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1968 J. Phys. A: Gen. Phys. 1 409

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Many-body optics

I. Dielectric constants and optical dispersion relations

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Communicated by S. F. Edwards; MS. received 18th July 1967, in final form 23rd January 1968

Abstract. This paper is the first of three papers constituting a preliminary mathematical discussion preparatory to the presentation of a series of papers on the observable macroscopic optical properties of a many-body molecular fluid. These properties are viewed wholly as consequences of microscopic many-body interactions, and the theory to be presented is largely concerned with a microscopic theory of the complex refractive index and associated optical response functions: it is nowhere phenomenological. In this paper the classical integral equation, which can be derived from the quantal theory and is fundamental to the optical theory, is presented in limited form (restricted to two-particle interactions) and rigorously solved. Both longitudinal and transverse dispersion relations are obtained and these are generalized to include correlations between sets of particles of any number and to two- (and by implication to multi-) component molecular-fluid systems. All the longitudinal dispersion relations are new results. The theory is strictly a refractive index theory and *not* a dielectric constant theory: in consequence, the longitudinal dispersion relations admit frequencies close to, but not precisely at, the zeros of the corresponding transverse wave number, and this departure from the conventional picture is associated with the theory of optical scattering. The 'local' optical field is due to two- and many-particle complex interaction terms: it mixes 'transverse photons' and 'longitudinal photons', and both kinds of photon contribute to each dispersion relation. The theory of how this complex local field describes external scattering, Cerenkov radiation and the contribution of virtual photon exchange to the ground-state energy will be developed later. For a theory of external scattering it is necessary to break translational invariance: as a consequence, the optical 'extinction theorem', due in the first instance to P. P. Ewald, plays a very significant role in the theory.

1. Introduction

In the course of the last few years the author has carried out a careful investigation of the microscopic processes whereby light is scattered from a fluid in thermal equilibrium. The work is a natural extension of the approach outlined by Rosenfeld (1951). The reason for doing it has been because of the importance of light-scattering measurements as a tool for investigating the microscopic structure of fluids and because of the intrinsic interest of the theory. Two points have emerged from this investigation: firstly, that all optical properties of a many-body fluid system of molecules bound only by van der Waals forces can be treated within a unified optical theory; secondly, that the machinery is so powerful and the light-scattering process so delicate that only the most searching investigation can rid the scattering theory of certain paradoxes that at first sight appear within it.

Preliminary reports of the theory acknowledging the existence of unresolved difficulties appear in the papers of the author (Bullough 1962, 1963, 1965, 1967). The theory has now been cast in an illuminating and simplified form and it is intended to present a series of papers outlining the form and scope of this theory. In three preliminary papers it is intended to investigate the structure and solution of the integral equation which lies at the heart of the whole theory: the present paper (I) is one of these.

The integral equation is an archetype of self-consistent molecular field calculations. It was first studied by Darwin (1924) and appears in generalized form in the work of Hoek (1939), the book of Rosenfeld (1951), and the work of Mazur and Mandel (1956),

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Mazur (1958), Mazur and Postma (1959), and Mazur and Terwiel (1964), as well as in that of the author. Darwin's integral equation is also treated in Born and Wolf's (1959) book, and it has been extended by Bloembergen and Pershan (1962) to the case of a non-linear response.

A significant feature of the theory is the emergence of the so-called 'extinction theorem' of Ewald (1912, 1916) and Oseen (1915). This elegant feature characterizes a certain type of optical theory. It does not appear in any of the current many-body theories of optical properties of the type described, for example, by Pines (1963), and it is of interest to discover why not. One reason is that in order to prepare for a discussion of the scattering of light *outside* a material medium it is necessary to break translational invariance: we do this here and hope to discuss the microscopic optics of a translationally invariant system on another occasion. A second reason is the emphasis of much of current many-body theory on 'longitudinal' rather than 'transverse' probes: the extinction theorem becomes irrelevant (but only in the very limited sense to be indicated in a subsequent paper, which is the second of these three preliminary papers (Bullough, to be published, to be referred to as II)) in the case of a longitudinal probe. A number of points concerning the extinction theorem in relation to current many-body theory will also be made in II. These points do not provide an all-embracing answer to the question of understanding implicit in these two contrasting approaches to many-body optical theories, but at least some of these contrasts are exposed there. The extinction theorem plays a curious and very significant role in the theory of external scattering, which we shall outline in the later papers of this series, and its existence also has important consequences for the understanding of the theory of binding energy and of virtual photons.

In the present paper we use the integral equation we study for two purposes: firstly, to provide an introduction to the general optical theory which is to follow later, and, secondly, to reach a new physical result. This result is a longitudinal dispersion relation for a many-body 'molecular' fluid: it does not seem to have been reached before and it is therefore given here in as complete a form as possible. This occasions the introduction of many-particle correlation functions which play an important role in the later presentation of the general theory but lie outside the consequences of the particular integral equation we study here. The longitudinal dispersion relation in either one- or multi-component systems seems to be of some importance in a later discussion of ground-state energy; but we can defer comment on this aspect of the longitudinal dispersion relation until then.

Likewise, a discussion of both the extinction theorem and other aspects of the physical significance of the longitudinal dispersion relation will be deferred until paper II. The consequences of breaking translational invariance and a number of mathematical and interpretative points are deferred until a third paper (Bullough, to be published, to be referred to as III). This third paper therefore constitutes something of a mathematical appendix to both I and II, and to all the consequent work which will rely upon it. The general optical theory can be developed most expeditiously only if the reader has early access to such an 'appendix'. It is for this reason that the 'appendix' must be presented as an early rather than last paper here.

This completes a first survey of the programme we shall adopt in presenting the microscopic optical theory. Now we turn to the specific problem of the present paper, the solution of the fundamental integral equation and the derivation of the dispersion relations.

2. The integral equation

The integral equation we shall study is

$$\mathbf{P}(\mathbf{x}, \omega) = \alpha(\omega) \left\{ \mathbf{E}(\mathbf{x}, \omega) + n \int \mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) g(\mathbf{x}, \mathbf{x}') \cdot \mathbf{P}(\mathbf{x}', \omega) d\mathbf{x}' \right\}. \quad (2.1)$$

This is not the integral equation which determines even the 'simplest' optical property of a many-body fluid, namely its true refractive index, but it will become plain from § 4, and indeed from the work which has appeared already, that the solutions of (2.1) in different circumstances cover all the situations that arise in the more complete many-body optical

theory of the fluid. The integral equation used by Rosenfeld (1951) is precisely (2.1); Darwin (1924) and Born and Wolf (1959) investigate the solution of

$$\mathbf{P}(\mathbf{x}, \omega) = \alpha(\omega) \left\{ \mathbf{E}(\mathbf{x}, \omega) + n \int \mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) \cdot \mathbf{P}(\mathbf{x}', \omega) d\mathbf{x}' \right\} \quad (2.2)$$

in the present notation. The integral equations of Mazur and the writer are more complicated, and the final result of this paper, the most general forms of the dispersion relations (4.11a) and (4.11b), is a consequence of the more general equations. The particular result of these more general equations is that equations (4.11) have to be taken with the interpretations (4.19a) and (4.19b), in which many-particle correlation functions appear, instead of the interpretations (4.12), in which only $g(\mathbf{x}, \mathbf{x}')$ appears. The result (4.11b) in either interpretation is believed to be new.

The essential physics contained in the integral equation (2.1) is as follows. The quantity $n\mathbf{P}(\mathbf{x}, \omega)$ is a 'classical' dipole moment per unit volume of the fluid induced by an incident electromagnetic field $\mathbf{E}(\mathbf{x}, \omega)$ of angular frequency ω ; n is a number density of particles so that \mathbf{P} is a dipole moment 'per particle'. The scalar $\alpha(\omega)$ is a 'classical' polarizability per particle, but is also strictly quantal in the sense that Kramers and Heisenberg (1925) showed long ago that the quantum theory of an isolated molecule interacting with a radiation field yields the natural generalization of the classical form

$$\alpha(\omega) = \frac{e^2}{m_e} \sum_k \frac{f_k}{\omega_k^2 - \omega^2} \quad (2.3)$$

in which e and m_e are the charge and mass of the electron and the ω_k are characteristic frequencies.

The f_k are pure numbers, the oscillator strengths, and are essentially matrix elements of the dipole operator $e\mathbf{r}$:

$$f_k = \frac{2m_e}{3\hbar} \omega_k |\langle k|\mathbf{r}|0\rangle|^2. \quad (2.4)$$

We assume that the states $\langle k|$ can be chosen so that $\langle k|\mathbf{r}|0\rangle$ is real. We also assume at this stage that the isolated molecules are spherically symmetrical so that we can treat both the f_k and $\alpha(\omega)$ as scalars.† The many-body quantum theory is also capable of yielding an integral equation like (2.1) with polarizabilities $\alpha(\omega)$ given by (2.3). The important point is that by choosing 'molecular' fluids for consideration the states $\langle k|$ of the isolated particles are (by definition of a molecular fluid) weakly perturbed in the many-body system, and quantal aspects of the theory can be carried through concealed in the $\alpha(\omega)$. It follows that the present investigation has direct application to the many-body optics of real molecular-fluid-like systems.

Implicit in these definitions is the time dependence $e^{+i\omega t}$ of the kernel of a time Fourier transformation and a time dependence $e^{-i\omega t}$ associated with a Fourier component of frequency ω .‡ As indicative of the structure of the time-dependent form of (2.1), we might remark that the polarizabilities $\alpha(\omega)$ in (2.3) are essentially the time Fourier transforms of the retarded commutators of the autocorrelated dipole moment $e\mathbf{r}(t)$. Let us define Heisenberg operators in terms of \mathcal{H}_0 , the Hamiltonian of a single *isolated* unperturbed

† More precisely as isotropic rather than anisotropic *second-rank* tensors, but the unit second-rank tensor can be dropped from the theory. The factor of $\frac{1}{3}$ follows from (with $\mathbf{r} = (x, y, z)$)

$$|\langle k|x|0\rangle|^2 = |\langle k|y|0\rangle|^2 = |\langle k|z|0\rangle|^2 = \frac{1}{3} |\langle k|\mathbf{r}|0\rangle|^2$$

and is a consequence of the assumption of spherical symmetry.

‡ In this choice the author does not follow his previous work. Classically the choice is entirely a matter of convention. On the other hand, when $\hbar\omega$ is identified with the photon energy E the time dependence is $\exp(+Et/i\hbar)$ and the photon energies are all positive. The author's previous work corresponds to negative photon energies, rotation of the complex ω plane by π and causality if, and only if, all singularities lie in the *upper* half-plane. In these papers we adopt the more usual choice.

molecule, by

$$\mathbf{r}(t) = \exp\left(\frac{i\mathcal{H}_0 t}{\hbar}\right) \mathbf{r}(0) \exp\left(\frac{-i\mathcal{H}_0 t}{\hbar}\right). \quad (2.5a)$$

Then, with $|0\rangle$ the unperturbed ground state,

$$\alpha(\omega) = -\frac{e^2}{3i\hbar} \text{Tr} \left[\int_0^\infty dt \exp\{i(\omega + i\epsilon)t\} \langle 0 | [\mathbf{r}(t), \mathbf{r}(0)] | 0 \rangle \right]. \quad (2.5b)$$

In the expression (2.5b) $\epsilon (> 0)$ is the usual positive infinitesimal. In this picture the poles of $\alpha(\omega)$ lie in the lower half-plane.† We comment on the effect of radiating boundary conditions and of complex ω (in the form $\omega + i\epsilon$) on the extinction theorem in II. It should be noted that the form (2.5b) replaces ω^2 in (2.3) by $(\omega + i\epsilon)^2$ and ω is necessarily positive if $\hbar\omega$ is positive. Thus (2.5b) means that the excited-state propagators $(\omega_k^2 - \omega^2)^{-1}$ contributing to $\alpha(\omega)$ in (2.3) are replaced by

$$\{\omega_k^2 - (\omega + i\epsilon)^2\}^{-1} = P(\omega_k^2 - \omega^2)^{-1} + i\pi(2\omega_k)^{-1}\delta(\omega - \omega_k); \quad \omega > 0. \quad (2.5c)$$

We discuss in later papers how external scattering, and particularly the radiation reaction field, replaces the infinitesimal ϵ by a finite width. The situation is such that we can use either form of the excited state propagators, depending on the context. Thus the δ function in (2.5c) has nothing to do with absorption and merely represents a formal loss of energy scattered into the sink at infinity, implicit in the choice of outgoing boundary conditions. The different forms (2.3) and (2.5b) are therefore wholly compatible with each other.

