{(1)}} \right] \Lambda_{13} \cdot \vec{P}_3^{(1)} \, d^3\vec{R}_3 \\ &+ \Lambda_{12} \cdot \Delta \vec{P}_{2;1}^{(2)} \\ &+ \int_V \frac{\rho^{(3)}}{\rho^{(2)}} \Lambda_{13} \cdot \left[\Delta \vec{P}_{3;1}^{(2)} + \Delta \vec{P}_{3;2}^{(2)} \right] d^3\vec{R}_3 \Big\}\end{aligned} \tag{6.12}$$

This is an inhomogeneous linear integral equation, and can be solved by various standard methods. The method used here is again that of series expansion. Define

$$\Delta \vec{P}_{1;2}^{(2)} = \sum_{K=0}^{\infty} \vec{f}_K (\vec{R}_1, \vec{R}_2) \, \alpha^K \tag{6.13}$$

and

$$\vec{D}_{12} = \Lambda_{12} \cdot \vec{P}_2^{(1)} + \int_V \left[\frac{\rho^{(3)}}{\rho^{(2)}} - \frac{\rho^{(2)}}{\rho^{(1)}} \right] \Lambda_{13} \cdot \vec{P}_3^{(1)} \, d^3\vec{R}_3 \tag{6.14}$$

Then, the usual procedure of expanding and collecting coefficients leads to

$$\vec{f}_0 = 0 \qquad ; \qquad \vec{f}_1 = \vec{\mathcal{D}}_{12}$$

$$\vec{f}_n(\vec{R}_1, \vec{R}_2) = \boldsymbol{\lambda}_{12} \cdot \vec{f}_{n-1}(\vec{R}_2, \vec{R}_1) + \int_V \frac{\rho^{(3)}}{\rho^{(2)}} \boldsymbol{\lambda}_{13} \cdot \left[\vec{f}_{n-1}(\vec{R}_3, \vec{R}_2) + \vec{f}_{n-1}(\vec{R}_3, \vec{R}_1) \right] d^3\vec{R}_3 \tag{6.15}$$

The loss in accuracy caused by the superposition is accompanied by the gain in convenience due to the appearance of only $\rho^{(2)}$ and $\rho^{(3)}$ in the expressions for the coefficients. It should be observed that the first order correction here, $\alpha \vec{\mathcal{D}}_{12}$, is the same as the one obtained by the more exact treatment. This state of affairs is reminiscent of the way in which the radial distribution function in the "second virial" approximation can be obtained using various procedures. The higher order corrections here can also be calculated. They are simpler than those calculated from the more exact theory, but are still too complicated to do much with at present.

A procedure that seems at first glance more attractive is the expansion of the function $\vec{P}^{(2)}$ as a power series in the density. However, this is mathematically a less natural procedure, and furthermore it would require the awkward expansion of $g^{(2)}$ in powers of density. Therefore, this procedure was not investigated.

This is a good place to point out a relation between this theory and that of Yvon$^{(15)}$. In his, the leading term in the expansion of $\vec{P}^{(2)}$ would be $\vec{E}^{(o)}$ instead of $\vec{P}^{(1)}$. Since $\vec{P}^{(1)}$ is a much better approximation for use in the scattering and index of refraction formulas, Yvon's procedure was not followed.

VII The Theory of the Index of Refraction

The index of refraction is a necessary variable in the light scattering theory, and also has its own intrinsic interest. A theory of the index of refraction follows from the integral equations of the preceding section, and will be developed here. This theory is similar in broad outline to Brown's$^{(17)}$ theory of the dielectric constant, and indeed should reduce to his in the limit of infinite wavelength.

The system to be considered is the same one that has been discussed in the preceding sections. The starting point is the equation

$$\vec{P}_1^{(1)} = \alpha \left\{ \vec{E}^{(0)}(R_1;t) + \int_V \frac{\rho_{12}^{(2)}}{\rho^{(1)}} \boldsymbol{\lambda}_{12} \cdot \vec{P}^{(2)}_{2;1} \, d^3\vec{R}_2 \right\} \qquad (7.1)$$

The following steps are the highpoints of the derivation: a suitable form for $\vec{P}^{(1)}$ is postulated, the higher order moment distribution function $\vec{P}^{(2)}$ is obtained using the solutions already obtained in section VI, and finally, the relationship between $\vec{P}^{(1)}$ and $\vec{E}^{(o)}$ is sought. This latter point leads to the index of refraction.

In order to specify $\vec{E}^{(o)}$ and $\vec{P}^{(1)}$ precisely, the geometry of the system is needed. In this section, the system is assumed to occupy a "half-space". That is, the universe is divided in two by a plane surface, with liquid on one side and vacuum on the other. The incident wave $\vec{E}^{(o)}$ is assumed to be plane, with its propagation vector normal to the plane surface (just for simplicity). The form of $\vec{E}^{(o)}$ is

$$\vec{E}^{(o)} = \vec{E}_o \, e^{i \vec{K}_0 \cdot \vec{R}} \, e^{-i \omega t} \tag{7.2}$$

where the magnitude of $\vec{k}_o$ is $K_0 = \frac{\omega}{c_0} = \frac{2\pi}{\lambda_0}$. In this case it is reasonable, on the basis of macroscopic electromagnetic field theory and one of the fundamental statistical postulates, to take for the average dipole wave the quantity

$$\vec{P}_1^{(1)} = \vec{P}_0 \, e^{i \vec{K}_1 \cdot \vec{R}_1} \, e^{-i \omega t} \tag{7.3}$$

Here, $\vec{k}_1 = n \vec{k}_o$ where n is the index of refraction of the fluid. It is necessary to show that this <u>assumed</u> solution provides a consistent solution of the chain of integral equations, and it is necessary to find the relation of $\vec{P}_o$ to $\vec{E}_o$.

Some algebraic manipulation casts the basic integral equation into a more convenient form

$$\begin{aligned}\vec{P}_1^{(1)} = {} & \alpha \left\{ \vec{E}_1^{(o)} + \rho^{(1)} \int_V \lambda_{12} \cdot \vec{P}_2^{(1)} \, d^3\vec{R}_2 \right\} \\ & + \alpha \rho^{(1)} \left\{ \int_V \left[g_{12}^{(2)} - 1 \right] \lambda_{12} \cdot \vec{P}_2^{(1)} \, d^3\vec{R}_2 \right. \\ & \left. + \int_V g_{12}^{(2)} \lambda_{12} \cdot \left[\vec{P}_{2;1}^{(2)} - \vec{P}_2^{(1)} \right] d^3\vec{R}_2 \right\}\end{aligned} \tag{7.4}$$

In the approximation that $\vec{P}^{(2)} = \vec{P}^{(1)}$, and with $g^{(2)} \equiv 1$, the integral equation takes on the very simple form

$$\vec{P}_1^{(1)} = \alpha\left\{ \vec{E}_1^{(0)} + \rho^{(1)} \int_V \lambda_{12} \cdot \vec{P}_2^{(1)} \, d^3\vec{R}_2 \right\} \qquad (7.5)$$

This equation has been solved exactly, for the $\vec{E}^{(0)}$ and $\vec{P}^{(1)}$ postulated here. The solution is presented in some detail by Born$^{(20)}$, and also by Darwin$^{(21)}$. The method of solution is referred to as the "Oseen" process. The problem in both the exact case (7.4) and in the approximate case (7.5) consists in evaluating the integrals on the right hand sides of the equations.

