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THE SCATTERING OF LIGHT. I. THE OPTICAL RESPONSE OF A FINITE MOLECULAR FLUID

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CONTENTS

We present a classical many-body theory of the optical response of a molecular fluid. The unified treatment provides mutually consistent expressions for the dielectric constant, the refractive index, the optical extinction coefficient, and the optical scattering cross section. The theory treats a finite material system and handles all surface effects associated with transmitted and scattered light. The complex refractive index and the scattering cross section will be analysed in two future papers.

1. Introduction

The present work is the first of a series of three papers reporting a classical many-body theory of the optics of molecular fluids. The quantum mechanical foundation and the corrections to the classical theory due to strictly quantal effects will be reported separately.

This series of papers, together with the quantum part still to be published, is the culmination of a study of optical processes in molecular fluids whose origins go back to before 1962 (Bullough 1962, 1965, 1967, 1968, 1969, 1970; Bullough *et al.* 1968; Bullough & Hynne 1968; Hynne & Bullough 1972, 1982; Hynne 1970, 1974, 1975, 1977, 1980, 1983). At that time (1962) a number of valuable papers on the optical many-body problem had already appeared (Yvon 1936, 1937; Kirkwood 1936; Hoek 1939; Rosenfeld 1951; De Boer *et al.* 1953; Fixman 1955; Buckingham & Pople 1955*a*, *b*; Mazur & Mandel 1956; Buckingham & Steven 1957; Mazur 1958; Mead 1958, 1960, 1962; Kielich 1960). It was clear, nevertheless that the theory contained a number of unsurmounted difficulties associated with a necessity of treating a *finite* material system.

The interest in molecular optics has continued ever since and has resulted in a large number of papers of which we can mention only examples (Abrikosov *et al.* 1965; Frisch & McKenna 1965; Linder & Hoernschemeyer 1967; Tanaka 1968; Mead 1968, 1972; Fulton 1969; Mountain 1972; Bedeaux & Mazur 1973; Felderhof 1974; Oxtoby & Gelbart 1974*a*, *b*; Dharma-wardana 1975, 1976*a*, *b*; Boots *et al.* 1975, 1976; Pasmanter *et al.* 1976; Samson *et al.* 1976; Sullivan & Deutch 1976; Keyes & Ladanyi 1978; Logan 1981, 1982; Logan & Madden 1982; Høye & Stell 1982; see also the book by Fabelinskii (1968) and the reviews by Gelbart (1974) and Fromhold (1981)).

But in spite of the striking role played by boundary surfaces of material media in classical optics, the presence of such surfaces has been largely ignored in these microscopic theories and never handled on a strictly microscopic level. Even the classical argument of Ewald (1912, 1916) and Oseen (1915), which deals with only part of the surface effect, is seldom used in molecular theories of the refractive index or light scattering.

The purpose of the present work is to give a complete and connected account of the many-body optics of a molecular fluid which solves all essential problems associated with the existence of a macroscopic surface. We shall refer to the three papers as I, II and III.

On the basis of classical electrodynamics and within a quasistatic approximation we develop a comprehensive theory of the response of a molecular fluid to incident light. This includes theories of the parameters that characterize that response, namely the dielectric constant, the complex refractive index, the extinction coefficient, and the differential and total cross sections of incoherent scattering.

These theories appear as branches of a single unified and internally consistent theory: various relations connect the different parts. For example, we prove that the total scattering cross section per unit volume equals the extinction coefficient obtained from the imaginary part of the refractive index, and we derive the Maxwell relation that identifies the dielectric constant with the square of the refractive index. In fact, there is a remarkable formal parallelism between the refractive index theory and the light scattering theory: one term at order p of a series expansion in the refractive index theory corresponds to $p-1$ terms of similar structure at the same order in the scattering theory.

The theory is developed in terms of infinite series, and to reach significant results it is necessary to handle these to all orders. For this purpose we develop an efficient machinery of integral equations. For example, the consistency proof referred to above is carried through in §5 without reference to series representations. Actually, the infinite series are themselves presented in very concise forms, which make them easy to handle and which make the relation between the refractive index theory and the light scattering theory particularly transparent. This is accomplished through definitions that initially appear as mere technical devices, but which will gain new physical significance through generalization in II.