The function $g(\mathbf{x}, \mathbf{x}')$ is a particle pair correlation function. The tensor $\mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega)$ is of the second rank and defined by

$$\mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) \equiv (\nabla_{\mathbf{x}} \nabla_{\mathbf{x}'} + k_0^2 \mathbf{U}) \frac{\exp(+ik_0 r)}{r}; \quad k_0 = \frac{\omega}{c}; \quad r = |\mathbf{x} - \mathbf{x}'|; \quad (2.6)$$

it is the dipole tensor Green function describing the vector field $\mathbf{e}_d(\mathbf{x})$, say, at \mathbf{x} due to the point dipole $\mathbf{P}(\mathbf{x}', \omega)$ at \mathbf{x}' , according to the classical formula

$$\mathbf{e}_d(\mathbf{x}) = \mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) \cdot \mathbf{P}(\mathbf{x}', \omega). \quad (2.7a)$$

In this sense it is a linear response function. Indeed, it is the time Fourier transform of the retarded commutator

$$\frac{i}{\hbar} \langle 0 | [\mathbf{e}(\mathbf{x}, t), \mathbf{e}(\mathbf{x}', t')] | 0 \rangle, \quad t > t' \quad (2.7b)$$

in which $\mathbf{e}(\mathbf{x}, t)$ is a Heisenberg operator. This compares with (2.5a, b), with \mathcal{H}_0 now the Hamiltonian of the free field $\mathbf{e}(\mathbf{x}, t)$.‡ The *coupled* quantized field $\mathbf{e}(\mathbf{x}, t)$ is the time analogue of that field

$$\mathbf{e}(\mathbf{x}, \omega) \equiv \{\alpha(\omega)\}^{-1} \mathbf{P}(\mathbf{x}, \omega) - \mathbf{E}(\mathbf{x}, \omega) \quad (2.7c)$$

which is implicit in the present discussion. With time dependence $e^{-i\omega t}$ associated with a Fourier component of frequency ω , the scalar Green function $\exp(+ik_0 r)r^{-1}$ in (2.6) is an *outgoing* wave.§

An explicit form for $\mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega)$ is

$$\mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) = \frac{2}{3} ik_0^3 \{h_0^{(1)}(k_0 r) \mathbf{U} + \frac{1}{2} h_2^{(1)}(k_0 r) (3\hat{\mathbf{f}}\hat{\mathbf{f}} - \mathbf{U})\} \quad (2.8a)$$

in which $\mathbf{r} = \mathbf{x}' - \mathbf{x}$, $\hat{\mathbf{f}}$ is a unit vector in the direction of \mathbf{r} and the $h_n^{(1)}(x)$ are spherical Hankel functions of the first kind (cf. Rosenfeld 1951, p. 102). It is worth remarking that

† See second footnote on page 411.

‡ The tensor \mathbf{F} of (2.6) is causal only because of the condition $t > t'$ in (2.7b): the commutator is the difference between a causal retarded part and a non-causal advanced part (cf. e.g. Power 1965).

§ See second footnote on p. 411.

implicitly we assume Lorentz rather than Coulomb gauge: this is, strictly speaking, irrelevant since the tensor \mathbf{F} defines the dipole electric field and so is gauge invariant. A formal definition of \mathbf{F} in Coulomb gauge is

$$\mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) = \nabla_{\mathbf{x}} \nabla_{\mathbf{x}'} |\mathbf{x} - \mathbf{x}'|^{-1} + \mathbf{R}(\mathbf{x}, \mathbf{x}'; \omega) \tag{2.8b}$$

in which \mathbf{R} defines the radiation field at \mathbf{x} due to a source at \mathbf{x}' and alone is frequency dependent. Since \mathbf{F} is given by equation (2.8a), we have explicitly that

$$\mathbf{R}(\mathbf{x}, \mathbf{x}'; \omega) = \frac{2}{3} ik_0^3 [\mathbf{U} h_0^{(1)}(k_0 r) + \{\frac{1}{2} h_2^{(1)}(k_0 r) - \frac{2}{3} (ik_0 r)^{-3}\} \{3\mathbf{f}\mathbf{f} - \mathbf{U}\}]. \tag{2.8c}$$

We make use of these forms (2.8b, c) in the discussion of § 4 and in II and III.

It is convenient to think of $g(\mathbf{x}, \mathbf{x}')\mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega)$ as a 'dipole photon'† Greenfunction weighted with the probability of finding a particle at \mathbf{x} when there is known to be an emitting source at \mathbf{x}' . In this picture $g(\mathbf{x}, \mathbf{x}')\mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega)$ is the probability amplitude of a 'dipole photon' emitted at \mathbf{x}' being absorbed at \mathbf{x} . For definiteness the existence of a particle at \mathbf{x} and the absorption of a photon at \mathbf{x} are taken to be synonymous: thus, by implication, every particle is in its ground state and if it is at \mathbf{x} will absorb a photon there. For our present purposes, of course we could define $g(\mathbf{x}, \mathbf{x}')\mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega)$ as the probability of a photon emitted at \mathbf{x}' being absorbed at \mathbf{x} . In practice, one needs to identify $g(\mathbf{x}, \mathbf{x}')$ as the usual particle pair correlation function (in this paper taken to be time or ω independent) unperturbed by light incident on the system. This identification will be valid if the number density of excited states is very small, and this will be the case when \mathbf{P} is very small. Since equation (2.1) is a linear integral equation, we expect that this will be achieved when (and even only when) \mathbf{E} is very small.‡ The demand for a low density of excited states is equivalent to the demand for a low density of quasi-particles as a condition for the validity of that concept in many-body theory (compare the quasi-bosons of Hopfield (1958), the discussion of quasi-fermions by Pines (1962) or see Abrikosov *et al.* (1965) perhaps more generally).

From the classical point of view, equation (2.1) is simply a statement that the total field at any point \mathbf{x} is given by the sum of the externally applied field $\mathbf{E}(\mathbf{x}, \omega)$ and the fields scattered from all particles at places other than \mathbf{x} . Multiplied by $\alpha(\omega)$, this total field yields the vector dipole moment $\mathbf{P}(\mathbf{x}, \omega)$ induced in a particle at \mathbf{x} . In fact, an equation very like (2.1) has been deduced from the many-electron Schrödinger equation of a molecular fluid in Hartree and Born–Oppenheimer approximations (Bullough 1964, unpublished). Although for fixed molecular sites these approximations reduce the problem to a sum of two-body interactions, the average over molecular sites now replaces the pair correlation function by a many-body kernel which can only be expressed in terms of an infinite set of particle correlation functions. The consequences of this generalization are shown in § 4 of this paper (compare the work of Mazur or Bullough's (1962) paper, and see the papers to follow). Thus the kernel of the integral equation describing the situation in the many-body system is indeed much more complicated than that of (2.1). Nevertheless, the methods of solution of (2.1) are very relevant to the more general case: that is why we study them here.

All we need to know about the kernel $\mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega)g(\mathbf{x}, \mathbf{x}')$ here is the definition (2.6) of $\mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega)$ and some general properties of $g(\mathbf{x}, \mathbf{x}')$, namely that§

$$\begin{aligned} g(\mathbf{x}, \mathbf{x}') &\rightarrow 0 & \text{as } |\mathbf{x} - \mathbf{x}'| &\rightarrow 0 \\ &\rightarrow 1 & \text{as } |\mathbf{x} - \mathbf{x}'| &\rightarrow \infty \end{aligned} \tag{2.9}$$

† The 'dipole photon' is asymptotically transverse and carries unit angular momentum. Its contribution to the longitudinal modes will become apparent in the following.

‡ We discuss later whether 'normal mode' solutions for \mathbf{P} exist when $\mathbf{E} \equiv \mathbf{0}$.

§ The short-range behaviour simply reflects the fact that two particles (conveniently thought of as molecules) cannot occupy the same space. The long-range behaviour is applicable to a fluid (no correlation at large pair separations), but not to a crystal where g oscillates finitely at infinity. Similar properties must be assumed for the many-particle correlation functions of the general theory which are introduced in § 4. It is not yet known if these assumed conditions are consistent with the many-body interactions we shall finally derive from the theory.

and the 'range' l of $g(\mathbf{x}, \mathbf{x}')$ is 'small'. By the second condition we shall mean that $g(\mathbf{x}, \mathbf{x}') - 1$ is sensibly different from zero† only for $|\mathbf{x} - \mathbf{x}'| < l$, which is 'small'. The criterion of smallness proves not to be one in comparison with the wavelength $2\pi k_0^{-1}$, but one in comparison with the macroscopic dimensions of the system.

The implied existence of dimensions to the system eliminates full translational invariance. Nevertheless, we also appeal to such translational invariance in writing $g(\mathbf{x}, \mathbf{x}')$ as a function $g(\mathbf{r})$ of $\mathbf{r} \equiv \mathbf{x}' - \mathbf{x}$ alone. We also appeal to macroscopic isotropy of the system to make $g(\mathbf{r})$ a function $g(r)$ of $r \equiv |\mathbf{r}|$ alone. The consequence of this incompatibility of our assumptions will be investigated in III.

This completes the essential physics contained in the integral equation (2.1). The rest of this paper is concerned with its solution and the dispersion relations consequent on that solution. For the solution of (2.1) we adapt the method employed by Born and Wolf (1959) in solving equation (2.2). We find dispersion relations for apparently acceptable longitudinal and transverse solutions of (2.1), but leave open until paper II the characterization of these modes and the investigation of their validity. The longitudinal dispersion relation with its many-particle generalization is the new physical result of this first paper. The generalization of both dispersion relations to include an infinite series of many-particle interactions is very important to the later work. The infinite series will be interpreted as multiple-scattering terms in the papers which are to follow I, II and III.

3. The method of Born and Wolf‡

Born and Wolf (1959) solve the integral equation (2.2). The integral equation (2.1) has been solved by Rosenfeld (1951) and later workers by rather less general methods. None of the methods indicates how complete are the solutions so obtained. We review here Born and Wolf's solution for the transverse modes of (2.2) and demonstrate that there are additional possible longitudinal modes. In § 4 we generalize the method to solve equations (2.1).

Equation (2.2) is a particular case of equation (2.1), with the choice $g(r) \equiv 1$, except that this choice does not satisfy the first of the conditions (2.9) that $g(r) \rightarrow 0$ as $r \rightarrow 0$. As a result the integral in (2.2) is undefined. This is so because, as $r \rightarrow 0$,§

$$\mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) \sim \nabla \nabla \left(\frac{1}{r} \right) = (3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathbf{U})r^{-3}. \quad (3.1a)$$

It is well known, however, that for any finite region V the integral

$$\int_{V-v} \nabla \nabla \left(\frac{1}{r} \right) d\mathbf{r} \quad (3.1b)$$

is conditionally convergent at $r = 0$ when a small region v about $r = 0$ is extracted from the region of integration. The usual choice for v is a small sphere of radius a , and the limit $a \rightarrow 0$ is taken. We shall define the integral in (2.2) in exactly this way. Unfortunately, if we choose a different shape for v the integral has a different value.¶ This non-physical result is, however, a consequence of the non-physical choice $g(r) \equiv 1$. We shall see that this non-physical result has no effect on the more physical equation (2.1), where $g(r) = 0$ at $r = 0$.||

† It is not rigorously necessary that $g(\mathbf{x}, \mathbf{x}') - 1 \sim A|\mathbf{x} - \mathbf{x}'|^{-\gamma}$ with $\gamma > 0$, providing any constant term ($\gamma = 0$) is properly accounted for: the larger γ is, the more convenient the theory becomes.

‡ This method has much in common with a remarkable paper by Planck (1902), who, however, does not explicitly demonstrate the optical extinction theorem.

§ $\mathbf{R}(\mathbf{x}, \mathbf{x}'; \omega) \sim O(r^{-1})$ as $r \rightarrow 0$ according to (2.8c).

¶ For example, an ellipsoid of variable semi-axes yields any magnitudes one cares to obtain for the elements of the tensor (3.1b), which is *not* isotropic, and subject only to a fixed trace.

|| The problem in a sense returns when we compute the 'self-energy' of the individual optical electrons: these appear as one-body terms in a theory of van der Waals forces (see the discussion in §4).

A second difficulty associated with the kernel \mathbf{F} in (2.2) is that

$$\mathbf{F} \sim k_0^2(\mathbf{U} - \hat{\mathbf{f}}\hat{\mathbf{f}}) \exp(ik_0r)r^{-1} \quad \text{as } r \rightarrow \infty. \quad (3.2)$$

The tensor is therefore 'long range' but not quite coulombic because of the oscillatory exponential factor. Even so, it does not follow that its integral over all space exists. We therefore restrict the region of integration in (2.2) to $V-v$, where V is finite. We explore the possibility of letting $V \rightarrow \infty$ in two or more of its dimensions in II.