The integral involved in the Oseen process will be considered first. With the explicit form of $\vec{P}^{(1)}$, the integral is

$$\vec{E}' = \int_V \lambda_{12} \cdot \vec{P}_0 \; e^{i\vec{K}_1 \cdot \vec{R}_2} \, d^3\vec{R}_2 \quad \left(e^{-i\omega t}\right)$$

The quantity $e^{i\vec{k}_1 \cdot \vec{R}_2}$ satisfies a wave equation, with the velocity c/n. The other factor, $\lambda_{12} \cdot \vec{P}_0$, also satisfies a wave equation. This can be seen most easily in this way: by the definition of the λ operator,

$$\lambda_{12} \cdot \vec{P}_0 = \nabla_{R_1} \times \nabla_{R_1} \times \left[\frac{e^{iK_0 R_{12}}}{R_{12}} \vec{P}_0 \right]$$

That is, the curl curl operator acts only on the retarded part of the retarded Hertz vector. The quantity in brackets is the propagation function for a spherical wave (the constant vector $\vec{P}_0$ does not matter) and therefore satisfies the wave equation. The curl curl operation commutes with the Laplacian, and therefore the entire quantity satisfies a wave equation with the velocity c. Therefore, following Born,

$$-\frac{\omega^2}{c^2}\vec{E}' = e^{-i\omega t}\int_V \left(\nabla^2_{R_2} \boldsymbol{\lambda}_{12}\cdot\vec{P}_0\right) e^{i\vec{K}_1\cdot\vec{R}_2}\, d^3\vec{R}_2$$

$$-n^2\frac{\omega^2}{c^2}\vec{E}' = e^{-i\omega t}\int_V \boldsymbol{\lambda}_{12}\cdot\vec{P}_0 \left(\nabla^2_{R_2} e^{i\vec{K}_1\cdot\vec{R}_2}\right) d^3\vec{R}_2$$

and subtraction leads to

$$\vec{E}' = \frac{c^2}{\omega^2(n^2-1)} e^{-i\omega t}\int_V \Big\{ \left(\nabla^2_{R_2} \boldsymbol{\lambda}_{12}\cdot\vec{P}_0\right) e^{i\vec{K}_1\cdot\vec{R}_2} - \boldsymbol{\lambda}_{12}\cdot\vec{P}_0 \left(\nabla^2_{R_2} e^{i\vec{K}_1\cdot\vec{R}_2}\right)\Big\}\, d^3\vec{R}_2$$

Then, Green's theorem transforms the volume integral into a surface integral,

$$\vec{E}' = \frac{c^2}{\omega^2(n^2-1)} e^{-i\omega t}\int_S \Big\{ \left(\frac{\partial}{\partial\nu_2} \boldsymbol{\lambda}_{12}\cdot\vec{P}_0\right) e^{i\vec{K}_1\cdot\vec{R}_2} - \boldsymbol{\lambda}_{12}\cdot\vec{P}_0 \left(\frac{\partial}{\partial\nu_2} e^{i\vec{K}_1\cdot\vec{R}_2}\right)\Big\}\, d^2\Omega_2 \qquad (7.5')$$

in which ν_2 is the normal to the surface in $\vec{R}_2$ space. This surface integral must now be evaluated over two surfaces. One of these is the external plane boundary, and the other is a spherical surface about the point $\vec{R}_1$, and is required because of the singularity in $\mathcal{A}_{12}$. The correct result is then obtained by taking the limit of the latter integral when the radius of the cavity vanishes. The cavity integral will lead to the Lorentz local field, and the outer surface integral will cancel $\vec{E}^{(o)}$ and provide a relationship between $\vec{P}_o$ and $\vec{E}_o$.

The cavity integral will now be discussed. A simple transformation, $e^{i\vec{K}_1\cdot\vec{R}_2} = e^{i\vec{K}_1\cdot\vec{R}_1}\, e^{i\vec{K}_1\cdot\vec{R}_{12}}$, allows a complete transfer to $\vec{R}_{12}$ space, with $\vec{R}_1$ always fixed. The surface involved is then $|\vec{R}_{12}| = a$, where a is the radius of the spherical cavity. Then $\frac{\partial}{\partial \nu_2} = \frac{\partial}{\partial R_{12}}$. The differentiations give rise to some trigonometric functions, and the surface integration requires integrating over angles at fixed $|\vec{R}_{12}|$. The integrations were performed by Born, who first expanded the exponentials in powers of $|\vec{R}_{12}|$, then integrated, and finally took the limit as $|\vec{R}_{12}| = a$ approached zero. The integrals can also be done exactly, for finite $\vec{R}_{12}$. The work is tedious, but quite simple. It will not be repeated here; however, a similar and more general calculation is described in the appendix. The result is in the limit the same as Born's, and leads to the following expression for the contribution to the total electric field:

$$\vec{E}'_{SPHERE} = \frac{4\pi}{3}\rho^{(1)}\,\frac{n^2+2}{n^2-1}\,\vec{P}_1^{(1)}(\vec{R}_1;t) \qquad (7.6)$$

The other contribution, due to the external plane boundary, has also been worked out by Born and by Darwin. Although their methods are faulty in some respects, it was not felt to be worthwhile to improve them. One source of discomfort is that it is necessary to throw away a diverging part of the integral, on the grounds that it should physically vanish. This situation is probably closely related to the one in which the potential due to a uniformly charged infinite plate is infinite, while the electric field is finite, and has something to do with interchanging differentiations and integrations when this is not permitted. However, the finite part of the integral works out very nicely to

$$\vec{E}'_{PLANE} = -\frac{2\pi}{n-1}\rho^{(1)}\vec{P}_0 e^{i\vec{K}_0\cdot\vec{R}_1} e^{-i\omega t} \qquad (7.7)$$

so that the entire term is

$$\vec{E}_1^{(0)} + \rho^{(1)}\left\{-\frac{2\pi}{n-1}\vec{P}_0 e^{i\vec{K}_0\cdot\vec{R}_1} e^{-i\omega t} + \frac{4\pi}{3}\frac{n^2+2}{n^2-1}\vec{P}_1^{(1)}\right\} \qquad (7.8)$$

This contains a term with the proper space dependence to cancel the external field,

$$\vec{E}_0 e^{i\vec{K}_0\cdot\vec{R}_1} e^{-i\omega t} = \frac{2\pi}{n-1}\rho^{(1)}\vec{P}_0 e^{i\vec{K}_0\cdot\vec{R}_1} e^{-i\omega t}$$

provided that

$$\vec{E}_0 = \frac{2\pi}{n-1} \rho^{(1)} \vec{P}_0 \qquad (7.9)$$

This agrees with the result obtained using electromagnetic field theory with continuous isotropic dielectrics, since $\rho^{(1)}\vec{P}_0 = \frac{n^2-1}{4\pi} \vec{E}^{+}$ within a dielectric, so that

$$\vec{E}_0 = \frac{n^2-1}{4\pi} \frac{2\pi}{n-1} \vec{E}^{+} = \frac{1}{2}(n+1)\vec{E}^{+}$$

which is the well known expression for the amplitude of the transmitted wave with normal incidence at a plane boundary$^{(22)}$. Therefore, the result of these integrations is that

$$\alpha\left\{ \vec{E}_1^{(0)} + \rho^{(1)} \int_V \Lambda_{12} \cdot \vec{P}_2^{(1)} d^3\vec{R}_2 \right\}$$

$$= \frac{4\pi}{3} \alpha \rho^{(1)} \frac{n^2+2}{n^2-1} \vec{P}_1^{(1)} \qquad (7.10)$$

In the approximation discussed by Born, this is set equal to $\vec{P}_1^{(1)}$ (equation (7.5)), and leads the well known Clausius-Mosotti (or Lorentz) formula for the index of refraction,

$$\frac{4\pi}{3} \rho^{(1)} \frac{n^2+2}{n^2-1} = \frac{1}{\alpha} \qquad (7.11)$$

The terms which Born neglected will of course lead to deviations from this simple formula.

There are two types of terms which give rise to deviations.

One of these containing $g^{(2)}-1$, can be integrated explicitly. The other, containing $\vec{P}^{(2)}-\vec{P}^{(1)}$, leads to a series in α, in which the higher terms than the first are very complicated. Some manipulation will be performed on the first term in the α expansion. It is an obvious requirement in this theory that the results of the integrations on these deviation terms be of the form of a constant times $\vec{P}^{(1)}$, so that the index of refraction may be isotropic. The requirement will be satisfied, at least for the simplest terms.