A characteristic feature of the optical response is its strong dependence on the geometry of the system, and conventional many-body techniques must fail. A major part of the surface dependence is handled through two distinct forms of the extinction theorem originally due to Ewald (1912, 1916) and Oseen (1915). Still, significant surface effects remain and complicate the theory from a computational point of view; but the theory explains all the surface effects in physical terms, as we shall see in II and III.

The more important results of the theory exploit the concept of dielectric screening:

corresponding to the usual 'photon' propagator, we introduce a screened photon propagator describing the average propagating field from a dipole in the presence of the many-body system, and similar screened propagators are introduced for (roughly) the radiation from a pair of dipoles to a distant detector.

A formulation in terms of these screened propagators, which is rigorously equivalent to the original unscreened formulation, is developed in §4. It is through such a screened formulation we are able to handle the intricate surface effects. The concept of screening is the usual one. But many-body optics has the unusual feature that one must treat the finite system, and the consequences of the existence of a bounding surface pervades the whole theory. Thus, in contradistinction to conventional many-body theory, we must introduce screening for the finite system, and the screened propagators depend strongly on the geometry. Of course such surface dependences must be contained in the theory, for they are essential to any proper description of the refraction and reflection of the scattered light at the surface. Moreover, the microscopic theory predicts macroscopic multiple light scattering too, and there must be surface dependences associated with this multiple scattering also. In this paper we develop certain key ideas for handling these surface effects. The actual solution to the problem of external scattering will be given in III.

We now indicate the organization of the three papers. In the present paper, we start in §2 with a derivation of the classical equations of molecular optics for the instantaneous response of a collection of molecules to an external electromagnetic field. In §3 and §4, we proceed to consider average values, and we develop the machinery of integral equations connecting macroscopic quantities like the polarization, electromagnetic field, and flux of scattered light. We obtain explicit expressions for the kernels of these integral equations, which generalize a macroscopic susceptibility and a scattering cross section. By their nature §3 and §4 may appear somewhat arid. But the concepts introduced there contain a lot of important physics, which will materialize as such during the subsequent analysis in II and III.

Sections 5 and 6 solve the response problem for the average polarization and the average electromagnetic field. We obtain expressions for the parameters of the response, the dielectric constant, the refractive index, and the total scattering cross section. We exhibit the actual solution to the response problem, in terms of the induced polarization and fields, for the particular geometry of a parallel sided slab and for an obliquely incident plane electromagnetic wave. We demonstrate that the solution agrees completely with macroscopic optics except for one feature: the microscopic theory predicts a small deviation from continuum behaviour in the field and polarization at points that lie within a few wavelengths from the surface. In §7 we summarize the result of the paper, and we indicate how some of the concepts introduced here will come to play important roles in the forthcoming papers II and III.

Paper II will develop the refractive index theory in two forms, one generalizing the Lorentz–Lorenz relation, the other, a dispersion relation due to Onsager (1936) and Böttcher (1942). The two related macroscopic models will be analysed and compared. The two-body corrections to the Lorentz–Lorenz relation will be obtained in closed form and computed numerically.

Paper III will treat the scattering of an incoming wave in vacuum into an outgoing wave in vacuum. It will demonstrate the refraction and reflection of scattered light at the surface and will treat macroscopic multiple light scattering, all handled in microscopic terms. It will derive the one- and two-body scattering in closed form and compute the depolarization ratio numerically. It will contain an analysis of the Einstein (1910) light scattering equation.

We now develop the foundation of the theory from classical electrodynamics in §2.