Equation (2.2) is a linear inhomogeneous integral equation for the vector field $\mathbf{P}(\mathbf{x}, \omega)$ once $\hat{\mathbf{E}}(\mathbf{x}, \omega)$ is given. We assume that $\mathbf{E}(\mathbf{x}, \omega)$ satisfies Maxwell's sourceless equations *in vacuo*:

$$\text{div } \mathbf{E}(\mathbf{x}, \omega) = 0 \quad (3.3a)$$

$$(\nabla^2 + k_0^2)\mathbf{E}(\mathbf{x}, \omega) = \mathbf{0}. \quad (3.3b)$$

Physically this assumes there are sources for \mathbf{E} at infinity. The boundary conditions on (2.2) are then radiating boundary conditions by (2.6) and sources at infinity by (3.3b). $\mathbf{E}(\mathbf{x}, \omega)$ is strictly 'transverse' by (3.3a).

These conditions seem to the author to be a natural description of a real physical situation, in which an external light source illuminates a necessarily finite material system. They seem to be rather different from what would seem to be implicit in much of current many-body theory. In the spirit of such work one would apparently assume the presence of imposed solenoidal currents of density $\mathbf{j}_t(\mathbf{x}, \omega)$ at finite points \mathbf{x} inside V . In the usual choices of gauge, Coulomb or Lorentz, one can choose a scalar potential $\varphi = 0$, if and only if, the imposed charge density $\rho(\mathbf{x}, \omega)$ is zero. This is consistent with the solenoidal condition $\text{div } \mathbf{j}_t(\mathbf{x}, \omega) = 0$.

With this choice (and time dependence $e^{-i\omega t}$)

$$\mathbf{E}(\mathbf{x}, \omega) = ik_0\mathbf{A}(\mathbf{x}, \omega) \quad (3.4a)$$

and $\text{div } \mathbf{A} = 0$ implies $\text{div } \mathbf{E} = 0$, whilst

$$(\nabla^2 + k_0^2)\mathbf{A}(\mathbf{x}, \omega) = -4\pi c^{-1}\mathbf{j}_t(\mathbf{x}, \omega). \quad (3.4b)$$

A space Fourier transform (with kernel $\exp(-i\mathbf{k} \cdot \mathbf{x})$) yields

$$\mathbf{A}(\mathbf{k}, \omega) = -4\pi c^{-1}\mathbf{j}_t(\mathbf{k}, \omega)(k_0^2 - \mathbf{k}^2)^{-1}. \quad (3.4c)$$

Since $\mathbf{j}_t(\mathbf{x}, \omega)$ is arbitrary \mathbf{k}, ω are four independent scalar variables. It is now apparently possible to discuss the response ϵ_t , say, of the system to the 'transverse probe' $\mathbf{A}(\mathbf{k}, \omega)$. Since \mathbf{k}, ω are independent, the response would be a function $\epsilon_t(\mathbf{k}, \omega)$, say, of them. We analyse this situation in more detail in II.†

In contrast, the assumption (3.3b) has Fourier transform

$$(k_0^2 - \mathbf{k}^2)\mathbf{E}(\mathbf{k}, \omega) = \mathbf{0} \quad (3.5a)$$

which can be satisfied only if the wave vector \mathbf{k} is real and satisfies the dispersion relation

$$|\mathbf{k}| = \omega c^{-1}. \quad (3.5b)$$

It follows that the Fourier transform $\mathbf{E}(\mathbf{k}, \omega)$ is orthogonal to the direction $\hat{\mathbf{k}}$ of \mathbf{k} by (3.3a), and is then specified as a function of ω alone once $\hat{\mathbf{k}}$ is given. A solution of (3.5a) is in fact

$$\mathbf{E}(\mathbf{k}, \omega) = k_0^{-2}\mathbf{E}_0(\hat{\mathbf{k}}, \omega)\delta(|\mathbf{k}| - k_0) \quad (3.5c)$$

where $\mathbf{E}_0(\hat{\mathbf{k}}, \omega)$ does not depend on $|\mathbf{k}|$. Dispersion relations completely control our discussion of the integral equations (2.1) and (2.2). We show, following Born and Wolf in

† Nozières and Pines (1958), on the other hand, use a 'longitudinal probe'. For example, let us set $\mathbf{A} = \mathbf{0}$, so that $\mathbf{j}_t \equiv \mathbf{0}$, φ satisfies $\nabla^2\varphi = -4\pi\rho$ and $\varphi(\mathbf{k}, \omega)$ has \mathbf{k}, ω independent when ρ is arbitrary. They actually make ρ an oscillating charge density with \mathbf{k} and ω independent. The 'close resemblance' between the theory of the transverse and longitudinal probes is noted by Pines (1963, p. 198). We shall emphasize the considerable differences.

particular, that the dispersion relation (3.5b) applicable *in vacuo* and outside V yields to a new dispersion relation inside V .†

Although \mathbf{E} satisfies (3.3b), we expect that \mathbf{P} satisfies an equation of the type

$$(\nabla^2 + m^2 k_0^2)\mathbf{P} = \mathbf{0} \tag{3.6}$$

where m is a pure number, possibly complex, and of value certainly not equal to ± 1 . The parameter m would be the natural choice for the refractive index of the medium lying in V .

The integral equation we now wish to solve is

$$\mathbf{P}(\mathbf{x}, \omega) = \alpha(\omega) \left\{ \mathbf{E}(\mathbf{x}, \omega) + n \int_{V-v} \mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) \cdot \mathbf{P}(\mathbf{x}', \omega) d\mathbf{x}' \right\}. \tag{3.7}$$

It is convenient first to take the tensor operator of (2.6) outside the integral, but if we do this we have to make a correction for a surface integral evaluated on the surface of v : we find (cf. Rosenfeld 1951, p. 104) that (3.7) becomes

$$\begin{aligned} \mathbf{P}(\mathbf{x}, \omega) = \alpha(\omega) \left\{ \mathbf{E}(\mathbf{x}, \omega) + n(\nabla_{\mathbf{x}} \nabla_{\mathbf{x}} + k_0^2 \mathbf{U}) \cdot \int_v \exp(ik_0 r) r^{-1} \mathbf{P}(\mathbf{x}', \omega) d\mathbf{x}' \right. \\ \left. + \frac{4\pi}{3} n \mathbf{P}(\mathbf{x}, \omega) \right\}. \end{aligned} \tag{3.8}$$

The number $4\pi/3$ is a direct consequence of the choice of a sphere for v , and does not depend on k_0 or \mathbf{x} when the radius a of the sphere tends to zero. Because \mathbf{P} satisfies the sourceless equation (3.6) by hypothesis, it will be without singularities and the surface integral correction is due entirely to the singularity in \mathbf{F} . For the same reason, there is no singularity in the remaining integral and we can integrate over V rather than $V-v$.

The integral is now easily evaluated using the condition (3.6), the equation for the Green function

$$(\nabla^2 + k_0^2) \exp(ik_0 r) r^{-1} = -4\pi \delta(\mathbf{r}) \tag{3.9}$$

and Green's second identity. We find when $m^2 \neq 1$ that

$$\int_v \exp(ik_0 r) r^{-1} \mathbf{P}(\mathbf{x}', \omega) d\mathbf{x}' = \frac{4\pi \mathbf{P}(\mathbf{x}, \omega)}{(m^2 - 1)k_0^2} + \frac{1}{(m^2 - 1)k_0^2} \boldsymbol{\Sigma}(\mathbf{x}, \omega) \tag{3.10a}$$

in which

$$\boldsymbol{\Sigma}(\mathbf{x}, \omega) \equiv \int_{\Sigma} \{ \mathbf{P}(\mathbf{x}', \omega) \nabla \exp(ik_0 r) r^{-1} \cdot d\mathbf{S} - \exp(ik_0 r) r^{-1} d\mathbf{S} \cdot \nabla \mathbf{P}(\mathbf{x}', \omega) \}. \tag{3.10b}$$

Thus, if \mathbf{P} satisfies (3.6), we have

$$\begin{aligned} \mathbf{P}(\mathbf{x}, \omega) = \alpha(\omega) \left\{ \mathbf{E}(\mathbf{x}, \omega) + (\nabla_{\mathbf{x}} \nabla_{\mathbf{x}} + k_0^2 \mathbf{U}) \cdot \frac{4\pi n \mathbf{P}(\mathbf{x}, \omega)}{(m^2 - 1)k_0^2} + \frac{4\pi}{3} n \mathbf{P}(\mathbf{x}, \omega) \right. \\ \left. + (\nabla_{\mathbf{x}} \nabla_{\mathbf{x}} + k_0^2 \mathbf{U}) \cdot \frac{n \boldsymbol{\Sigma}(\mathbf{x}, \omega)}{(m^2 - 1)k_0^2} \right\}. \end{aligned} \tag{3.11}$$

We now reach a crucial step in the argument. \mathbf{P} by hypothesis satisfies (3.6) and \mathbf{E} satisfies (3.3b). Further, $\boldsymbol{\Sigma}(\mathbf{x}, \omega)$ satisfies (3.3b) because the Green function satisfies (3.9), \mathbf{x} is interior to the surface Σ of V and $r = |\mathbf{x}' - \mathbf{x}| \neq 0$. Thus, at all interior points \mathbf{x} , terms in (3.11) satisfy either (3.6) or (3.3b). When $m^2 \neq 1$, this is possible if, and only if, equation (3.11) breaks up into *two* equations, which are

$$\mathbf{P}(\mathbf{x}, \omega) = \alpha(\omega) \left\{ (\nabla_{\mathbf{x}} \nabla_{\mathbf{x}} + k_0^2 \mathbf{U}) \cdot \frac{4\pi n \mathbf{P}(\mathbf{x}, \omega)}{(m^2 - 1)k_0^2} + \frac{4\pi}{3} n \mathbf{P}(\mathbf{x}, \omega) \right\} \tag{3.12}$$

† This is not, of course, a new result!

and

$$\mathbf{0} = \mathbf{E}(\mathbf{x}, \omega) + \frac{\nabla_{\mathbf{x}} \nabla_{\mathbf{x}} + k_0^2 \mathbf{U}}{(m^2 - 1)k_0^2} \cdot n \boldsymbol{\Sigma}(\mathbf{x}, \omega). \quad (3.13)$$

We can suppose† that $\mathbf{P}(\mathbf{x}, \omega)$ can be split into irrotational and solenoidal parts: we set

$$\mathbf{P}(\mathbf{x}, \omega) = \mathbf{P}_i(\mathbf{x}, \omega) + \mathbf{P}_t(\mathbf{x}, \omega) \quad (3.14a)$$

with

$$\operatorname{div} \mathbf{P}_t(\mathbf{x}, \omega) = 0; \quad \operatorname{curl} \mathbf{P}_i(\mathbf{x}, \omega) = \mathbf{0}. \quad (3.14b)$$

Then, by operating on (3.12) with the vector operator $\operatorname{curl} \operatorname{curl}$ and assuming that both $\mathbf{P}_t(\mathbf{x}, \omega)$ and $\mathbf{P}_i(\mathbf{x}, \omega)$ separately satisfy (3.6),‡ we readily find that (3.12) again splits into

$$\mathbf{P}_i(\mathbf{x}, \omega) = \alpha(\omega) \left\{ \frac{4\pi n \mathbf{P}_i(\mathbf{x}, \omega)}{m^2 - 1} + \frac{4\pi}{3} n \mathbf{P}_t(\mathbf{x}, \omega) \right\} \quad (3.15)$$

and an expression which reduces to

$$\mathbf{P}_i(\mathbf{x}, \omega) = \alpha(\omega) \left\{ (\nabla^2 + k_0^2) \frac{4\pi n \mathbf{P}_i(\mathbf{x}, \omega)}{(m^2 - 1)k_0^2} + \frac{4\pi}{3} n \mathbf{P}_t(\mathbf{x}, \omega) \right\}. \quad (3.16a)$$

Because of (3.6), equation (3.16a) is

$$\mathbf{P}_i(\mathbf{x}, \omega) = -\frac{8\pi}{3} n \alpha(\omega) \mathbf{P}_i(\mathbf{x}, \omega). \quad (3.16b)$$

For non-trivial $\mathbf{P}_i(\mathbf{x}, \omega)$ equation (3.15) implies the dispersion relation

$$\frac{m^2 - 1}{m^2 + 2} = \frac{4\pi}{3} n \alpha(\omega) \quad (3.17a)$$

or

$$m^2 - 1 = 4\pi n \alpha(\omega) \left\{ 1 - \frac{4\pi}{3} n \alpha(\omega) \right\}^{-1}. \quad (3.17b)$$

This is, of course, just the Lorentz-Lorenz expression for the refractive index m . It is quadratic in m with precisely two roots, $+|m|$ and $-|m|$. If \mathbf{P}_t is a plane-wave solution, for example, the two roots correspond to backward- and forward-going waves. We assume that the denominator of (3.17b) is positive.