One of the deviation integrals is

$$\vec{E}^{II} = \int_V \left[g^{(2)}(R_{12}) - 1 \right] \lambda_{12} \cdot \vec{P}_2^{(1)} \, d^3\vec{R}_2 \tag{7.12}$$

In this, it is probably quite safe to extend the domain of integration over all space, since $g^{(2)}-1$ is essentially a short range term. Then, after transforming coordinates to the relative configuration space $\vec{R}_{12}$, the integration over angles is the same as in the preceding evaluation. This must then be followed by an integration over scalar $\vec{R}_{12}$. The result is a special case of a more general result derived in the appendix. The answer is

$$\vec{E}^{II} = 2\pi \vec{P}_1^{(1)} \int_0^\infty \left[g^{(2)}(R) - 1 \right] F(R) \, dR \qquad = G P_1^{(1)}$$

$$\begin{aligned} F(R) = {} & 2 e^{iK_0R} j_0(K_1R) \left(-\frac{1}{R} + iK_0 + K_0^2 R \right) \\ & + e^{iK_0R} \left[j_0(K_1R) + j_0''(K_1R) \right] \left(\frac{3}{R} - 3iK_0 - K_0^2 R \right) \end{aligned} \tag{7.13}$$

Here, $j_0(k_1R)$ is the spherical Bessel function of 1/2 order

$$j_0(k_1R) = \frac{\sin k_1R}{k_1R}$$

and the primes denote differentiation with respect to the argument. If F(R) is expanded in powers of R, a simpler and probably more useful result is obtained as a first approximation:

$$\vec{E}^{II} \cong \frac{32\pi^3}{3}\,\frac{1}{\lambda_0^2}\,\frac{n^2+10}{10}\,\vec{P}_1^{(1)}\int_0^\infty \left[g^{(2)}(R)-1\right]R\,dR \qquad (7.14)$$

This expression was first obtained by Wood(23). It is clear that the $g^{(2)}$-1 term does give rise to the proper $\vec{P}^{(1)}$ dependence.

The other deviation integral is

$$\vec{E}^{III} = \int_V g^{(2)}(R_{12})\,\boldsymbol{\lambda}_{12}\cdot\left[\vec{P}_{2;1}^{(2)} - \vec{P}_1^{(1)}\right]d^2\vec{R}_2 \qquad (7.15)$$

With the expansion of $\vec{P}^{(2)}$ in α,

$$\vec{E}^{III} = \sum_{s=1}^{\infty}\alpha^s\int_V g^{(2)}(R_{12})\,\boldsymbol{\lambda}_{12}\cdot\vec{P}_{2;1}^{(2)(s)}\,d^3\vec{R}_2$$

The first term will be considered here. This is

$$\alpha\int_V g^{(2)}(R_{12})\,\boldsymbol{\lambda}_{12}\cdot\left[\boldsymbol{\lambda}_{12}\cdot\vec{P}_1^{(1)} + \int_V \boldsymbol{\lambda}_{23}\cdot\left\{\frac{\rho_{123}^{(3)}}{\rho_{12}^{(2)}} - \frac{\rho_{23}^{(2)}}{\rho^{(1)}}\right\}\vec{P}_3^{(1)}\,d^3\vec{R}_3\right]d^3\vec{R}_2$$

$$= H\,\vec{P}_1^{(1)}$$

(anticipating the proof that the value of the integral is proportional to $\vec{P}_1^{(1)}$). The integral is evaluated in two parts: the actual integrations are also performed in the appendix. The first part,

$$H_1 \vec{P}_1^{(1)} = \alpha \int_V g^{(2)}(R_{12}) \, \lambda_{12}^2 \, d^3\vec{R}_2 \cdot \vec{P}_1^{(1)}$$

has the value

$$H_1 = \frac{8\pi}{3} K_0^4 \alpha \int_0^\infty \left[g^{(2)}(R) - 1 \right] e^{2iK_0R} \, dR$$

$$+ \frac{4\pi}{3} \alpha \int_0^\infty g^{(2)}(R) \left\{ \frac{4iK_0^3}{R} - \frac{10 K_0^2}{R^2} - \frac{12 i K_0}{R^3} + \frac{6}{R^4} \right\} e^{2iK_0R} \, dR \tag{7.16}$$

The second part,

$$H_2 \vec{P}_1^{(1)} = \alpha \int_V \int_V g^{(2)}(R_{12}) \left[\frac{\rho_{123}^{(3)}}{\rho_{12}^{(2)}} - \frac{\rho_{23}^{(2)}}{\rho^{(1)}} \right] e^{i \vec{K}_1 \cdot \vec{R}_{13}} \lambda_{13} \cdot \lambda_{23} \cdot \vec{P}_1^{(1)} d^3\vec{R}_2 \, d^3\vec{R}_3$$

presents greater difficulty, because of the presence of two variables of integration which are mixed in the integrand. Only certain parts of this integration were performed, namely those which show that H_2 is a scalar. The details again are given in the appendix. Since the integrations are to be performed over all space, and since the only directional quantity in the integrand is $\vec{k}_1$, the following device proved useful: The integration was divided into two parts, one of which involves an integration over the relative configuration of the particles in a fixed plane, and the other an integration over the relative orientation of this plane with respect to $\vec{k}_1$. It is the latter integration that has been carried out, and which shows that H_2 is a scalar. With the definitions

$$\mathcal{G} = g^{(2)}(R_{12})\left[\frac{\rho_{123}^{(3)}}{\rho_{12}^{(2)}} - \frac{\rho_{23}^{(2)}}{\rho^{(1)}}\right]$$

$$\lambda_{12} = M_{12}\,\vec{e}_{12}\,\vec{e}_{12} + N_{12}\,\underset{\sim}{1}$$

$$\cos\theta_{1223} = \vec{e}_{12}\cdot\vec{e}_{23}$$

and so on, the result of the integration over angles is

$$4\pi^2\,\mathcal{G}\,\vec{P}_1^{(1)}\,\{\ \} \qquad (7.17)$$

where

$$\begin{aligned}\{\ \} = 2\Big[&N_{12}N_{23} - \tfrac{1}{2}M_{12}M_{23}\cos\theta_{1223}\big(\cos\theta_{1312}\cos\theta_{1323} \\ &\qquad - \cos\theta_{1223}\big) \\ &+ \tfrac{1}{2}M_{12}N_{23}\sin^2\theta_{1312} + \tfrac{1}{2}N_{12}M_{23}\sin^2\theta_{1323}\Big]\,j_0(K_1R_{13}) \qquad (7.18) \\ + \tfrac{1}{2}\Big[&M_{12}M_{23}\cos\theta_{1223}\big(3\cos\theta_{1312}\cos\theta_{1323} - \cos\theta_{1223}\big) \\ &+ M_{12}N_{23}\big(3\cos^2\theta_{1312} - 1\big) + N_{12}M_{23}\big(3\cos^2\theta_{1323} - 1\big)\Big]\times \\ &\times\Big[j_0(K_1R_{13}) - j_0''(K_1R_{13})\Big]\end{aligned}$$

This must then be integrated over the relative configurations of the particles in a plane, and involves, of course, the distances R_{12}, R_{23}, and R_{13}, and the angles $\theta_{13\,12}$, θ_{1323}, and θ_{1223}. The result is therefore:

$$4\pi^2\int \mathcal{G}(\vec{R}_1,\vec{R}_2,\vec{R}_3)\left\{\ \right\} dR_{13}\ R_{12}\,dR_{12}\ d\theta_{1213} \qquad (7.19)$$

While it is certainly possible to carry out further computations on the H term, this hardly seems to be worth while in view of the length of even the simplest parts of this term. However, it has been shown that this correction term is proportional to $\vec{P}_1^{(1)}$, in a first approximation.

The calculation of the index of refraction can now be made complete:

$$\frac{4\pi}{3}\alpha\rho^{(1)}\,\frac{n^2+2}{n^2-1} = 1 + \alpha\rho^{(1)}G + \alpha^2\rho^{(1)}H \qquad (7.20)$$

where G is defined in equation (7.13) and H (= $H_1 + H_2$) is defined in equation (7.16) and the following text. It would probably be preferable to have this expansion in powers of density, but then it would be far more difficult to evaluate the coefficients. Brown has claimed that the dielectric constant ϵ can be best fitted by the equation

$$\frac{\epsilon+2}{\epsilon-1} = \frac{d_0}{\rho^{(1)}} + c_0 + c_1\frac{\rho^{(1)}}{d_0} + c_2\left(\frac{\rho^{(1)}}{d_0}\right)^2 + \cdots$$

where d_0, c_1, c_2... are constants, on the basis of a theory similar to this. From a practical point of view, this may be the case for the index of refraction too. At least in principle, it is possible to expand the right hand side of (7.20) in powers of the density, so that it has the form of Brown's equation.

VIII Corrections to the Light Scattering Formula

In section V, the exact light scattering theory was described, and the customary approximation was obtained. Calculation of the correction terms required knowledge of the quantity $\vec{P}^{(2)}-\vec{P}^{(1)}$, which was obtained in section VI. In this section, the corrections will be discussed.