A note on notation

We use bold type for vectors and tensors and employ a dyadic notation. Vectors are bold italic as in $\boldsymbol{x}$ or $\boldsymbol{P}$, for example, or bold sloping greek as in $\boldsymbol{\varepsilon}$ or $\boldsymbol{\Sigma}$. Tensors are bold roman sans serif as in F, or bold upright greek as in $\mathbf{\Lambda}$. The scalar product of two vectors $\boldsymbol{k}$ and $\boldsymbol{x}$ is $\boldsymbol{k}\cdot\boldsymbol{x}$ and is a scalar; the outer product $\boldsymbol{e}^*\boldsymbol{e}$ is a dyadic (a second rank tensor); the product $\mathbf{\Pi}\cdot\boldsymbol{P}$ is a vector when $\mathbf{\Pi}$ is a second rank tensor and is the same vector as $\boldsymbol{P}\cdot\mathbf{\Pi}$ only if $\mathbf{\Pi}$ is a symmetric tensor; the product $\mathsf{F}\cdot\mathbf{\Pi}$ is a second rank tensor when F and $\mathbf{\Pi}$ are.

We also use bold script letters: for example $\boldsymbol{\mathscr{E}}$ is a vector. But the tensor F (which is a free electromagnetic field or 'photon' propagator) is generalized in the paper to a new tensor, which is a bold script $\boldsymbol{\mathscr{F}}$. It will always be clear that this must be second rank tensor rather than a vector.

2. ELECTRODYNAMICAL FOUNDATION

In this section we shall derive the classical integral equation of molecular optics and an expression for the flux of light radiated from a molecular system.

We consider a system of isotropically polarizable, non-polar molecules in an instantaneous state with molecules at sites $\boldsymbol{x}_j$ exposed to an external coherent electromagnetic field $\boldsymbol{E}(\boldsymbol{x},\omega)$ of frequency ω. A stationary situation is assumed, and we work in terms of time Fourier-transformed functions. We shall use a quasistatic approximation in which we solve the electrodynamical problem for a fixed configuration of molecules and subsequently take a statistical average. The quasistatic approximation means that there is no dependence on the molecular velocity distribution, and the averaging is effectively over molecular configurations only. The theory takes no account of momentum transfer between photons and molecules in microscopic scattering processes, and this excludes a proper treatment of Doppler broadening and Brillouin scattering for example. On the other hand, we believe the theory provides a valid theory of the integrated scattering (integrated over the frequency spectrum of the scattered light).

We shall work in a dipole approximation in which the state of polarization of the system is determined by the dipole moments of individual molecules. The total electromagnetic field at the point $\boldsymbol{x}$ is then the sum of the external field $\boldsymbol{E}(\boldsymbol{x},\omega)$ at $\boldsymbol{x}$ and the fields radiated to $\boldsymbol{x}$ from each dipole, namely

$$\boldsymbol{\mathscr{E}}(\boldsymbol{x},\omega) = \boldsymbol{E}(\boldsymbol{x},\omega) + \sum_j \mathsf{F}(\boldsymbol{x},\boldsymbol{x}_j;\omega)\cdot\boldsymbol{P}_j(\omega). \tag{2.1}$$

We shall need to change the notation later to distinguish between instantaneous configurations $\{\boldsymbol{x}_j\}$ of molecules and their averages. Thus (2.1) is rewritten in (2.24) with $\boldsymbol{\mathscr{E}}^{\text{in}}(\boldsymbol{x},\omega)$ written for $\boldsymbol{\mathscr{E}}(\boldsymbol{x},\omega)$ and, in (3.1*a*) $\boldsymbol{\mathscr{E}}(\boldsymbol{x},\omega)$ is reintroduced as the ensemble average of $\boldsymbol{\mathscr{E}}^{\text{in}}(\boldsymbol{x},\omega)$. This change in notation is introduced after (2.21) and is then used consistently throughout the paper.