For non-trivial $\mathbf{P}_i(\mathbf{x}, \omega)$ equation (3.16b) yields a set of characteristic frequencies. If $\alpha(\omega)$ is given by (2.3), these frequencies are the roots of

$$1 + \frac{8\pi}{3} n \frac{e^2}{m_e} \sum_k f_k (\omega_k^2 - \omega^2)^{-1} = 0. \quad (3.18)$$

For example, were there only one oscillator of strength unity contributing to $\alpha(\omega)$, the root would be

$$\omega = (\omega_k^2 + \frac{2}{3} \omega_p^2)^{1/2}$$

where $\omega_p = (4\pi n e^2 m_e^{-1})^{1/2}$ is the classical plasma frequency for n (optical) electrons per unit volume: we accept positive roots only.

The result (3.18), together with the observation that the roots $\omega = \omega_k$, say, of that equation are the zeros of m^2 in the transverse dispersion relations (3.17), is well known (cf. Knox 1963, Hubbard 1955, for example). As far as the writer is aware, it has not been obtained before from the integral equation (2.2). We shall therefore clarify the nature of the solution for $\mathbf{P}_i(\mathbf{x}, \omega)$.

† Usual proofs make use of the vanishing of $\mathbf{P}(\mathbf{x}, \omega)$ at infinity. This condition would not necessarily be applicable here unless, for example, $\mathbf{P}(\mathbf{x}, \omega) = \mathbf{0}$ by definition outside V and V is finite.

‡ We do not assume that the value of m is the same in each case.

Before doing this, however, it may be helpful if we first interpolate a comment on other particularly relevant work on longitudinal modes. Firstly, Born and Wolf (1959), explicitly using the integral equation (2.2), seek only transverse solutions. On the other hand, a number of people have derived longitudinal dispersion relations for what is usually the cubic crystal by semi-phenomenological arguments which are to that extent comparable with the use of (2.2): Hall (1962), Amos (1963) and Fowler (1964 a), who work with excitons, thus use longitudinal-time-like photons, i.e. $\nabla_{\mathbf{x}} \nabla_{\mathbf{x}'} |\mathbf{x} - \mathbf{x}'|^{-1}$ of (2.8b) alone, for their microscopic particle interactions (compare therefore (4.23) below), vest transverse photons in a transverse field mode and conserve \mathbf{k} (cf. § 4). In a comparable calculation exhibiting longitudinal modes Ball and McLachlan (1964) use Lorentz gauge and the tensor \mathbf{F} of (2.8a). Other relevant work is that of Huang (1951) and Born and Huang (1954); we should also cite, for example, Agranovitch (1960) in a less than exhaustive list.†

Hopfield (1958) and Anderson (1964) have considered the longitudinal and transverse excitons of a cubic molecular crystal, but explicitly invoke periodic boundary conditions, again vest radiation-field interactions in transverse field modes, conserve \mathbf{k} and do not find any condition comparable with the extinction theorem. We comment on this treatment of the radiation field in III: it does not agree in its detailed consequences with those of our approach to the problem and cannot yield an external scattering theory when applied to the molecular fluid (fully ordered crystals, of course, do not scatter light). In contrast, the integral equation (2.1) has recently been applied by Obada (1967) to the finite 'cold' molecular crystal of arbitrary symmetry by choosing a set of periodic δ functions for the pair correlation function $g(r)$. The long range of $g(r)$ modifies the extinction theorem (cf. § 4). Both transverse and longitudinal modes associated with each principal crystalline axis are obtained. The new physical feature is a set of frequency-dependent local radiation-field terms which do not vanish even for cubic symmetry (these terms are comparable with the integrals (4.12) below and are non-zero for the cubic crystal only because of the presence of the radiation-field tensors $\mathbf{R}(\mathbf{x}, \mathbf{x}'; \omega)$ of (2.8b)). Nevertheless, there is no external scattering. Obada also attempts to marry the extinction theorem into an argument directly comparable with that of Hopfield (1958) with only partial success. Fowler (1964 b) has also considered the contribution of the radiation field to the local field in the pseudocrystal of DNA. We shall consider these problems of the radiation field raised by work already in the literature in III and elsewhere. Now we revert again to a discussion of the nature of the solution we have obtained here for the longitudinal dipole function $\mathbf{P}_l(\mathbf{x}, \omega)$.

If w_k is a root of the equation (3.18), an apparent solution of the time-dependent version of (2.2) is

$$\mathbf{P}_l(\mathbf{x}, t) = \exp(-iw_k t) \mathbf{P}_l(\mathbf{x}, w_k)$$

where \mathbf{P}_l is irrotational and satisfies (3.6) with no condition on m^2 , that is, that parameter is arbitrary. In particular, if the functional form

$$\mathbf{P}_l(\mathbf{x}, \omega) = \mathbf{P}_l \exp(+i\mathbf{k} \cdot \mathbf{x}) \quad (3.19b)$$

is acceptable, \mathbf{P}_l is parallel to \mathbf{k} and \mathbf{k}^2 is entirely arbitrary. In contrast, at an arbitrary frequency ω a plane-wave solution for \mathbf{P}_l is

$$\mathbf{P}_l(\mathbf{x}, t) = \mathbf{P}_l \exp\{-i(\omega t - \mathbf{k} \cdot \mathbf{x})\}; \quad \mathbf{P}_l \cdot \mathbf{k} = 0; \quad \mathbf{k}^2 = \{m(\omega)\}^2 \omega^2 c^{-2}. \quad (3.20a)$$

At the frequency w_k this solution would reduce to

$$\mathbf{P}_l(\mathbf{x}, t) = \mathbf{P}_l \exp(-iw_k t) \quad (3.20b)$$

since $\mathbf{k}^2 = 0$ there. This is not a propagating wave, but the arguments we have used still apply since $m^2 \neq 1$.

We now discuss equation (3.13). The solutions whose form we have discussed so far are acceptable if, but only if, equation (3.13) is also satisfied. This remarkable equation is the

† We must also quote the important and comprehensive paper by Fano (1956), who studies longitudinal and transverse modes in an arbitrary but rather intuitive many-body quantal oscillator model.

'extinction theorem' introduced by Ewald (1912, 1916) in a more physical way. The physical content of the equation is that scattering from induced dipole sources on the boundary Σ of V is always precisely sufficient to extinguish the incident field at all points inside V . The mathematical content is that (3.13) is an integro-differential equation for $\mathbf{P}(\mathbf{x}, \omega)$ and the normal component of $\nabla\mathbf{P}(\mathbf{x}, \omega)$ on the surface Σ of V , given $\mathbf{E}(\mathbf{x}, \omega)$ at all points \mathbf{x} inside V . Once $\mathbf{P}(\mathbf{x}, \omega)$ and $\nabla\mathbf{P}(\mathbf{x}, \omega)$ on Σ are determined, $\mathbf{P}(\mathbf{x}, \omega)$ at all \mathbf{x} in V is determined from (3.6) as a boundary-value problem, with the values of $\mathbf{P}(\mathbf{x}, \omega)$ and $\nabla\mathbf{P}(\mathbf{x}, \omega)$ on Σ as boundary conditions. We show in II, however, by an actual choice of V and Σ that, because of the existence of the longitudinal solutions, the solution for $\mathbf{P}(\mathbf{x}, \omega)$ is not necessarily unique. This question is tied up with the characterization of the solutions as 'forced' solutions or 'normal-mode' solutions. A normal-mode solution of (2.2) is defined to be one which satisfies the homogeneous integral equation obtained by setting $\mathbf{E}(\mathbf{x}, \omega) \equiv 0$. We leave the actual characterization of the solutions until paper II: there we characterize the solutions of (2.1) rather than those of (2.2), though the characterization is in fact the same for both equations.

Before we extend the argument of this section to the solution of (2.1) we should prove that $m^2 = 1$ is not acceptable for a *transverse* solution of the equation (2.2). With $m^2 = 1$, it is necessary in order to satisfy (3.8) that

$$(\nabla_{\mathbf{x}}\nabla_{\mathbf{x}} + k_0^2\mathbf{U}) \cdot \left\{ (\nabla^2 + k_0^2) \int_V \exp(ik_0r)r^{-1}\mathbf{P}(\mathbf{x}', \omega) d\mathbf{x}' \right\} = 0 \quad (3.21)$$

(apply the scalar operator $\nabla^2 + k_0^2$ to equation (2.2)). If we take the scalar operator inside, it is now necessary that

$$-4\pi(\nabla_{\mathbf{x}}\nabla_{\mathbf{x}} + k_0^2\mathbf{U}) \cdot \mathbf{P}(\mathbf{x}, \omega) = 0. \quad (3.22a)$$

Then

$$\mathbf{P}_t(\mathbf{x}, \omega) \equiv 0 \quad (3.22b)$$

whilst (using $\text{curl } \mathbf{P}_t = 0$)

$$(\nabla^2 + k_0^2)\mathbf{P}_l(\mathbf{x}, \omega) = 0. \quad (3.22c)$$

Equation (3.22b) shows that there are no transverse solutions. Equation (3.22c) shows that there are potential longitudinal solutions, but this reflects the fact that since (3.16b) leaves m arbitrary it can indeed be unity.

4. Solution of the more general integral equation

The method of Born and Wolf has the important property of finding an expression for the refractive index of a material without demanding an explicit solution for the dipole field $\mathbf{P}(\mathbf{x}, \omega)$. In this respect it is superior to the methods used by Rosenfeld, Mazur and the author.† In order to extend the method to equation (2.1), we must acknowledge that $g(\mathbf{x}, \mathbf{x}')$ depends on $r = |\mathbf{x}' - \mathbf{x}|$ alone only in a translationally invariant isotropic system. Further, statistical mechanics defines $g(r)$ only in the limit $V \rightarrow \infty$. This suggests we either assume *a priori* that V is three-dimensionally infinite, or at least we let $V \rightarrow \infty$ at the close of the calculation. In the second case we certainly first break translational invariance. In either case we must ask for the role of the extinction theorem in the theory since the surface Σ is *a priori* or ultimately a surface at infinity. It is intuitively plain that the breaking of translational invariance is essential to the theory; for then, and only then, is momentum not 'a good quantum number', and we may expect that then, and only then, does the momentum \mathbf{k}_0 of the 'wave function' $\mathbf{E}(\mathbf{x}, \omega)$ become replaced by the momentum $\mathbf{k} \neq \mathbf{k}_0$ (with $|\mathbf{k}| = m(\omega)k_0 \neq k_0$) of the 'wave function' $\mathbf{P}(\mathbf{x}, \omega)$.

Intuitively we can break translational invariance without introducing any complication in $g(r)$. We take V to be very large (that is of dimensions much greater than the correlation length l of $g(r)$) and work at points \mathbf{x} well inside V . Then $g(\mathbf{x}, \mathbf{x}') \rightarrow 1$ well inside V , and $g(\mathbf{x}, \mathbf{x}') - 1$ will depend on $\mathbf{r} = \mathbf{x}' - \mathbf{x}$, insignificantly on \mathbf{x} alone, and then by *local* isotropy almost solely on r .

† It is not clear from the argument of these authors that the explicit solution, which apparently appears in the expression for m , does not in fact affect the form of that expression.

With this result, we rewrite (2.1) as

$$\mathbf{P}(\mathbf{x}, \omega) = \alpha(\omega) \left\{ \mathbf{E}(\mathbf{x}, \omega) + n \int_{v-v} \mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) \cdot \mathbf{P}(\mathbf{x}', \omega) d\mathbf{x}' + n \mathcal{J}(\mathbf{x}, \omega; \mathbf{P}) \right\}. \quad (4.1a)$$

The linear vector functional \mathcal{J} is defined by

$$\mathcal{J}(\mathbf{x}, \omega; \mathbf{P}) \equiv \int_{v-v} \mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) \cdot \mathbf{P}(\mathbf{x}', \omega) \{g(r) - 1\} d\mathbf{x}'. \quad (4.1b)$$

Obviously the whole of the argument of the previous section can be applied if we can show that \mathcal{J} satisfies either of the wave equations (3.3b) or (3.6) (or splits into parts which do).