The extra term is

$$\Delta \vec{S}_0 = \int_v\!\!\int_v \rho_{12}^{(2)} \{\Delta\}\, d^3\vec{R}_1\, d^3\vec{R}_2$$

$$\begin{aligned} \{\Delta\} = {} & (\lambda_{01}\cdot \Delta \vec{P}^{(2)}_{1;2}) \times (\vec{\mu}^{\,*}_{02} \times \vec{P}^{(1)*}_2) \qquad (8.1) \\ & + (\lambda_{01}\cdot \vec{P}^{(1)}_1) \times (\vec{\mu}^{\,*}_{02} \times \Delta \vec{P}^{(2)*}_{2;1}) \\ & + (\lambda_{01}\cdot \Delta \vec{P}^{(2)}_{1;2}) \times (\vec{\mu}^{\,*}_{02} \times \Delta \vec{P}^{(2)*}_{2;1}) \end{aligned}$$

With the use of the approximations in λ and $\vec{\mu}$, and simplification according to equation (5.9), this becomes

$$\{\Delta\} = \vec{e}_{10} \frac{C_0 K_0^4}{R_{01}^2} e^{i \vec{K}_0 \cdot \vec{R}_{12}} \Big\{ (\vec{P}_2^{(1)*} \cdot \vec{e}_{01})(\Delta \vec{P}_{1;2}^{(2)} \cdot \vec{e}_{01})$$

$$- (\vec{P}_2^{(1)*} \cdot \Delta \vec{P}_{1;2}^{(2)}) + (\Delta \vec{P}_{2;1}^{(2)*} \cdot \vec{e}_{01})(\vec{P}_1^{(1)} \cdot \vec{e}_{01}) - (\Delta \vec{P}_{2;1}^{(2)*} \cdot \vec{P}_1^{(1)})$$

$$+ (\Delta \vec{P}_{2;1}^{(2)*} \cdot \vec{e}_{01})(\Delta \vec{P}_{1;2}^{(2)} \cdot \vec{e}_{01}) - (\Delta \vec{P}_{2;1}^{(2)*} \cdot \Delta \vec{P}_{1;2}^{(2)}) \Big\}$$

Then, making the expansion of $\vec{P}^{(2)}$ in powers of α,

$$\Delta \vec{P}_{1;2}^{(2)} = \vec{P}_{1;2}^{(2)} - \vec{P}_1^{(1)} = \sum_{s=1}^{\infty} \alpha^s \vec{P}_{1;2}^{(2)(s)} , \qquad (8.2)$$

the moment dependence of the scattering correction becomes

$$\{\Delta\} = \vec{e}_{10} \frac{C_0 K_0^4}{R_{01}^2} e^{i \vec{K}_0 \cdot \vec{R}_{12}} \sum_{s=1}^{\infty} \alpha^s F^{(s)}$$

$$F^{(s)} = (\vec{P}_2^{(1)*} \cdot \vec{e}_{01})(\vec{P}_{1;2}^{(2)(s)} \cdot \vec{e}_{01}) - (\vec{P}_2^{(1)*} \cdot \vec{P}_{1;2}^{(2)(s)})$$

$$+ (\vec{P}_{2;1}^{(2)(s)*} \cdot \vec{e}_{01})(\vec{P}_1^{(1)} \cdot \vec{e}_{01}) - (\vec{P}_{2;1}^{(2)(s)*} \cdot \vec{P}_1^{(1)}) \qquad (8.3)$$

$$+ \sum_{\substack{j=1\\K=1\\j+K=S}} (\vec{P}_{2;1}^{(2)(j)*} \cdot \vec{e}_{01})(\vec{P}_{1;2}^{(2)(K)} \cdot \vec{e}_{01}) - (\vec{P}_{2;1}^{(2)(j)*} \cdot \vec{P}_{1;2}^{(2)(K)})$$

Only the first order correction will be considered here: the higher order terms can be written down, but are too long and involved to receive much consideration at the present time. The first order correction is

$$\Delta \vec{S}_0 = \vec{e}_{10} \, \frac{C_0 K_0^{\,4}}{R_{01}^2} \, \alpha \int_v \int_v \rho_{12}^{(2)} \, e^{i \vec{K}_0 \cdot \vec{R}_{12}} \, F^{(1)} \, d^3\vec{R}_1 \, d^3\vec{R}_2$$

$$F^{(1)} = \left(\vec{P}_2^{(1)*} \cdot \vec{e}_{01} \right)\left(\vec{P}_{1;2}^{(2)(1)} \cdot \vec{e}_{01} \right) - \left(\vec{P}_2^{(1)*} \cdot \vec{P}_{1;2}^{(2)(1)} \right) \qquad (8.4)$$

$$+ \left(\vec{P}_{2;1}^{(2)(1)*} \cdot \vec{e}_{01} \right)\left(\vec{P}_1^{(1)} \cdot \vec{e}_{01} \right) - \left(\vec{P}_{2;1}^{(2)(1)*} \cdot \vec{P}_1^{(1)} \right)$$

The quantities that appear in this expression are

$$\vec{P}_1^{(1)} = \vec{P}_0 \, e^{i \vec{K}_1 \cdot \vec{R}_1} \, \left(e^{-i\omega t} \right)$$

$$\vec{P}_{1;2}^{(2)(1)} = \lambda_{12} \cdot \vec{P}_2^{(1)} + \int_V \lambda_{13} \cdot \vec{P}_3^{(1)} \left[\frac{\rho_{123}^{(3)}}{\rho_{12}^{(2)}} - \frac{\rho_{13}^{(2)}}{\rho^{(1)}} \right] d^3\vec{R}_3 \qquad (8.5)$$

$F^{(1)}$ can be simplified by noting that in the integral in which $F^{(1)}$ appears, the coordinates 1 and 2 are interchangeable, and that with such a change the second two terms are complex conjugates of the first two terms:

$$F^{(1)} = a + a^*$$

$$a = \left(\vec{P}_2^{(1)*} \cdot \vec{e}_{01} \right)\left(\vec{P}_{1;2}^{(2)(1)} \cdot \vec{e}_{01} \right) - \left(\vec{P}_2^{(1)*} \cdot \vec{P}_{1;2}^{(2)(1)} \right) \qquad (8.6)$$

After substituting,

$$a = \vec{P}_0^{\,*} \cdot \left(\vec{e}_{01} \vec{e}_{01} - \underset{\sim}{1} \right) \cdot \left(e^{-i \vec{K}_1 \cdot \vec{R}_2} \, \vec{P}_{1;2}^{(2)(1)} \right) \qquad (8.7)$$

Therefore, the scattering correction is

$$\Delta \vec{S}_{01} = \vec{e}_{10} \; \frac{c_0 K_0^4}{R_{01}^2} \; \alpha \left(J + J^* \right)$$

$$J = \vec{P}_0^{\,*} \cdot \left(\vec{e}_{01} \vec{e}_{01} - \underset{\sim}{1} \right) \cdot \vec{L} \qquad (8.8)$$

$$\vec{L} = \iint\limits_{v\,v} \rho_{12}^{(2)} \, e^{i \vec{K}_0 \cdot \vec{R}_{12}} \, e^{-i \vec{K}_1 \cdot \vec{R}_2} \; \vec{P}_{1;2}^{(2)(1)} \, d^3\vec{R}_1 \, d^3\vec{R}_2$$

Putting in the explicit form of $\vec{P}^{(2)(1)}$,

$$\vec{L} = \iint\limits_{v\,v} \rho_{12}^{(2)} \, e^{i \vec{K}_0 \cdot \vec{R}_{12}} \, \boldsymbol{\lambda}_{12} \cdot \vec{P}_0 \, d^3\vec{R}_1 \, d^2\vec{R}_2$$

$$+ \iint\limits_{v\,v} \rho_{12}^{(2)} \, e^{i \vec{K}_0 \cdot \vec{R}_{12}} \left\{ \int\limits_{\infty} e^{i \vec{K}_1 \cdot \vec{R}_{23}} \left[\frac{\rho_{123}^{(3)}}{\rho_{12}^{(2)}} - \frac{\rho_{13}^{(2)}}{\rho^{(1)}} \right] \boldsymbol{\lambda}_{13} \cdot \vec{P}_0 \, d^3\vec{R}_3 \right\} d^3\vec{R}_1 \, d^3\vec{R}_2 \qquad (8.9)$$