While working in terms of (2.1) for the present, the electromagnetic field (or 'photon') propagator $\mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)$ gives the electric field at $\boldsymbol{x}$ from a dipole $\boldsymbol{P}$ at $\boldsymbol{x}'$ as $\mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{P}$, and it can be derived classically from this definition (for example, via the Hertz potential) in the form

$$\mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega) = (\nabla\nabla + k_0^2\,\mathsf{U})\exp(\mathrm{i}k_0 r)/r. \tag{2.2a}$$

In (2.2*a*) k_0 denotes the wavenumber of radiation of frequency ω propagating in empty space,

$k_0 = \omega/c$ (c is the velocity of light in vacuum); U is the unit tensor and $r = |\boldsymbol{x}-\boldsymbol{x}'|$. Direct evaluation gives the explicit form of F:

$$\mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega) = \left[k_0^2(\mathsf{U}-\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}) + \left(\frac{1}{r^2}-\frac{\mathrm{i}k_0}{r}\right)(3\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}-\mathsf{U})\right]\frac{\exp(\mathrm{i}k_0 r)}{r}. \tag{2.2b}$$

It may also be written in terms of spherical Hankel functions of the first kind, $h_n^{(1)}$, as (Rosenfeld 1951)

$$\mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega) = \tfrac{2}{3}\mathrm{i}k_0^3\,[h_0^{(1)}(k_0 r)\,\mathsf{U} + \tfrac{1}{2}h_2^{(1)}(k_0 r)\,(3\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}-\mathsf{U})]. \tag{2.2c}$$

Here $\boldsymbol{r} = \boldsymbol{x}-\boldsymbol{x}'$, $r = |\boldsymbol{r}|$, and $\hat{\boldsymbol{r}} = \boldsymbol{r}/r$. (Throughout this paper we shall use a similar notation to denote the length of a vector and a unit vector in the direction of a given vector.)

At zero frequency, $k_0 = 0$, (2.2b) goes into the well known static (or strictly longitudinal) form (see, for example, Jackson 1975)

$$\mathsf{F}(\boldsymbol{x},\boldsymbol{x}';0) = r^{-3}(3\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}-\mathsf{U}). \tag{2.3a}$$

This is also the part of F that dominates at distances r small compared to k_0^{-1} for finite frequencies. For large r, $\mathsf{F}(\boldsymbol{x},\boldsymbol{x}';0)$ behaves asymptotically as

$$\mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega) \sim k_0^2(\mathsf{U}-\hat{\boldsymbol{r}}\hat{\boldsymbol{r}})\exp(\mathrm{i}k_0 r)/r, \quad r\rightarrow\infty, \tag{2.3b}$$

and is transverse.

Since the molecules are assumed non-polar, the dipoles in (2.1) can only arise as a result of the external field $\boldsymbol{E}$. Actually, the dipole $\boldsymbol{P}_j(\omega)$ of molecule j is induced directly by the total field $\boldsymbol{\mathscr{E}}$ at the site $\boldsymbol{x}_j$ of the molecule, and it is given by the linear relation

$$\boldsymbol{P}_j(\omega) = \alpha(\omega)\,\boldsymbol{\mathscr{E}}(\boldsymbol{x}_j,\omega) \tag{2.4}$$

provided we ignore all nonlinear effects. We shall therefore assume a weak-field limit since we are specifically interested in linear optics. Classically, the linear relation (2.4) is an assumption. Indeed it is assumed both linear and local. The quantum theory shows that in the weak field limit the Kramers–Heisenberg (1925) expression for $\alpha(\omega)$ is correct for isolated molecules. But it also shows that there are additional many body contributions to any effective polarizability. We analyse these in the quantum foundation to be published separately.

Classically, by combining (2.1) and (2.4) we obtain a set of equations for the induced dipole moments $\boldsymbol{P}_j$:

$$\boldsymbol{P}_i(\omega) = \alpha(\omega)\,[\boldsymbol{E}(\boldsymbol{x}_i,\omega) + \sum_j \mathsf{F}(\boldsymbol{x}_i,\boldsymbol{x}_j;\omega)\cdot\boldsymbol{P}_j(\omega)]. \tag{2.5}$$