We assume $\mathbf{P}(\mathbf{x}', \omega)$ has the Fourier resolution

$$\mathbf{P}(\mathbf{x}', \omega) = (2\pi)^{-3} \int \mathbf{P}(\mathbf{k}, \omega) \exp(i\mathbf{k} \cdot \mathbf{x}') d\mathbf{k} \quad (4.2)$$

so that

$$\begin{aligned} \mathcal{J}(\mathbf{x}, \omega; \mathbf{P}) &= (2\pi)^{-3} \int \exp(i\mathbf{k} \cdot \mathbf{x}) d\mathbf{k} \\ &\times \int_{v-v} \mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) \cdot \mathbf{P}(\mathbf{k}, \omega) \exp\{i\mathbf{k} \cdot (\mathbf{x}' - \mathbf{x})\} \{g(r) - 1\} d\mathbf{x}'. \end{aligned} \quad (4.3)$$

The tensor

$$\mathbf{J}(\mathbf{k}, \omega) \equiv \int_{v-v} \mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) \exp\{i\mathbf{k} \cdot (\mathbf{x}' - \mathbf{x})\} \{g(r) - 1\} d\mathbf{x}' \quad (4.4)$$

can, by our assumptions about $g(r) - 1$, be evaluated over all of space (except for the small sphere at \mathbf{x}). The integrand is a function of $\mathbf{r} = \mathbf{x}' - \mathbf{x}$ alone, so that $\mathbf{J}(\mathbf{k}, \omega)$ does not depend on \mathbf{x} . That tensor is one of the second rank depending only on a single vector \mathbf{k} . It must therefore be of the form†

$$\mathbf{J}(\mathbf{k}, \omega) = J_t(|\mathbf{k}|, \omega)(\mathbf{U} - \hat{\mathbf{k}}\hat{\mathbf{k}}) + J_l(|\mathbf{k}|, \omega)\hat{\mathbf{k}}\hat{\mathbf{k}} \quad (4.5)$$

(in which $\hat{\mathbf{k}}$ is a unit vector in the direction of \mathbf{k}). The scalar quantities J_t and J_l depend only on $|\mathbf{k}|$ (and ω). Here and throughout $|\mathbf{k}| \equiv (\mathbf{k}^2)^{1/2}$ and is *not* $(\mathbf{k}^* \cdot \mathbf{k})^{1/2}$ with \mathbf{k}^* the complex conjugate of \mathbf{k} . Thus $|\mathbf{k}|$ can be, and is, complex.

We now split $\mathbf{P}(\mathbf{k}, \omega)$ into irrotational and solenoidal parts. These are $\mathbf{P}_l(\mathbf{k}, \omega)$ and $\mathbf{P}_t(\mathbf{k}, \omega)$, where

$$\mathbf{P}_l(\mathbf{k}, \omega) \wedge \hat{\mathbf{k}} = \mathbf{0} \quad \text{and} \quad \mathbf{P}_t \cdot \hat{\mathbf{k}} = 0. \quad (4.6)$$

Then

$$\mathcal{J}(\mathbf{x}, \omega; \mathbf{P}) = (2\pi)^{-3} \int \exp(i\mathbf{k} \cdot \mathbf{x}) d\mathbf{k} \{J_t(|\mathbf{k}|, \omega)\mathbf{P}_l(\mathbf{k}, \omega) + J_l(|\mathbf{k}|, \omega)\mathbf{P}_t(\mathbf{k}, \omega)\}. \quad (4.7)$$

Since, by hypothesis, $\mathbf{P}(\mathbf{x}, \omega)$ satisfies (3.6) and $\mathbf{P}_l(\mathbf{x}, \omega)$ and $\mathbf{P}_t(\mathbf{x}, \omega)$ do so separately, these quantities have Fourier transforms‡

$$\mathbf{P}_l(\mathbf{k}, \omega) = m^{-2}k_0^{-2}\mathbf{P}_{l0}(\hat{\mathbf{k}}, \omega)\delta(|\mathbf{k}| - mk_0) \quad (4.8a)$$

$$\mathbf{P}_t(\mathbf{k}, \omega) = m^{-2}k_0^{-2}\mathbf{P}_{t0}(\hat{\mathbf{k}}, \omega)\delta(|\mathbf{k}| - mk_0). \quad (4.8b)$$

† There are two tensors isotropic in the 2-space orthogonal to $\hat{\mathbf{k}}$, namely $\mathbf{U} - \hat{\mathbf{k}}\hat{\mathbf{k}}$ and $\mathbf{u}(\hat{\mathbf{k}})\mathbf{t}(\hat{\mathbf{k}}) - \mathbf{t}(\hat{\mathbf{k}})\mathbf{u}(\hat{\mathbf{k}})$. In the latter \mathbf{u} , \mathbf{t} , $\hat{\mathbf{k}}$ are unit vectors forming an orthogonal right-handed system. This tensor is excluded since (4.4) is invariant under $\hat{\mathbf{k}} \rightarrow -\hat{\mathbf{k}}$ because $g(r)$ and \mathbf{F} are invariant under $\mathbf{r} = \mathbf{x}' - \mathbf{x} \rightarrow -\mathbf{r}$. If $g(r)$ is generalized so that it depends on the orientations of the particles at \mathbf{x} and \mathbf{x}' and is not invariant under $\mathbf{r} \rightarrow -\mathbf{r}$, \mathbf{J} is a potential source of coupled oscillator optical rotation (Bullough 1962).

‡ \mathbf{P}_{l0} and \mathbf{P}_{t0} could depend on $|\mathbf{k}|$; but we show that this satisfies a dispersion relation and so depends on ω (i.e. we show that m depends only on ω).

We now find that

$$\begin{aligned} \mathcal{F}(\mathbf{x}, \omega; \mathbf{P}) &= J_t(mk_0, \omega)(2\pi)^{-3} \int \exp(i\mathbf{k} \cdot \mathbf{x}) d\mathbf{k} \mathbf{P}_t(\mathbf{k}, \omega) \\ &\quad + J_l(mk_0, \omega)(2\pi)^{-3} \int \exp(i\mathbf{k} \cdot \mathbf{x}) d\mathbf{k} \mathbf{P}_l(\mathbf{k}, \omega) \\ &= J_t(mk_0, \omega)\mathbf{P}_t(\mathbf{x}, \omega) + J_l(mk_0, \omega)\mathbf{P}_l(\mathbf{x}, \omega). \end{aligned} \quad (4.9)$$

Hence \mathcal{F} satisfies the wave equation (3.6). Thus it follows that the whole of the argument of § 3 is valid, the extinction theorem (3.13) is unchanged but the dispersion relations are now derived from

$$\mathbf{P}_t(\mathbf{x}, \omega) = \alpha(\omega) \left[\frac{4\pi n \mathbf{P}_t(\mathbf{x}, \omega)}{m^2 - 1} + \left\{ \frac{4\pi}{3} n + n J_t(mk_0, \omega) \right\} \mathbf{P}_t(\mathbf{x}, \omega) \right] \quad (4.10a)$$

and

$$\mathbf{P}_l(\mathbf{x}, \omega) = \alpha(\omega) \left[(\nabla^2 + k_0^2) \frac{4\pi n \mathbf{P}_l(\mathbf{x}, \omega)}{(m^2 - 1)k_0^2} + \left\{ \frac{4\pi}{3} n + n J_l(mk_0, \omega) \right\} \mathbf{P}_l(\mathbf{x}, \omega) \right]. \quad (4.10b)$$

These are, of course, the transverse dispersion relation

$$m_t^2 - 1 = 4\pi n \alpha(\omega) \left\{ 1 - \frac{4\pi}{3} n \alpha(\omega) - n \alpha(\omega) J_t(m_t k_0, \omega) \right\}^{-1} \quad (4.11a)$$

instead of (3.17*b*) and the longitudinal dispersion relation

$$n \alpha(\omega) J_l(m_l k_0, \omega) = 1 + \frac{8\pi}{3} n \alpha(\omega) \quad (4.11b)$$

instead of (3.16*b*).

The quantities J_t and J_l can be evaluated from (4.4) and their definition (4.5). In terms of the spherical Hankel and Bessel functions introduced in (2.8) they prove to be†

$$J_t(mk_0, \omega) = +\frac{2}{3} i k_0^3 \int_{-v}^v \{g(r) - 1\} \{j_0(mk_0 r) h_0^{(1)}(k_0 r) + \frac{1}{2} j_2(mk_0 r) h_2^{(1)}(k_0 r)\} dr \quad (4.12a)$$

$$J_l(mk_0, \omega) = +\frac{2}{3} i k_0^3 \int_{-v}^v \{g(r) - 1\} \{j_0(mk_0 r) h_0^{(1)}(k_0 r) - j_2(mk_0 r) h_2^{(1)}(k_0 r)\} dr. \quad (4.12b)$$

The transverse dispersion relation (4.11*a*) with (4.12*a*) was first obtained by Rosenfeld (1951)‡. The longitudinal dispersion relation (4.11*b*) with (4.12*b*) has not been reported before as far as the present author is aware.

Perhaps the most interesting feature of (4.11*b*) is that, in contrast with (3.16*b*), it is a dispersion relation which fixes the longitudinal refractive index m_l at a given frequency ω . On the other hand, (4.11*b*) depends very weakly on m_l since $J_l(m_l k_0, \omega)$ is very small. Since

$$h_0^{(1)}(k_0 r) j_0(mk_0 r) \sim (ik_0 r)^{-1} \{1 + ik_0 r + O(k_0^2 r^2)\} \quad (4.13a)$$

$$h_2^{(1)}(k_0 r) j_2(mk_0 r) \sim (ik_0 r)^{-1} \{\frac{1}{3} m^2 + O(k_0^2 r^2)\} \quad (4.13b)$$

we can see that

$$J_l(mk_0, \omega) = (1 - \frac{1}{3} m^2) J_l(0, \omega) \{1 + O(k_0 l)\} \quad (4.14a)$$

where l is the correlation length of $g(r) - 1$ and

$$\begin{aligned} J_l(0, \omega) &= J_t(0, \omega) = \frac{8\pi}{3} k_0^2 \int_a^\infty \{g(r) - 1\} r dr \\ &\simeq \frac{2}{3} k_0^2 l^{-1} \int \{g(r) - 1\} dr. \end{aligned} \quad (4.14b)$$

† Unfortunately, there is a glaring error in the paper of Bullough (1963). It was stated, in effect, that $J_t(mk_0, \omega)$ and $J_l(mk_0, \omega)$ were identical. This would mean that $\mathbf{J}(\mathbf{k}, \omega)$ was isotropic. In fact, the distinction between J_t and J_l was irrelevant to the argument of that paper.

‡ The radiation damping term has been omitted here.

To order of magnitude we can identify

$$\int \{g(r) - 1\} d\mathbf{x} = \kappa k_B T$$

where κ is the isothermal compressibility of the fluid at temperature T and k_B is Boltzmann's constant. We then find (roughly) that

$$J_i(0, \omega) \sim \frac{2}{3} k_0^2 l^{-1} \times 10^{-25} \sim k_0^2 l^2 \times 10^{-4}. \quad (4.15)$$

The last step assumes $l \sim 10^{-7}$ cm. Hence the right-hand side of (4.15) is probably rather smaller than the figure quoted. It follows that, although (4.11*b*) is a dispersion relation for m_i , longitudinal modes lie at frequencies ω rather close to the roots of the equation (3.18), and any small change in frequency induces an enormous change in the wave number of the mode $m_i \omega c^{-1}$. Evidently in the long wavelength limit $m_i \rightarrow 0$ there are acceptable frequencies at the roots of

$$n\alpha(\omega) J_i(0, \omega) = 1 + \frac{8\pi}{3} n\alpha(\omega) \quad (4.16)$$

and the wave number $|\mathbf{k}|$ is essentially arbitrary, providing it is 'long', i.e. providing $|\mathbf{k}|^{-1} \gg l$. It follows from this discussion that, although the longitudinal modes *no longer* lie at the zeros of the transverse dispersion relation (4.11*a*) for m_i , they do lie close to these zeros when the wave number is long. The zeros of (4.11*a*) are the roots of (4.16) since $J_i(0, \omega) = J_t(0, \omega)$.

The mathematical formulation of the idea that longitudinal modes should lie at the zeros of the transverse refractive index m (or the transverse 'dielectric constant' m^2) is demonstrated in (4.10). Because $\mathbf{P}_i(\mathbf{x}, \omega)$ satisfies (3.6),

$$(\nabla^2 + k_0^2) \mathbf{P}_i(\mathbf{x}, \omega) = -(m^2 - 1) k_0^2 \mathbf{P}_i(\mathbf{x}, \omega)$$

and the *first* term in the curly bracket in (4.10*b*) reduces to $-4\pi n \mathbf{P}_i(\mathbf{x}, \omega)$. This result is precisely obtained in (4.10*a*) by putting $m^2 = 0$ in the first term (and replacing \mathbf{P}_i by \mathbf{P}_t). Similar considerations do not apply to other terms where m appears in (4.10), that is in J_i and J_t , and the longitudinal modes are not exact zeros of the transverse dispersion relation. For another interpretation we show in this section (near equations (4.23)) that transverse photons alone contribute to the term in $(m^2 - 1)^{-1}$ in (4.10*a*) and that longitudinal time-like photons alone contribute to the corresponding term reducing to $-4\pi n \mathbf{P}_i(\mathbf{x}, \omega)$ in (4.10*b*).

The interpretation of (4.11*b*) as a dispersion relation for m_i assumes that that equation, which is a transcendental equation for m_i^2 , has actual roots for m_i^2 .[†] Within the same type of assumption, the transverse dispersion relation now has more than one root for m_i^2 . For example, to the algebraic approximation (4.13) at least, there are obviously two roots for m_i^2 . The additional roots for m_i are damped but not spectacularly more heavily than the 'fundamental' root close to the root of (3.17*b*).