The integrals involved here are very much like those required in the index of refraction theory. However, they differ in the domains of integration and in some small but significant details. In these integrals both variables must remain within the domain v of integration. However, this volume is of macroscopic size: it is large compared with molecular dimensions and also with the wavelength of the light. The integrands are essentially short-range, so that one of the volume integrals may be replaced by an integration over all space. That is,

$$\vec{L} = \left(\rho^{(1)} \right)^2 v \int\limits_{\infty} g_{12}^{(2)} \, e^{i \vec{K}_0 \cdot \vec{R}_{12}} \, \boldsymbol{\lambda}_{12} \cdot \vec{P}_0 \, d^3\vec{R}_{12}$$

$$+ \left(\rho^{(1)} \right)^2 v \int\limits_{\infty} g_{12}^{(2)} \, e^{i \vec{K}_0 \cdot \vec{R}_{12}} \left\{ \int\limits_{\infty} e^{i \vec{K}_1 \cdot \vec{R}_{23}} \left[\frac{\rho_{123}^{(3)}}{\rho_{12}^{(2)}} - \frac{\rho_{13}^{(2)}}{\rho^{(1)}} \right] \right. \qquad (8.10)$$

$$\left. \times \; \boldsymbol{\lambda}_{13} \cdot \vec{P}_0 \, d^3\vec{R}_3 \right\} d^3\vec{R}_{12}$$

If the volume v is symmetrical about the direction of propagation $\vec{k}_0$ (and $\vec{k}_1$), then these integrals are special cases of the more general type worked out in the appendix, with the result that $\vec{L}$ is proportional to $\vec{P}_0$ and in the same direction. This will be expressed

$$\vec{L} = n_v \rho^{(1)} W \vec{P}_0 \tag{8.11}$$

where W is now the magnitude of the corresponding dyadic integral. The evaluation of W should proceed along much the same lines as the evaluation of the correction to the index of refraction formula. The actual evaluation will not be performed here. Collecting terms, the light scattering correction is

$$\Delta \vec{S}_{01} = \vec{e}_{10} \frac{C_0 K_0^4}{R_{01}^2} \alpha \rho^{(1)} n_v (W + W^*)(\vec{P}_0^* \cdot \vec{P}_0) \sin^2\theta \tag{8.12}$$

and the whole intensity is

$$\langle \vec{S} \rangle_{AV} = \vec{e}_{10} \left\{ \frac{1}{2} \frac{C_0 K_0^4}{R_{01}^2} n_v (\vec{P}_0^* \cdot \vec{P}_0) \sin^2\theta \right\} \times$$

$$\times \left\{ 1 + \rho^{(1)} \int_0^\infty \left[g^{(2)}(R) - 1 \right] 4\pi R^2 \frac{\sin sR}{sR} dR \right. \tag{8.13}$$

$$\left. + \alpha \rho^{(1)} (W + W^*) \right\}$$

In this, $\vec{e}_{10}$ is the unit vector from the scattering volume to the observer, c_o is the velocity of light in vacuo, k_o is $2\pi/\lambda_o$ where λ_o is the wavelength of the light in vacuo, R_{01} is the distance from the scattering volume to the observer, n_v is the number of particles in the scattering volume v, $\vec{P}_o$ is the magnitude of the macroscopic dipole wave, and θ is the angle between the direction of polarization of the incoming light and direction of observation. In the brace, $\rho^{(1)}$ is the density of the fluid, $g^{(2)}$ is the radial distribution function, s is the magnitude of $\vec{k}_{10}-\vec{k}_1$ (and contains another angular dependence, in general), α is the polarizibility of a particle, and W is a numerical constant defined earlier in the section.

Since most scattering measurements start with unpolarized light, a more useful expression is obtained by averaging this over directions of polarization. Then, $\sin^2\theta$ is replaced by $\frac{1+\cos^2\varphi}{2}$, where φ is the angle between the direction of propagation of the incoming light and the direction of the observer. It is also desirable to express the result in terms of an "initial intensity" I_o which is taken to be the magnitude of the Poynting vector of the electromagnetic field that is traveling through the liquid. The electric field is

$$\begin{aligned}\vec{E}_1^{(1)} &= \vec{E}_o^{(1)}\, e^{i\vec{K}_1\cdot\vec{R}_1}\, e^{-i\omega t} \\ &= \frac{1}{\alpha}\,\vec{P}_1^{(1)}\end{aligned} \tag{8.14}$$

and the energy flow is therefore

$$I_0 = n c_0 \frac{1}{2} \left(\vec{E}_1^{(1)*} \cdot \vec{E}_1^{(1)}\right) = \frac{n c_0}{2 \alpha^2} \left(\vec{P}_0^{*} \cdot \vec{P}_0\right) \tag{8.15}$$

so that the first part of the scattering intensity formula (8.13) is

$$\frac{1}{2} \frac{c_0 K_0^4}{R_{01}^2} \left(\vec{P}_0^* \cdot \vec{P}_0\right) = \frac{K_0^4 \alpha^2}{R_{01}^2 \, n} I_0 \tag{8.16}$$

(The definition of I_0 varies from author to author: the one used here is convenient from the point of view of a "scattering cross-section". This formula differs from most in having the index of refraction in the denominator, which is just a result of the definition of I_0.)

The scattering cross-section, which gives the intensity of light scattered into a solid angle $d\Omega$, from a volume v, with density $\rho^{(1)}$ and incident intensity I_0, is

$$d I = \frac{v}{R_{01}^2} \sigma I_0 \, d\Omega$$

$$\sigma = \frac{8 \pi^4 \alpha^2}{\lambda_0^4 \, n} \rho^{(1)} (1 + \cos^2\varphi) \times \left\{ 1 + \rho^{(1)} \int_0^\infty \left[g^{(2)}(R) - 1 \right] \times 4\pi R^2 \frac{\sin sR}{sR} \, dR + \alpha \rho^{(1)} (W + W^*) \right\} \tag{8.17}$$

with

$$W = \left| \int_\infty g^{(2)}(R_{12}) e^{i\vec{K}_0 \cdot \vec{R}_{12}} \lambda_{12} \, d^3\vec{R}_{12} + \int_\infty g^{(2)}(R_{12}) e^{i K_0 \cdot \vec{R}_{12}} \left\{ \int_\infty e^{i\vec{K}_1 \cdot \vec{R}_{23}} \left[\frac{\rho_{123}^{(3)}}{\rho_{12}^{(2)}} - \frac{\rho_{13}^{(2)}}{\rho^{(1)}} \right] \lambda_{13} \, d^3\vec{R}_3 \right\} d^3\vec{R}_{12} \right| \tag{8.18}$$

The other symbols have all been defined after the equation (8.12). To carry this a bit further, the polarizibility is determined, although indirectly, by the index of refraction:

$$\frac{4\pi}{3}\alpha\rho^{(1)}\,\frac{n^2+2}{n^2-1} = 1+\alpha\rho^{(1)}G+\alpha^2\rho^{(1)}H+\cdots$$

which is equation (7.20). Therefore it is possible to evaluate the light scattering intensity, if one knows the index of refraction and the radial distribution function. This concludes the rigorous derivation of the light scattering intensity from a fluid of spherically symmetric, optically isotropic particles.

IX Appendix

In the text, we promised that some of the more involved calculations would be described in an appendix. These are the fundamental cavity integral which leads to the Lorentz-Lorenz field, and the simplification of the correction terms in the index of refraction and light scattering theory. These are all of the form of volume integrals or surface integrals, and the parts that will be performed here involve the angular dependence of the integrands.

The first integral to be evaluated is the general one

$$\mathbb{I}_1 = \int f(\vec{K}_1 \cdot \vec{R}_{12})\left[M(R_{12})\,\vec{e}_{12}\vec{e}_{12} + N(R_{12})\,\frac{1}{m}\right] d\Omega_{12} \tag{9.1}$$

over the surface of a sphere, $|\vec{R}_{12}| = R_{12}$. The functions M and N are arbitrary functions of scalar distance, the vectors $\vec{e}_{12}$ are unit vectors

$$\vec{e}_{12} = \frac{\vec{R}_{12}}{R_{12}}$$

and f is an arbitrary function of the scalar product of $\vec{R}_{12}$ and a constant vector $\vec{k}_1$.