The term of the sum (2.5) with $j = i$ is not defined yet. Physically, it represents the field on a molecule arising from a dipole in the molecule itself. The divergence is part of the intricate problem of the interaction of an electron with its own radiation field, and is handled by renormalization in the quantum theory. The problem was first studied classically by Abraham and Lorentz (e.g. Lorentz 1909) and it is discussed in classical terms in many books (see, for example, Rosenfeld 1951). The result of the classical analysis is that the self-field contains a finite part, the radiation reaction, which in the present context may be introduced formally by defining the propagator $\mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)$ at $\boldsymbol{x} = \boldsymbol{x}'$ as a purely imaginary quantity,

$$\mathsf{F}(\boldsymbol{x},\boldsymbol{x};\omega) = \tfrac{2}{3}\mathrm{i}k_0^3\,\mathsf{U}. \tag{2.6}$$

(We show elsewhere how the quantum theory substantiates this view.)

The radiation reaction (2.6) plays a vital role in the present theory. It is essential for the internal consistency of the theory and it can be generalized to include intermolecular self-interactions related to the macroscopic reaction field introduced by Onsager (1936). It is possible to carry the effect of radiation reaction through the theory concealed in a polarizability. In (2.5), the term $j = i$ contains $\boldsymbol{P}_i(\omega)$, and it may be combined with the term on the left side to yield an equation of the same form as (2.5). In the resulting equation the sum excludes the term $j = i$ and the polarizability $\alpha(\omega)$ is replaced by a complex polarizability

$$\gamma(\omega) = \frac{\alpha(\omega)}{1-\frac{2}{3}\mathrm{i}k_0^3\,\alpha(\omega)}. \tag{2.7}$$

Although we shall have occasion to use the form (2.7), it proves to be advantageous in the general development to keep the radiation reaction explicitly as a self-interaction through the definition (2.6).

We have now obtained the equations that determine the polarization (equation (2.5)) and the field (equation (2.1) with (2.5)) induced in response to the external field $\boldsymbol{E}$. For the treatment of light scattering we shall also need the flux of energy radiated in a given direction.

From the asymptotic form (2.3*b*) we find at a distant point $\boldsymbol{R}$, where $\boldsymbol{E}$ vanishes,

$$\mathscr{E}(\boldsymbol{R},\omega) = \sum_j k_0^2\,(\mathbf{U}-\hat{\boldsymbol{R}}_j\,\hat{\boldsymbol{R}}_j)\cdot\boldsymbol{P}_j\exp{(\mathrm{i}k_0\,R_j)}/R_j, \tag{2.8}$$

in which $\boldsymbol{R}_j = \boldsymbol{R}-\boldsymbol{x}_j$. Let V denote the region containing the molecular system (for any configuration) and choose the origin of the coordinate system inside V. If $R \gg \max x_j$ we may write (recall that x_j denotes $|\boldsymbol{x}_j|$ for example)

$$R_j = R-\hat{\boldsymbol{R}}\cdot\boldsymbol{x}_j+O(x_j/R)\,x_j. \tag{2.9}$$

Since we are ultimately interested in the limit $R\rightarrow\infty$ we may neglect terms of relative order $O(x_j/R)$ for all j. Defining $\boldsymbol{k} = k_0\,\hat{\boldsymbol{R}}$ we may then write (2.8) as

$$\mathscr{E}(\boldsymbol{R},\omega) = R^{-1}\exp{(\mathrm{i}k_0\,R)}\,k_0^2(\mathbf{U}-\hat{\boldsymbol{k}}\hat{\boldsymbol{k}})\cdot\sum_j\boldsymbol{P}_j\exp{(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}_j)}. \tag{2.10}$$

From a homogeneous Maxwell equation we find the magnetic field at $\boldsymbol{R}$. The Poynting vector then gives the intensity and, upon multiplication by R^2, the flux per unit solid angle in the direction of $\boldsymbol{k}$, $I(\boldsymbol{k})$, which may be written

$$I(\boldsymbol{k}) = \frac{ck_0^2}{8\pi}\sum_{i,j}\boldsymbol{P}_i^*\cdot\mathbf{S}(\boldsymbol{x}_i,\boldsymbol{x}_j;\boldsymbol{k})\cdot\boldsymbol{P}_j. \tag{2.11}$$