These particular roots are, however, a consequence of the algebraic approximation and it seems probable that any additional solutions of the transcendental equation for m_i^2 are necessarily heavily damped. Even so, such possible additional roots are not fully understood. We have not yet discussed whether or not the extinction theorem fixes the amplitude of a transverse mode. We show in II that it is so fixed, providing there is only *one* root for m_i^2 . If there is more than one root for m_i^2 , the solution contains an arbitrary ratio of the amplitudes of the corresponding modes.

We must also remember that we still have to show that the extinction theorem (3.13) can actually be satisfied. However, we show in II that it can be and that therefore both of the dispersion relations (4.11) are acceptable. It is therefore convenient to exhibit here the many-body generalization of the longitudinal dispersion relation (4.11*b*).

From Bullough's (1962) paper and from the work of Mazur and Mandel (1956) and Mazur (1958) we discover that it is not possible to express the refractive index of a molecular

[†] One can always expect to solve (4.11*b*) for admissible $\omega(|\mathbf{k}|)$.

fluid in terms of the pair correlation function $g(r)$ alone. From, for example, equation (B 10) of Bullough's (1962) paper applied to equation (4.08) of the same paper (and here simplified to the case of isotropically polarizable particles in a one-component system) we find that the generalization of the tensor $\mathbf{J}(\mathbf{k}, \omega)$ of our equation (4.4) is

$$\mathbf{J}(\mathbf{k}, \omega) = \sum_{s=1}^{\infty} \{n\alpha(\omega)\}^{s-1} \mathbf{J}_s(\mathbf{k}, \omega) \tag{4.17}$$

where $\mathbf{J}_1(\mathbf{k}, \omega)$ is defined by the right-hand side of (4.4), and $\mathbf{J}_2(\mathbf{k}, \omega)$ and $\mathbf{J}_3(\mathbf{k}, \omega)$ take the form

$$\begin{aligned} \mathbf{J}_2(\mathbf{k}, \omega) = & \iint \{g_{123}(\mathbf{r}, \mathbf{r}') - g_{12}(r)g_{23}(r')\} \exp\{i\mathbf{k} \cdot (\mathbf{r} + \mathbf{r}')\} \mathbf{F}(\mathbf{r}, \omega) \cdot \mathbf{F}(\mathbf{r}', \omega) \, d\mathbf{r} \, d\mathbf{r}' \\ & + n^{-1} \int g_{12}(r) \mathbf{F}(\mathbf{r}, \omega) \cdot \mathbf{F}(\mathbf{r}, \omega) \, d\mathbf{r} \end{aligned} \tag{4.18a}$$

$$\begin{aligned} \mathbf{J}_3(\mathbf{k}, \omega) = & \iiint \{g_{1234}(\mathbf{r}, \mathbf{r}', \mathbf{r}'') - g_{12}(r)g_{234}(\mathbf{r}', \mathbf{r}'') - g_{123}(\mathbf{r}, \mathbf{r}')g_{34}(r'') \\ & + g_{12}(r)g_{23}(r')g_{34}(r'')\} \exp\{i\mathbf{k} \cdot (\mathbf{r} + \mathbf{r}' + \mathbf{r}'')\} \mathbf{F}(\mathbf{r}, \omega) \cdot \mathbf{F}(\mathbf{r}', \omega) \mathbf{F}(\mathbf{r}'', \omega) \, d\mathbf{r} \, d\mathbf{r}' \, d\mathbf{r}'' \\ & + n^{-1} \iint \{g_{123}(\mathbf{r}, \mathbf{r}') - g_{12}(r)g_{23}(r')\} \exp(i\mathbf{k} \cdot \mathbf{r}) \\ & \times \mathbf{F}(\mathbf{r}, \omega) \cdot \mathbf{F}(\mathbf{r}', \omega) \cdot \mathbf{F}(\mathbf{r}', \omega) \, d\mathbf{r} \, d\mathbf{r}' \\ & + n^{-1} \iint \{g_{123}(\mathbf{r}, \mathbf{r}') - g_{12}(r)g_{13}(|\mathbf{r} + \mathbf{r}'|)\} \exp\{i\mathbf{k} \cdot (\mathbf{r} + \mathbf{r}')\} \\ & \times \mathbf{F}(\mathbf{r}, \omega) \cdot \mathbf{F}(\mathbf{r}, \omega) \cdot \mathbf{F}(\mathbf{r} + \mathbf{r}', \omega) \, d\mathbf{r} \, d\mathbf{r}' \\ & + n^{-1} \iint \{g_{123}(\mathbf{r}, \mathbf{r}')\} \mathbf{F}(\mathbf{r}, \omega) \cdot \mathbf{F}(\mathbf{r}', \omega) \cdot \mathbf{F}(\mathbf{r} + \mathbf{r}', \omega) \, d\mathbf{r} \, d\mathbf{r}' \\ & + n^{-2} \int \{g_{12}(r)\} \exp(i\mathbf{k} \cdot \mathbf{r}) \mathbf{F}(\mathbf{r}, \omega) \cdot \mathbf{F}(\mathbf{r}, \omega) \cdot \mathbf{F}(\mathbf{r}, \omega) \, d\mathbf{r}. \end{aligned} \tag{4.18b}$$

In these expressions g_{1234} is a four-particle correlation function, g_{123} is a three-particle correlation function and $g_{12}(r) \equiv g(r)$. $\mathbf{J}_4(\mathbf{k}, \omega)$, for example, would contain a leading term in g_{12345} , a five-particle correlation function. We shall introduce a 'cluster' diagrammatic notation to handle these terms in later papers, and so it is not worth quoting any more of the $\mathbf{J}_s(\mathbf{k}, \omega)$ explicitly here.†

Important points about the $\mathbf{J}_s(\mathbf{k}, \omega)$ are, first, that because the g 's are zero whenever two particles approach each other closely we need not exclude the small sphere from any region of integration; secondly, the regions of integration are assumed to be over all space, although there is a peculiar difficulty in demonstrating the validity of the step of replacing integrations over V in (4.18a) and (4.18b) (which is what the theory demands) by integration over all space as these expressions assume. We shall discuss this very important difficulty in later papers because it plays an important role in the theory of extinction due to external scattering. Strictly speaking, the expressions (4.18) cannot be correctly written in precisely these forms. We shall also show that in discussing the extinction due to scattering we to some extent need, and after correcting for this difficulty are certainly able to handle, the tensors $\mathbf{J}_s(\mathbf{k}, \omega)$ at all orders s .

Therefore leaving this difficulty aside here, we see that, because $\mathbf{J}_2(\mathbf{k}, \omega)$ and $\mathbf{J}_3(\mathbf{k}, \omega)$ (and indeed all the $\mathbf{J}_s(\mathbf{k}, \omega)$) are tensors of the second rank depending only on the single vector \mathbf{k} , everything we have said in showing that the functional $\mathcal{F}(\mathbf{x}, \omega; \mathbf{P})$ of (4.3) takes

† Nor do we include radiation reaction in (4.18b): it does not occur in (4.18a).

the form (4.7) still applies, and consequently the dispersion relations (4.11) still follow, providing only that we interpret $J_t(mk_0, \omega)$ and $J_l(mk_0, \omega)$ to be given by

$$J_t(m_i k_0, \omega) = \sum_{s=1}^{\infty} \{n\alpha(\omega)\}^{s-1} \mathbf{u}(\hat{\mathbf{k}}) \cdot \mathbf{J}_s(m_i k_0 \hat{\mathbf{k}}, \omega) \cdot \mathbf{u}(\hat{\mathbf{k}}) \quad (4.19a)$$

and

$$J_l(m_i k_0, \omega) = \sum_{s=1}^{\infty} \{n\alpha(\omega)\}^{s-1} \hat{\mathbf{k}} \cdot \mathbf{J}_s(m_i k_0 \hat{\mathbf{k}}, \omega) \cdot \hat{\mathbf{k}} \quad (4.19b)$$

in which $\mathbf{u}(\hat{\mathbf{k}})$ is a unit vector orthogonal to $\hat{\mathbf{k}}$. The longitudinal dispersion relation (4.11b), with the interpretation of $J_l(m_i k_0, \omega)$ given by (4.19b), is the new physical result constituting the main result of this paper. We now discuss it.

It is plain that everything we have said so far about J_t and J_l still applies: in particular,

$$J_t(0, \omega) = J_l(0, \omega). \quad (4.20a)$$

Further, (4.18a, b), for example, depend weakly on m_i^\dagger ; so also do all the \mathbf{J}_s . Hence the longitudinal dispersion relation still lies close to the zeros of m_i^2 in the transverse dispersion relation (4.11a), with $J_t(0, \omega)$ given now by (4.19a). It is not, however, any true zero of the dispersion relation since

$$J_l(m_i k_0, \omega) \neq J_l(0, \omega)$$

and it is a dispersion relation since J_l depends on m_l (or $|\mathbf{k}|$).

There is also the dielectric constant approximation in which ω (rather than m) tends to zero. Since, by (4.20a),

$$J_t(0, 0) = J_l(0, 0) \quad (4.20b)$$

(and $m k_0 = 0$ when $\omega = 0$, even though $m \neq 0$), the 'transverse' dielectric constant $\epsilon \equiv m_i^2(0)$ is given by (4.11a) as

$$\epsilon - 1 = 4\pi n\alpha(0) \left\{ 1 - \frac{4\pi}{3} n\alpha(0) - n\alpha(0) J_t(0, 0) \right\}^{-1} \quad (4.21)$$

with $J_t(0, 0)$ obtained from (4.19a). Since at $\omega = 0$ the $\mathbf{J}_s(m k_0 \hat{\mathbf{k}}, \omega)$ do not depend on m (or m^2), it is not possible to define a longitudinal dielectric constant. Indeed, a longitudinal mode as $\omega \rightarrow 0$ is itself a valid concept only if the equation

$$n\alpha(0) J_t(0, 0) = 1 + \frac{8\pi}{3} n\alpha(0) \quad (4.22a)$$

is satisfied. If this is so

$$-4\pi n\alpha(0) = 1 - \frac{4\pi}{3} n\alpha(0) - n\alpha(0) J_t(0, 0). \quad (4.22b)$$

But equation (4.22b) shows that the denominator of (4.21) is negative. Hence (since $\alpha(0) > 0$) $\epsilon - 1$ is negative and this means that $m_i^2(\omega) - 1$ is real and negative when $\omega \simeq 0$. But this can only mean that the Lorentz-field term $(4\pi/3)n\alpha(\omega)$ and the 'local-field' term $n\alpha(\omega) J_t(m k_0, \omega)$ have together moved the poles of $\alpha(\omega)$ to new poles of $m_i^2(\omega) - 1$ and, further, that one of these poles has been pushed[†] so that $m_i^2(\omega) - 1$ has a pole on the

[†] The quantities $J_t(k, \omega)$ and $J_l(k, \omega)$ depend weakly on k , providing $k \simeq m_i k_0$. This is so because the cluster dimensions (correlation range) in $\mathbf{J}_2(\mathbf{k}, \omega)$, $\mathbf{J}_3(\mathbf{k}, \omega)$, etc., are much smaller than $2\pi/m_i k_0$ when $c k_0 = \omega$ is an optical frequency (and $m_i \sim 1.5$). Even this situation assumes that the system is not on the verge of phase separation (when the correlation range becomes very large). At x-ray frequencies the reciprocal wave number is comparable with, or less than, the correlation range, but a multipole expansion is not valid then and the theory needs correcting. It is more relevant here that it does not follow that k , as a root of the longitudinal dispersion relation, is necessarily approximately equal to $m_i k_0 \sim 1.5 k_0$ at optical frequencies. If the additional roots for m_i are significant, the same may be true of these.

[‡] We discuss the changed poles of $m_i^2(\omega)$ and how they are pushed by $J_t(m k_0, \omega)$ in later papers.

imaginary ω axis. Such a pole is usually interpreted as evidence of a ferroelectric phase transition or some analogous structural change. Therefore we may exclude such a pole from the present discussion. It follows that (4.22*b*) cannot be satisfied and therefore that (4.22*a*) cannot be satisfied.

If equation (4.22*a*) cannot be satisfied we must infer that there is some least frequency $\omega_0 > 0$ such that the longitudinal dispersion relation (4.11*b*) is valid for some $\omega \geq \omega_0$. We have not, of course, demonstrated that the longitudinal modes exhibit a continuous frequency spectrum, and, although (4.11*b*) is a dispersion relation, admissible ω (viewed as functions $\omega(|\mathbf{k}|)$ of $|\mathbf{k}|$) may lie in discrete ranges as $|\mathbf{k}|$ changes.†

Despite the existence of this lower bound to the admissible longitudinal frequencies which satisfy the dispersion relation (4.11*b*), we shall show later that an integral over all frequencies, which in effect contains this longitudinal dispersion relation, taken with the interpretation (4.19*b*)‡ is an important contributor to the ground-state energy of the system. This is probably the main importance of this relation and why we have devoted much of this first paper to obtaining it. We obtain its two-component generalization immediately below.