We transform from spherical to rectangular coordinates,

$$X = R \sin\theta \cos\varphi$$

$$Y = R \sin\theta \sin\varphi$$

$$Z = R \cos\theta$$

For convenience, we also take the dot product of the integrand with an arbitrary fixed vector $\vec{a}$ perpendicular to $\vec{k}_1$. The integral is then

$$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta \, d\theta \quad f(\vec{K}_1 \cdot \vec{R}_{12}) \left[M_{12}\, \vec{e}_{12} (\vec{e}_{12} \cdot \vec{a}) + N_{12}\, \vec{a} \right]$$

Select a special coordinate system in which the x axis is in the $\vec{a}$ direction, and the z axis is in the $\vec{k}_1$ direction. Then

$$\vec{K}_1 \cdot \vec{R}_{12} = K_1 R_{12} \cos\theta \quad ; \quad \vec{e}_{12} (\vec{e}_{12} \cdot \vec{a}) = \vec{b}$$

$$b_x = |\vec{a}| \sin^2\theta \cos^2\varphi$$

$$b_Y = |\vec{a}| \sin^2\theta \sin\varphi \cos\varphi$$

$$b_z = |\vec{a}| \sin\theta \cos\theta \cos\varphi$$

When we integrate over φ, the b_Y and b_z terms vanish, and since

$$\int_0^{2\pi} \cos^2\varphi \, d\varphi = \pi$$

we get as a result

$$\Pi_1 \cdot \vec{a} = \pi \left\{ M_{12} \int_0^{\pi} f(K_1 R_{12} \cos\theta) \sin^3\theta \, d\theta \right. \tag{9.2}$$

$$\left. + 2 N_{12} \int_0^{\pi} f(K_1 R_{12} \cos\theta) \sin\theta \, d\theta \right\} \vec{a}$$

It should be observed that $\mathbb{I}_1$ behaves like a constant times the unit dyad, when it operates on a vector perpendicular to $\vec{k}_1$. As a further result, which is easily seen, if we integrate the same integrand over any surface which is symmetrical about $\vec{k}_1$, with $\vec{k}_1$ perpendicular to $\vec{a}$, the result is in the direction $\vec{a}$. Going back to the spherical case, we now take

$$f(\vec{K}_1 \cdot \vec{R}_{12}) = e^{i \vec{K}_1 \cdot \vec{R}_{12}}$$

Then, the integrals are

$$\int_{-1}^{+1} e^{i K_1 R_{12} x}\, dx = \frac{2}{K_1 R_{12}} \sin K_1 R_{12} = 2 j_0(K_1 R_{12})$$

and

$$\int_{-1}^{+1} e^{i K_1 R_{12} x} x^2\, dx = -2 \frac{d^2}{d(K_1 R_{12})^2} j_0(K_1 R_{12}) = -2 j_0''(K_1 R_{12})$$

In this case,

$$\mathbb{I}_1 \cdot \vec{a} = 2\pi \Big\{ M_{12}\big[j_0(K_1 R_{12}) + j_0''(K R_{12})\big] + 2 N_{12}\, j_0(K_1 R_{12}) \Big\} \vec{a} \qquad (9.3)$$

This may be used to obtain the integral

$$\vec{E}^{\mathrm{I}} = \int^{\infty} \left[g^{(2)}(R_{12}) - 1 \right] \lambda_{12} \cdot \vec{P}_2^{(1)}\, d^3 \vec{R}_2 \qquad (9.4)$$

which was required as a correction in the index of refraction theory (equations (7.12-7.14)). This is just

$$\int_0^\infty R_{12}^2 \left[g^{(2)}(R_{12}) - 1 \right] \mathbb{I}_1 \cdot \vec{P}_1^{(1)} \, dR_{12}$$

since the integration over angles on the surface of the sphere $|\vec{R}_{12}| = R_{12}$ leads to $\mathbb{I}_1 \cdot \vec{P}_1^{(1)}$. In this M and N are determined by $\boldsymbol{\lambda}_{12}$:

$$\boldsymbol{\lambda}_{12} = M_{12} \, \vec{e}_{12} \vec{e}_{12} + N_{12} \underset{\sim}{1}$$

Performing the substitutions and some simple algebra leads to equation (7.13).

This basic integral may also be used to get the cavity surface integral needed in the Oseen process. This integral is

$$\vec{E}^{I} = \frac{c^2}{(m^2-1)\,\omega^2} e^{-i\omega t} \int_s \left\{ \left(\frac{\partial}{\partial \nu_2} \boldsymbol{\lambda}_{12} \cdot \vec{P}_0 \right) e^{i \vec{K}_1 \cdot \vec{R}_2} - \boldsymbol{\lambda}_{12} \cdot \vec{P}_0 \left(\frac{\partial}{\partial \nu_2} e^{i \vec{K}_1 \cdot \vec{R}_2} \right) \right\} d\Omega_2 \tag{9.5}$$

Here

$$\frac{\partial}{\partial \nu_2} = \frac{\partial}{\partial R_{12}}$$

and the integration is over the surface of a sphere. By simple manipulation, the integral (without the constant factors) is

$$\int_{s} e^{i\vec{K}_1\cdot\vec{R}_{12}}\left\{\frac{\partial \lambda_{12}}{\partial R_{12}} - i\vec{K}_1\cdot\vec{e}_{12}\,\lambda_{12}\right\}\cdot\vec{P}_1^{\prime\prime\prime}\,d\Omega \qquad (9.6)$$

which is of the general type (9.1) and can be handled easily. The calculation in Born's Optik sooner or later comes to the series expansion of this form. Since this has been worked out in sufficient detail in other places, no farther attention will be given to it here.

Another correction in the index of refraction theory can be evaluated using the same basic integral. This is equation (7.16),

$$H_1\vec{P}_1^{(1)} = \alpha\int_{V} g^{(2)}(R_{12})\,\lambda_{12}^{2}\cdot\vec{P}_1^{(1)}\,d^3\vec{R}_2 \qquad (9.7)$$

Here, the quantities of importance are

$$f(\vec{K}_1\cdot\vec{R}_{12}) = 1$$

$$M = M_0^2 + 2M_0N_0$$

$$N = N_0^2$$

$$\lambda_{12} = M_0\,\vec{e}_{12}\,\vec{e}_{12} + N_0\,\underline{1}$$

The integrations over θ are easy:

$$\int_0^{\pi}\sin^3\theta\,d\theta = \frac{4}{3}$$

$$\int_0^{\pi}\sin\theta\,d\theta = 2$$

and therefore

$$H_1 \vec{P}_1^{(1)} = \alpha \frac{4\pi}{3} \int_0^\infty R^2 g^{(2)}(R) \left[M+3N \right] dR \quad \vec{P}_1^{(1)}$$

Direct substitution gives the value of M + 3N:

$$M+3N = e^{2iK_0R} \left(\frac{6}{R^6} - \frac{12iK_0}{R^5} - \frac{10K_0^2}{R^4} + \frac{4iK_0^3}{R^3} + \frac{2K_0^4}{R^2} \right)$$

Some attention must be paid to the convergence of the resulting integral. All the terms converge at the origin because of the cutoff character of $g^{(2)}$. At infinity, the only term that will cause trouble is

$$\frac{4\pi}{3} \int_0^\infty R^2 g^{(2)}(R) \frac{2K_0^4}{R^2} e^{2iK_0R} \, dR$$

$$= \frac{8\pi K_0^4}{3} \int_0^\infty \left[g^{(2)} - 1 \right] e^{2iK_0R} dR + \frac{8\pi K_0^4}{3} \int_0^\infty e^{2iK_0R} dR$$

The second part gives rise to a delta function singularity, $\delta_+(K_0)$, but the coefficient k_0^4 will dominate this, since the δ function contributes for small k, where the factor k_0^4 which multiplies it is also small. Therefore, the result is the one given in equation (7.16).

For the remaining integrals in the index of refraction theory, called $H_2\vec{P}_1^{(1)}$, it is convenient to use the device of averaging a function of points on a plane over all orientations of that plane with respect to a fixed axis. For this purpose, a lemma is derived first.

We are given a dyad, $\vec{A}\,\vec{B}$, and we wish to rotate this dyad about a fixed axis $\vec{r}_0$. What is the average value (or the corresponding integral) of the dyad? Take $\vec{r}_0$ in the z direction, and have both vectors start at the origin. If the spherical polar coordinates of the vactors are

$$\vec{A} : \quad a, \ \theta_1, \ \varphi_1$$

$$\vec{B} : \quad b, \ \theta_2, \ \varphi_2$$

the the dyad is

$$\begin{aligned}
\vec{A}\,\vec{B} = \ & \vec{i}\,\vec{i} \quad a\,b \sin\theta_1 \sin\theta_2 \cos\varphi_1 \cos\varphi_2 \\
& + \vec{j}\,\vec{j} \quad a\,b \sin\theta_1 \sin\theta_2 \sin\varphi_1 \sin\varphi_2 \\
& + \vec{K}\,\vec{K} \quad a\,b \cos\theta_1 \cos\theta_2 \\
& + \vec{i}\,\vec{j} \quad a\,b \sin\theta_1 \sin\theta_2 \cos\varphi_1 \sin\varphi_2 \\
& + \vec{j}\,\vec{i} \quad a\,b \sin\theta_1 \sin\theta_2 \sin\varphi_1 \cos\varphi_2 \\
& + \vec{i}\,\vec{K} \quad a\,b \sin\theta_1 \cos\theta_2 \cos\varphi_1 \\
& + \vec{K}\,\vec{i} \quad a\,b \cos\theta_1 \sin\theta_2 \cos\varphi_2 \\
& + \vec{j}\,\vec{K} \quad a\,b \sin\theta_1 \cos\theta_2 \sin\varphi_1 \\
& + \vec{K}\,\vec{j} \quad a\,b \cos\theta_1 \sin\theta_2 \sin\varphi_2
\end{aligned}$$

The integration is performed with θ_1, θ_2, and $\psi = \varphi_1 - \varphi_2$ fixed, allowing φ_1 to go from 0 to 2π. The result of this integration is

$$\begin{aligned}\langle \vec{A}\,\vec{B} \rangle = {} & \vec{i}\,\vec{i}\ \tfrac{1}{2}\, a b \sin\theta_1 \sin\theta_2 \cos\psi \\ & + \vec{j}\,\vec{j}\ \tfrac{1}{2}\, a b \sin\theta_1 \sin\theta_2 \cos\psi \\ & + \vec{i}\,\vec{j}\ \tfrac{1}{2}\, a b \sin\theta_1 \sin\theta_2 \sin\psi \\ & - \vec{j}\,\vec{i}\ \tfrac{1}{2}\, a b \sin\theta_1 \sin\theta_2 \sin\psi \\ & + \vec{K}\,\vec{K}\ a b \cos\theta_1 \cos\theta_2 \end{aligned}$$

and going over to the rectangular components of the dyads, this is

$$\begin{aligned}\langle \vec{A}\ \vec{B} \rangle = {} & \tfrac{1}{2}\left(a_x b_x + a_y b_y\right)\left(\vec{i}\,\vec{i} + \vec{j}\,\vec{j}\right) \\ & + \tfrac{1}{2}\left(a_x b_y - a_y b_x\right)\left(\vec{i}\,\vec{j} - \vec{j}\,\vec{i}\right) \\ & + \left(a_z b_z\right) \quad \left(\vec{K}\,\vec{K}\right) \end{aligned}$$

This can also be written in a form which does not depend on the coordinate axes: if $\vec{e}$ is the unit vector in the direction of the axis of rotation,

$$\begin{aligned}\langle \vec{A}\,\vec{B} \rangle = {} & \tfrac{1}{2}\left(3\, \vec{e}\cdot\vec{A}\ \vec{e}\cdot\vec{B} - \vec{A}\cdot\vec{B}\right) \vec{e}\,\vec{e} \\ & - \tfrac{1}{2}\left(\vec{e}\cdot\vec{A}\ \vec{e}\cdot\vec{B} - \vec{A}\cdot\vec{B}\right) \underset{\sim}{1} \\ & - \tfrac{1}{2}\left(\vec{A}\times\vec{B}\cdot\vec{e}\right) \ \vec{e}\times\underset{\sim}{1} \end{aligned} \qquad (9.8)$$

in which $\underset{\sim}{1}$ is the unit dyad.

Now it is possible to evaluate the desired integral,

$$H_2 \vec{P}_1^{(1)} = \alpha \iint g^{(2)}(R_{12}) \left[\frac{\rho_{123}^{(3)}}{\rho_{12}^{(2)}} - \frac{\rho_{13}^{(2)}}{\rho^{(1)}} \right] e^{i\vec{K}_1 \cdot \vec{R}_{13}} \lambda_{12} \cdot \lambda_{23} \cdot \vec{P}_0 \; d^3\vec{R}_2 \, d^3\vec{R}_3$$

For convenience, take

$$\mathcal{G}(R_{12}, R_{13}, R_{23}) = g^{(2)}(R_{12}) \left[\frac{\rho_{123}^{(3)}}{\rho_{12}^{(2)}} - \frac{\rho_{13}^{(2)}}{\rho^{(1)}} \right]$$

This is a function only of the relative positions of the three particles in a plane. The integral is then

$$H_2 \vec{P}_1^{(1)} = \alpha \, \mathbb{H} \cdot \vec{P}_1^{(1)}$$

$$\mathbb{H} = \iint \mathcal{G} \quad e^{i K_1 \cdot R_{13}} \lambda_{12} \cdot \lambda_{23} \; d^3\vec{R}_2 \, d^3\vec{R}_3$$

The only thing which contains any absolute direction is $\vec{k}_1$. The integration is therefore performed in two parts, the first being over the relative positions of the points in a foxed plane, and the second being over all orientations of this plane with respect to $\vec{k}_1$. Now, a dyad appears in the integrand,

$$\lambda_{12} = M_{12} \, \vec{e}_{12} \, \vec{e}_{12} + N_{12} \, \underset{\sim}{1}$$

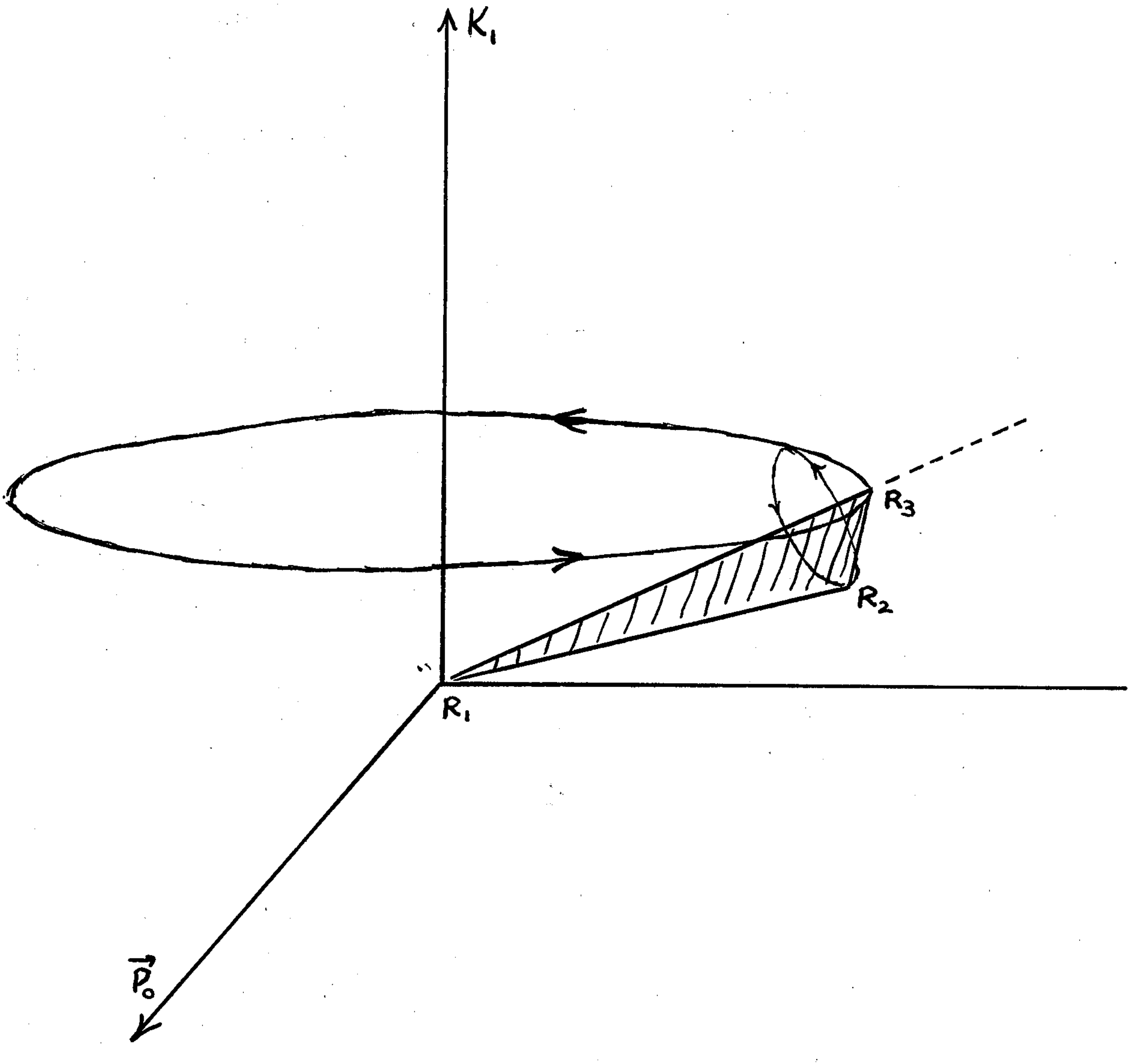
$$\lambda_{23} = M_{23} \, \vec{e}_{23} \, \vec{e}_{23} + N_{23} \, \underset{\sim}{1}$$