Since the longitudinal modes are governed by the extinction theorem which depends on the surface integral (3.10*b*) and thus on the surface geometry of V , we are ultimately obliged to consider the effect of that surface geometry. The simplest choice for this certainly shows that none of the longitudinal modes governed by the longitudinal dispersion relations which we have obtained in this paper is excited by light. This is a well-accepted concept in dielectric theory (cf. e.g. Pines 1963, pp. 201–2), although we are here no longer talking about the zeros of a transverse dielectric constant. In fact, we shall see in II that the extinction theorem means that in this single simplest case the longitudinal modes cannot be excited by light whether that light is strictly transverse or not, and in the author's view this explicit demonstration is particularly perspicuous. However, we shall see that such an understanding is very incomplete with other geometries. It has not been possible to eliminate the possibility that the longitudinal modes can be excited by transverse light of the proper frequencies, whilst the case of a longitudinal exciting field needs additional comment. Both situations are analysed in II, and we show in particular that forcing longitudinal modes have a response.

Perhaps the most interesting feature exhibited by the microscopic theory is the way in which the 'longitudinal photons' help to build up the transverse modes, whilst 'transverse photons' help to build up the longitudinal modes. That this is so in the dipole approximation, to which we are limited here, follows from the fact that (2.8*b*) shows that in the dielectric constant approximation of (4.21) only longitudinal-time-like photons (i.e. the coulombic part $\nabla_{\mathbf{x}} \nabla_{\mathbf{x}'} |\mathbf{x} - \mathbf{x}'|^{-1}$ of $\mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega)$ in (2.8*b*)) contribute to the local-field term which is $J_\ell(0, 0)$. We have noted that $J_\ell(mk_0, \omega)$ depends rather weakly on m and also on ω at optical or lower frequencies. Therefore longitudinal photons continue to play an important role in the local-field term $J_\ell(mk_0, \omega)$ at these finite frequencies. Likewise, transverse photons are contained in the radiation-field tensor $\mathbf{R}(\mathbf{x}, \mathbf{x}'; \omega)$ of (2.8*b*), and therefore appear in the \mathbf{F} tensors in the local-field term $J_\ell(mk_0, \omega)$ of the longitudinal dispersion relation (4.11*b*). Coupling of this kind is essential to a phenomenon like Čerenkov radiation. We show later that the theory of such radiation is contained within the theory associated with the transverse and longitudinal modes.

Despite this coupling, it is interesting to see that longitudinal photons are explicitly eliminated from the term in $(m^2 - 1)^{-1}$ in (3.12) in the passage to the transverse dispersion relation implicit in (3.15), and this of course still applies in the passage to the more general

† We have noted that, whilst $|\mathbf{k}| = m(\omega)k_0$ depends strongly on ω , $\omega(|\mathbf{k}|)$ correspondingly depends weakly on $|\mathbf{k}|$. A possible spectrum for the real part of $|\mathbf{k}(\omega)|$ is a series of steeply rising lines starting close to the roots of (3.18) (or more precisely at the roots of (4.11*b*) when $m_l = 0$, so that $|\mathbf{k}| = 0$ there).

‡ The integrand has the dispersion relation (4.11*b*) as its poles. It follows that there are longitudinal modes which contribute to the ground-state energy which are not acceptable in the way that the modes (4.11*b*) (with (4.19*b*)) are acceptable. The situation once again depends very much on the extinction theorem and is analysed in II.

transverse dispersion relation (4.11a). It is also interesting to see that transverse photons are eliminated from the term in $(m^2-1)^{-1}$ in the passage from (3.12) to (3.16a), and this still applies to the passage to the general longitudinal dispersion relation (4.11b); for the quantity

$$(\nabla^2 + k_0^2) \frac{4\pi n \mathbf{P}_i(\mathbf{x}, \omega)}{(m^2-1)k_0^2} = -4\pi n \mathbf{P}_i(\mathbf{x}, \omega) \quad (4.23a)$$

can be thought of, rather roughly, as the Fourier transform

$$\begin{aligned} & n(2\pi)^{-3} \int \exp(i\mathbf{k} \cdot \mathbf{x}) d\mathbf{k} \mathbf{P}_i(\mathbf{k}, \omega) \cdot \int (\nabla \nabla |\mathbf{x} - \mathbf{x}'|^{-1}) \exp\{i\mathbf{k} \cdot (\mathbf{x}' - \mathbf{x})\} d\mathbf{x}' \\ &= n(2\pi)^{-3} \int \exp(i\mathbf{k} \cdot \mathbf{x}) d\mathbf{k} \mathbf{P}_i(\mathbf{k}, \omega) \cdot \left(\frac{-4\pi \mathbf{k}\mathbf{k}}{|\mathbf{k}|^2} \right) \\ &= -4\pi n \mathbf{P}_i(\mathbf{x}, \omega). \end{aligned} \quad (4.23b)$$

Particular attention must still be paid to the role of the extinction theorem, and this we must discuss in II. It is, however, plain from (4.23b) that only the Fourier transform $-4\pi \mathbf{k}\mathbf{k}/|\mathbf{k}|^2$ of $\nabla \nabla |\mathbf{x} - \mathbf{x}'|^{-1}$ contributes to (3.16b) and the radiation-field tensor $\mathbf{R}(\mathbf{x}, \mathbf{x}'; \omega)$ of (2.8b) is eliminated here. It is plain therefore that coupling between longitudinal and transverse photons is largely due to the intervention of the spatial correlation between the particles described by the correlation functions $g_{12}(r)$, $g_{123}(\mathbf{r}, \mathbf{r}')$, etc. In fact, only the Lorentz-field term (which, though longitudinal, i.e. coulombic, in origin, still contributes to the transverse dispersion relation) is not a consequence of particle correlation in the theory.

We now turn to the problem of the form assumed by the dispersion relations (4.11) in a system of more than one component. The extension of the dispersion relations (4.11) with (4.19) to multi-component systems is, in fact, rather obvious. We consider the case of two-component systems only. Instead of (4.10a) we shall obtain

$$\begin{aligned} \mathbf{P}_{ta}(\mathbf{x}, \omega) = \alpha(\omega) \left\{ \frac{4\pi n_a}{m_t^2-1} \mathbf{P}_{ta}(\mathbf{x}, \omega) + \frac{4\pi}{3} n_a \mathbf{P}_{ta}(\mathbf{x}, \omega) + n_a J_{taa}(mk_0, \omega) \mathbf{P}_{ta}(\mathbf{x}, \omega) \right. \\ \left. + \frac{4\pi n_b}{m_t^2-1} \mathbf{P}_{tb}(\mathbf{x}, \omega) + \frac{4\pi}{3} n_b \mathbf{P}_{tb}(\mathbf{x}, \omega) + n_b J_{tab}(mk_0, \omega) \mathbf{P}_{tb}(\mathbf{x}, \omega) \right\} \end{aligned} \quad (4.24a)$$

$$\begin{aligned} \mathbf{P}_{tb}(\mathbf{x}, \omega) = \beta(\omega) \left\{ \frac{4\pi n_a}{m_t^2-1} \mathbf{P}_{ta}(\mathbf{x}, \omega) + \frac{4\pi}{3} n_a \mathbf{P}_{ta}(\mathbf{x}, \omega) + n_a J_{tba}(mk_0, \omega) \mathbf{P}_{ta}(\mathbf{x}, \omega) \right. \\ \left. + \frac{4\pi n_b}{m_t^2-1} \mathbf{P}_{tb}(\mathbf{x}, \omega) + \frac{4\pi}{3} n_b \mathbf{P}_{tb}(\mathbf{x}, \omega) + n_b J_{tbb}(mk_0, \omega) \mathbf{P}_{tb}(\mathbf{x}, \omega) \right\}. \end{aligned} \quad (4.24b)$$

These two equations are compatible if, and only if,

$$m_t^2 - 1 = \frac{4\pi \{n_a \alpha + n_b \beta - n_a n_b \alpha \beta (J_{taa}' + J_{tbb}' - J_{tab}' - J_{tba}')\}}{1 - n_a \alpha J_{taa}' - n_b \beta J_{tbb}' + n_a n_b \alpha \beta (J_{taa}' J_{tbb}' - J_{tab}' J_{tba}')} \quad (4.24c)$$

in which for compactness here $J_{t\gamma\delta}' \equiv 4\pi/3 + J_{t\gamma\delta}$ ($\gamma, \delta = a$ or b).

Similarly, (4.10b) becomes

$$\begin{aligned} \mathbf{P}_{ia}(\mathbf{x}, \omega) = \alpha(\omega) \left\{ -\frac{8\pi}{3} n_a \mathbf{P}_{ia}(\mathbf{x}, \omega) + n_a J_{iaa} \mathbf{P}_{ia}(\mathbf{x}, \omega) \right. \\ \left. - \frac{8\pi}{3} n_b \mathbf{P}_{ib}(\mathbf{x}, \omega) + n_b J_{iab} \mathbf{P}_{ib}(\mathbf{x}, \omega) \right\} \end{aligned} \quad (4.25a)$$

$$\begin{aligned} \mathbf{P}_{ib}(\mathbf{x}, \omega) = \beta(\omega) \left\{ -\frac{8\pi}{3} n_a \mathbf{P}_{ia}(\mathbf{x}, \omega) + n_a J_{iba} \mathbf{P}_{ia}(\mathbf{x}, \omega) \right. \\ \left. - \frac{8\pi}{3} n_b \mathbf{P}_{ib}(\mathbf{x}, \omega) + n_b J_{ibb} \mathbf{P}_{ib}(\mathbf{x}, \omega) \right\}. \end{aligned} \quad (4.25b)$$

This yields the longitudinal dispersion relation

$$\begin{aligned} n_a \alpha J_{laa} + n_b \beta J_{lbb} + n_a n_b \alpha \beta \left\{ \frac{8\pi}{3} (J_{laa} + J_{lbb} - J_{lab} - J_{lba}) - (J_{laa} J_{lbb} - J_{lab} J_{lba}) \right\} \\ = 1 + \frac{8\pi}{3} (n_a \alpha + n_b \beta). \end{aligned} \quad (4.25c)$$

The quantities which appear in the dispersion relations (4.24c) and (4.25c) are the obvious analogues in the two-component system consisting of n_a a particles and n_b b particles per unit volume of the one-component quantities defined in § 2 for n particles of a single kind per unit volume. When the a and b particles are identical (so that $\alpha = \beta$) and $n_a + n_b = n$, equation (4.24c) reduces to (4.11a), and (4.25c) to (4.11b).

The only complication in this extension is the definition of the J_i and J_l . Instead of (4.19) we obtain, for example,

$$J_{lab}(m_l k_0, \omega) = \sum_{s=1}^{\infty} \mathbf{u}(\mathbf{k}) \cdot \mathbf{G}_{sab}(m_l k_0 \mathbf{k}, \omega) \cdot \mathbf{u}(\mathbf{k}) \quad (4.26a)$$

$$J_{lab}(m_l k_0, \omega) = \sum_{s=1}^{\infty} \mathbf{k} \cdot \mathbf{G}_{sab}(m_l k_0 \mathbf{k}, \omega) \cdot \mathbf{k} \quad (4.26b)$$

in which

$$\mathbf{G}_{sab} = \sum_{\gamma=0}^{s-1} (n_a \alpha)^{s-\gamma-1} (n_b \beta)^{\gamma} \sum \mathcal{P} \mathbf{J}_{a\delta\dots\mu b}(m_l k_0 \mathbf{k}, \omega) \quad (4.26c)$$

and \mathcal{P} is any distinct permutation of $\delta \dots \mu$ (γ of which quantities are b 's and the remainder of which are a 's). Thus, in particular,

$$\begin{aligned} \mathbf{G}_{2ab} &= (n_a \alpha \mathbf{J}_{aab} + n_b \beta \mathbf{J}_{abb}) \\ \mathbf{G}_{3ab} &= (n_a^2 \alpha^2 \mathbf{J}_{aaa} + n_a n_b \alpha \beta \mathbf{J}_{aba} + n_a n_b \alpha \beta \mathbf{J}_{abb} + n_b^2 \beta^2 \mathbf{J}_{bbb}). \end{aligned}$$

An example of the tensors \mathbf{J} is

$$\begin{aligned} \mathbf{J}_{aab}(\mathbf{k}, \omega) &= \iint \{g_{aab}(\mathbf{r}, \mathbf{r}') - g_{aa}(r)g_{ab}(r')\} \\ &\quad \times \exp\{i\mathbf{k} \cdot (\mathbf{r} + \mathbf{r}')\} \mathbf{F}(\mathbf{r}, \omega) \cdot \mathbf{F}(\mathbf{r}', \omega) \, d\mathbf{r} \, d\mathbf{r}'; \end{aligned} \quad (4.27a)$$

on the other hand,

$$\begin{aligned} \mathbf{J}_{aba}(\mathbf{k}, \omega) &= \iint \{g_{aba}(\mathbf{r}, \mathbf{r}') - g_{ab}(r)g_{ba}(r')\} \exp\{i\mathbf{k} \cdot (\mathbf{r} + \mathbf{r}')\} \mathbf{F}(\mathbf{r}, \omega) \cdot \mathbf{F}(\mathbf{r}', \omega) \, d\mathbf{r} \, d\mathbf{r}' \\ &\quad + n_a^{-1} \int \{g_{ab}(r)\} \mathbf{F}(\mathbf{r}, \omega) \cdot \mathbf{F}(\mathbf{r}, \omega) \, d\mathbf{r}. \end{aligned} \quad (4.27b)$$

The dispersion relation (4.24c) has already been presented in greater generality by Bullough (1962).† The dispersion relation (4.25c) is (again as far as the author is aware) a new physical result. Everything we have said about the relationship between the two dispersion relations (4.11) still applies to the dispersion relations of the two-component system. In particular, when $m_l = 0$, equation (4.25c) is a zero of m_l^2 in the transverse dispersion relation (4.24c), since

$$J_{l\gamma\delta}(0, \omega) = J_{l\gamma\delta}(0, \omega); \quad \gamma, \delta = a \text{ or } b.$$

More generally, the modes which satisfy (4.25c) continue to lie close to the zeros of (4.24c). The discussion of longitudinal dispersion relations following equation (4.16) still entirely applies.

† It has also been given independently by Terwiel (1964) as far as the $\mathbf{G}_{2\gamma\delta}$ of (4.26c).

The longitudinal dispersion relation (4.25c) apparently makes an important contribution in the theory of the ground-state energy of a two-component system in the formulation we present later.

We are now in a position to treat the many-body theory of a molecular fluid in relation to (i) optical scattering, both elastic and, in principle, inelastic; (ii) microscopic theories of critical opalescence in fluids; (iii) optical screening and resonance broadening; (iv) certain many-body aspects of the theory of optical absorption; (v) ground-state energy (a many-body theory of van der Waals forces).

For the scattering phenomena we need to observe only that both m_t and m_l , as given by (4.11) or by (4.24c) and (4.25c), are complex since the J_t and J_l are complex: they implicitly contain therefore the theory of extinction due to external scattering.† The scattering of light is, of course, concerned with the transverse modes; but we can also treat the stopping power of the fluid to an incident fast electron which engages the longitudinal modes. In the second problem the theory displays the loss of energy as scattered light (partly Čerenkov radiation) as we have briefly noted already, and in this it seems rather more satisfactory than the treatment given, for example, by Nozières and Pines (1958) who, however, were concerned solely with the plasma.‡ We hope to present the essential parts of the theory of scattering, and particularly of optical scattering, in later papers: because of several intricacies of detail in this theory of optical scattering we shall there attempt to indicate only the broad features of the theory and its consequences.

The theory of optical screening emerges in part in the course of the study of external scattering: it is hoped, however, to present an explicitly screened formulation of the microscopic optics of a fluid in a later paper. So far this theory appears to be the only one which is really applicable to a translationally invariant system (see Bullough 1967).

The theory of absorption that we are able to present exploits the microscopic optics implicit in the dispersion relations (4.11a) and (4.24c); the theory therefore deals with problems of frequency shifts, changes of absorption intensity induced by local fields and screening problems, but the treatment of the actual absorption process is rather rudimentary. It must be discussed later.

The theory of van der Waals forces which we can develop from the work of this first paper is built round a variant of the integral equations we have studied here. The theory seems easily to yield low-energy quantum electrodynamic results like those of Casimir and Polder (1948), generalized to all orders of a perturbation theory for polarizable particles *and* in a form applicable to the finite-temperature many-body fluid. It is a virtual photon theory directly related to the real photon theory of external scattering. It exhibits of necessity and without contrivance a Lamb-type level shift of the ground state consequent upon the coupling to the radiation field, and it also displays all the currently accepted divergences of quantum electrodynamics (necessarily in non-relativistic form). Thus this aspect of the theory is surprisingly complete.§

An attempt to relate the theory explicitly to the refractive index (motivated by the semi-phenomenological approach of Lifshitz and co-workers (cf. e.g. Lifshitz 1956, Dzyaloshinskii *et al.* 1961) has so far failed to surmount the following difficulty. Within the sequence of terms (4.18) contributing to (4.17) is a sequence of 'closed-loop' multiple-scattering terms. On integration over frequency *and* coupling constant (e^2) this sequence is an expression for the binding energy of the system. Unfortunately, (4.18) contains many additional terms, which apparently do not contribute to the binding energy and yet cannot be eliminated. In this respect the longitudinal dispersion relation of this paper offers much greater scope for manipulation. It can be exhibited as the surface of singularity of a longitudinal response function, which can then be related directly to the 'longitudinal'

† The important contribution of the radiation reaction field has been omitted so far, however.

‡ But compare Fano (1956).

§ These one-body terms are numerically significant only in very dilute gases. They emerge so naturally from the theory, however, that they must be considered to be a significant part of it.

part of the total binding energy; and this is why we consider the study of the longitudinal modes of the present paper to be important.†

The difficulty in relating the theory of van der Waals forces *directly* to the refractive index alone stems from two facts: first, the existence of all powers of the coupling constant e^2 in (4.19) above; secondly, the role of the radiation field and the consequent dispersion relations of (4.11) connecting \mathbf{k} and ω in the theory. Because of the first point, for example, it has proved possible to reach the zero-temperature result of Dzyaloshinskii *et al.* (1961) (a semi-phenomenological theory) only by the drastic approximation of basing the theory on the integral equation (2.2) instead of on that most general form of the integral equation (2.1) which leads to the results of § 4 above. It is still necessary to eliminate the Lorentz-field term.

Despite such particular difficulties, the microscopic theories of these several phenomena all appear as different aspects of one unified theory based essentially on the generalized form of the integral equation (2.1) which is treated in § 4 and on the dispersion relations (4.11) (with (4.19)) derived from it. They are, of course, all limited by the approximations of the theory which are to the following: to molecular fluids, to second-order time-dependent perturbation theory applied to the (non-relativistic) time-dependent Schrödinger equation and so to the linear perturbing field approximation (linearity in the *external* field), to a self-consistent Hartree (or Hartree-Fock) approximation for the many-body electron motions and to a Born-Oppenheimer‡ approximation for the molecular motions. We largely work in the dipole approximation, but this is by no means necessary. Likewise, we usually assume that the particles are isotropically polarizable, but, again, this is not always necessary.

Within these approximations the theory permits a rather striking view of the detailed mechanism of the optics of a many-body molecular system. On the other hand, it is important as far as possible to cast the theory into one in terms of easily measurable macroscopic quantities like the refractive index. We have briefly considered the problem of doing this for the binding energy above. Another very important example of this is the passage from a microscopic theory of external light scattering to a macroscopic theory, and this problem like the van der Waals problem will be taken up in later papers.

Before doing so, it is convenient to complete the investigation of the several primarily mathematical aspects of the theory which have emerged so far. These points are concerned with the characterization of transmitted modes and the role of the extinction theorem (to be considered with an extension of the physical content of the theory of longitudinal modes in II), and with the destruction of translational invariance and the theory of response functions to be developed in a mathematical 'appendix' as paper III. We return again to the main theme and physical content of the theory thereafter.

References

- ABRIKOSOV, A. A., GORKOV, L. P., and DZYALOSHINSKII, I. YE., 1965, *Quantum Field Theoretical Methods in Statistical Physics* (Oxford: Pergamon Press), pp. 4-5, 16-17.
 AGRANOVITCH, V. M., 1960, *Sov. Phys.-JETP*, **10**, 307-13 (*Zh. Eksp. Teor. Fiz.*, **37**, 430-41 (1959)).
 AMOS, A. T., 1963, *Molec. Phys.*, **6**, 393-407.
 ANDERSON, P. W., 1964, *Concepts in Solids* (New York: W. A. Benjamin), pp. 132-52.
 BALL, M. A., and McLACHLAN, A. D., 1964, *Proc. R. Soc. A*, **282**, 433-45.
 BLOEMBERGEN, N., and PERSHAN, P. S., 1962, *Phys. Rev.*, **128**, 606-22.

† There is, nevertheless, a comparable transverse response function, and transverse contributions to the binding energy can be expressed in terms of it. The theory in this form may be incomplete because of the complication of surface contributions, which appear partly in the guise of the surface integral (3.10*b*) of the extinction theorem (3.13). The response function theory of binding energy is examined in II, but the complete theory will be presented later.

‡ By a 'Born-Oppenheimer approximation' is meant that the consequences of electronic motions are computed with molecular sites held fixed. The subsequent statistical average over molecular sites generates the spatial correlation functions of this paper. The approximation has been called quasi-static (Lax 1951). Conservation of both energy *and* momentum in the microscopic scattering, processes may be assured by using time-dependent (Van Hove type) molecular correlation functions, but the theory is still approximate (see later).

- BORN, M., and HUANG, K., 1954, *Dynamical Theory of Crystal Lattices* (Oxford: Clarendon Press), pp. 248-77.
- BORN, M., and WOLF, E., 1959, *Principles of Optics* (Oxford: Pergamon Press), pp. 98-107.
- BULLOUGH, R. K., 1962, *Phil. Trans. R. Soc. A*, **254**, 397-440.
- 1963, *Proc. R. Soc. A*, **275**, 271-83.
- 1965, *Phil. Trans. R. Soc. A*, **258**, 387-420.
- 1967, *Proc. 2nd Interdisciplinary Conf. on Electromagnetic Scattering* (New York: Gordon and Breach), pp. 537-77.
- CASIMIR, H. B., and POLDER, D., 1948, *Phys. Rev.*, **73**, 360-72.
- DARWIN, C. G., 1924, *Trans. Camb. Phil. Soc.*, **23**, 137-67.
- DZYALOSHINSKII, I. YE., LIFSHITZ, E. M., and PITAEVSKII, L. P., 1961, *Adv. Phys.*, **10**, 165-209.
- EWALD, P. P., 1912, *Dissertation*, Munich.
- 1916, *Ann. Phys., Lpz.*, **49**, 1-38.
- FANO, U., 1956, *Phys. Rev.*, **103**, 1202-18.
- FOWLER, G. N., 1964 a, *Molec. Phys.*, **8**, 375-82.
- 1964 b, *Molec. Phys.*, **8**, 383-6.
- HALL, G. G., 1962, *Proc. R. Soc. A*, **270**, 285-94.
- HOEK, H., 1939, *Thesis*, Leiden.
- HOPFIELD, J. J., 1958, *Phys. Rev.*, **112**, 1555-67.
- HUANG, K., 1951, *Proc. R. Soc. A*, **208**, 352-65.
- HUBBARD, J., 1955, *Proc. Phys. Soc. A*, **68**, 441-3.
- KNOX, R. S., 1963, *Theory of Excitons* (New York: Academic Press), pp. 107-11.
- KRAMERS, H. A., and HEISENBERG, W., 1925, *Z. Phys.*, **31**, 681-712.
- LAX, M., 1951, *Rev. Mod. Phys.*, **23**, 287-310.
- LIFSHITZ, E. M., 1956, *Sov. Phys.-JETP*, **2**, 73-83 (*Zh. Eksp. Teor. Fiz.*, **29**, 94-110 (1955)).
- MAZUR, P., 1958, *Advances in Chemical Physics*, Vol. 1 (New York: Interscience), pp. 309-60.
- MAZUR, P., and MANDEL, M., 1956, *Physica*, **22**, 289-310.
- MAZUR, P., and POSTMA, B. J., 1959, *Physica*, **25**, 251-67.
- MAZUR, P., and TERWIEL, R. H., 1964, *Physica*, **30**, 625-64.
- NOZIÈRES, P., and PINES, D., 1958, *Nuovo Cim.*, [10], **9**, 470-90.
- OBADA, A.-S. F., 1967, *Ph.D. Thesis*, University of Manchester.
- OSEEN, C. W., 1915, *Ann. Phys., Lpz.*, **48**, 1-56.
- PINES, D., 1962, *The Many Body Problem* (New York: W. A. Benjamin), pp. 26-34.
- 1963, *Elementary Excitations in Solids* (New York: W. A. Benjamin), chap. IV.
- PLANCK, M., 1902, *Sber. Preuss. Akad. Wiss.*, 470-94.
- POWER, E. A., 1965, *Introductory Quantum Electrodynamics* (New York: Elsevier), pp. 139-41.
- ROSENFELD, L., 1951, *Theory of Electrons* (Amsterdam: North-Holland), chap. VI.
- TERWIEL, R. H., 1964, *Physica*, **30**, 1027-37.