$$\begin{aligned} \lambda_{12} \cdot \lambda_{23} \quad = \quad & M_{12} M_{23} \, (\vec{e}_{12} \cdot \vec{e}_{23}) \, \vec{e}_{12} \, \vec{e}_{23} \\ & + M_{12} N_{23} \quad \vec{e}_{12} \, \vec{e}_{12} \\ & + N_{12} M_{23} \quad \vec{e}_{23} \, \vec{e}_{23} \\ & + N_{12} N_{23} \quad \underset{\sim}{1} \end{aligned}$$

so that it will be necessary to average dyads by rotation about an axis. This is the reason for the preceding lemma. The accompanying diagram may help to clarify the process. To cover all orientations, the plane is rotated about the line $\vec{R}_{13}$, and then this result is averaged by taking all positions of the line $\vec{R}_{13}$ with respect to $\vec{k}_1$. Since during the rotations, M, N, and $\mathcal{G}$ are constant (depending only on relative positions in a plane), the quantities to be integrated are

$$e^{i K_1 R_{13} \vec{e}_1 \cdot \vec{e}_{13}} \left\{ \begin{array}{c} \vec{e}_{12} \cdot \vec{e}_{23} \quad \vec{e}_{12}\,\vec{e}_{23} \\ \vec{e}_{12}\,\vec{e}_{12} \\ \vec{e}_{23}\,\vec{e}_{23} \\ \underset{\sim}{1} \end{array} \right\}$$

Combinations like $\vec{e}_{12} \cdot \vec{e}_{23}$ are just functions of the relative positions of the points in the plane, and are constant during the averaging process. The result of the rotation around $\vec{R}_{13}$ is another dyad, with components $\vec{e}_{13}\,\vec{e}_{13}$ and $\underset{\sim}{1}$. Next, this is rotated about $\vec{k}_1$, with a constant angle between $\vec{e}_{13}$ and $\vec{k}_1$. The result of this rotation is a dyad with components $\vec{K}_1\,\vec{K}_1$ and $\underset{\sim}{1}$. This may be simplified now by taking the required dot product with $\vec{P}_0$. Since $\vec{k}_1$ and $\vec{P}_0$ are perpendicular, that part vanishes, and the result of these two rotations ia a constant times the unit dyad. This must still be integrated over the angle between $\vec{e}_{13}$ and $\vec{k}_1$. This introduces the spherical bessel functions. The result


K_1
R_3
R_2
R_1
$\vec{P}_0$

of all this calculation is stated in equation (7.18). So far, only three integrations have been performed, but six are required. The other three involve moving R_3 along the line whose direction is $\vec{e}_{13}$, and then taking R_2 anywhere in the plane.

REFERENCES

1. G. Oster, Chem. Rev., 43, 319 (1948).
2. J. A. Stratton, Electromagnetic Theory, p. 434, McGraw Hill 1941.
3. R. Gans, Ann. Physik, 62, 330 (1920).
4. F. Möglich, Ann. Physik, 83, 609 (1927).
5. G. Mie, ibid., 25, 377 (1908).
6. P. Debye, ibid., 30, 59 (1909).
7. P. Debye, Lecture given at the Polytechnic Institute of Brookly, November 25, 1944.
8. B. Zinn, R. Stein, and P. Doty, Polymer Bull., 1, 90 (1945).
9. A. Einstein, Ann. Physik, 33, 1275 (1910).
10. M. Smoluchowski, Ann. Physik, 25, 205 (1908).
11. J. G. Kirkwood and R. J. Goldberg, J. Chem. Phys.
12. P. Debye and H. Menke, Forts. Röntgenforschung, 2, 1 (1931).
13. N. Gingrich, Rev. Mod. Phys.
14. B. Zimm, J. Chem. Phys., 13, 141 (1945).
15. J. Yvon, Actualites Scientifiques et Industrielles, No.543 "La Propagation et la Diffusion de la Lumiere" Hermann et Cie, 1937.
16. J. G. Kirkwood, J. Chem. Phys., 7, 911 (1939).
17. W. F. Brown, J. Chem. Phys., 18, 1193 (1950).
18. J. G. Kirkwood, E. K. Maun, and B. J. Alder, J. Chem. Phys., 18, 1040 (1950).
19. J. DeBoer, Reports on Progress in Physics XII, pp. 305-374, The Physical Society, 1949.
20. M. Born, Optick, pp. 313-327, Berlin, 1933.
21. S. Darwin, Trans. Camb. Soc., 23, 137 (1924).

22. J. A. Stratton, op cit, pp. 490-497.

23. W. Wood, Dissertation, California Institute of Technology, 1950.

PROPOSITIONS

1. There is a close formal relationship between the "Feynman kernel" and the density matrix of a system in canonical equilibrium. This may be used to obtain the density matrix of a harmonic oscillator in closed form (something which was accomplished by Erdelyi using advanced mathematical analysis), rather than as a series of Hermite functions. It may also be of use in other systems, although the application will not be quite so simple.(1,2)

2. A new set of integral equations can be derived which may be used to get the radial distribution function both in classical and in quantum statistics. This is the first set of integral equations derived quantum mechanically which contains the temperature explicitly.

3. As an application of this set of integral equations, the second virial coefficient of a quantum gas may be derived. A case of special interest is that of rigid spheres. This requires the solution of the quantum mechanical problem of the energy levels and eigenfunctions of two rigid spheres in a box.

4. The analogue of the Kirkwood approach to the free volume theory of liquids can be developed in quantum statistical mechanics(3).

5. The theory of light scattering developed in this thesis can be extended to multicomponent systems. In this way, it should be possible to provide the statistical mechanical basis for the Kirkwood-Goldberg expressions(4).

6. A general scattering theory may be worked out, in which explicit allowance is made for the effect of particle dependence on the scattering cross section (for example, the polarizibility). The important quantities in this are the wave function of the scattered particle at 1 when 2 is fixed and the other scattering centers are averaged out, and the scattering cross section of 1 when 2 is fixed and the others are averaged out.

7. It has been claimed that the lambda point transition in liquid helium II may be due to a condensation in "momentum space". The scattering of slow neutrons from liquid helium may give a method of obtaining the pair density matrix, and hence the momentum distribution of liquid helium. This should be a way of checking the above hypothesis(5,6).

8. Existing forms of statistical mechanics are not relativistically invariant. There are several good reasons for wanting to cast the theory into invariant form. Some of the basic notions of statistical mechanics will have to be reconsidered carefully. It should prove possible to obtain an invariant Liouville equation using modern classical field theory, and maybe even using quantum field theory.

9. Purcell and Pound have claimed that they have obtained a negative thermodynamic temperature in the laboratory. I believe that the operational significance of a negative temperature is doubtful, and that their results should be interpreted in some other way(7,8).

10. a) A possible inhibition caused by an electric current of the decomposition of a solution of potassium in liquid ammonia on a platinum surface should be investigated. This effect has been observed, but not corroborated, and is unexplained.

b) Solutions of alkali metals in liquid ammonia-ether mixtures should be investigated. Preliminary observations have shown some peculiar effects.