A superscript asterisk denotes complex conjugation, and we have introduced a tensor kernel $\mathbf{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k})$ by the definition

$$\mathbf{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k}) = k_0^2\,(\mathbf{U}-\hat{\boldsymbol{k}}\hat{\boldsymbol{k}})\exp{[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')]}. \tag{2.12a}$$

For the case where the radiation is analysed by a polarizer of direction $\boldsymbol{v}$, the resulting flux is given by (2.11) with $\mathbf{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k})$ replaced by

$$\mathbf{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}) = k_0^2\,\boldsymbol{v}\boldsymbol{v}\exp{[\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}-\boldsymbol{x}')]}. \tag{2.12b}$$

Plainly, we obtain $\mathbf{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k})$ from $\mathbf{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})$ by summing over two orthogonal polarization vectors $\boldsymbol{v}_1$ and $\boldsymbol{v}_2$, perpendicular to $\boldsymbol{k}$,

$$\mathbf{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k}) = \sum_{j=1,2}\mathbf{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}_j). \tag{2.13}$$

It is therefore convenient to use the same symbol $\mathbf{S}$ for both quantities and distinguish them by the presence or absence of an argument $\boldsymbol{v}$. When the symbol $\mathbf{S}$ appears without arguments below, either interpretation can be adopted at will because the light scattering theory in terms of $\mathbf{S}$ is formally independent of whether the scattering is analysed for polarization or not.

The quantity $\mathbf{S}$ is closely related to the propagator $\mathbf{F}$, and because of this propagator character we shall call it a 'radiator' (or more precisely a 'dipole radiator' corresponding to the dipole photon propagator $\mathbf{F}$). We now show that the polarization-independent form (2.12*a*) is connected with the imaginary part of $\mathbf{F}$ by the Bohr–Peierls–Placzek type relation (compare with Sakurai (1967), for example)

$$\int \mathbf{S}(\boldsymbol{x}, \boldsymbol{x}'; \boldsymbol{k})\, \mathrm{d}\Omega = 4\pi\, k_0^{-1}\, \mathrm{Im}\{\mathbf{F}(\boldsymbol{x}, \boldsymbol{x}'; \omega)\}, \tag{2.14}$$

in which the integration is to be taken over all directions of $\boldsymbol{k}$. This relation will come to play a decisive part in the unified theory as a connection between the refractive index theory and the scattering theory: we show later that the theory is rigorously internally consistent in that the total scattering (integrated over all directions) agrees with the extinction calculated from the imaginary part of the refractive index.

To prove (2.14) we resolve the tensor in (2.12*a*) into irreducible parts

$$\mathbf{U} - \hat{\boldsymbol{k}}\hat{\boldsymbol{k}} = \tfrac{2}{3}\mathbf{U} - \tfrac{1}{3}(3\hat{\boldsymbol{k}}\hat{\boldsymbol{k}} - \mathbf{U}). \tag{2.15}$$

We evaluate the integral in (2.14) in polar coordinates with polar axis along $\boldsymbol{r} = \boldsymbol{x} - \boldsymbol{x}'$. The exponential is constant under integrations over the azimuthal angle:

$$\int \mathbf{S}(\boldsymbol{x}, \boldsymbol{x}'; \boldsymbol{k})\, \mathrm{d}\Omega = 2\pi\, k_0^2 \int_{-1}^{1} \exp\,(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})\, [\tfrac{2}{3}\mathbf{U}\, P_0(z) - \tfrac{1}{3}(3\hat{\boldsymbol{r}}\hat{\boldsymbol{r}} - \mathbf{U})\, P_2(z)]\, \mathrm{d}z \tag{2.16}$$

with $z = \hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{r}}$. By substituting the Rayleigh spherical wave expansion for the plane wave (Abramowitz & Stegun 1964)

$$\exp\,(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}) = \sum_{n=0}^{\infty} \mathrm{i}^n (2n+1)\, j_n(k_0 r)\, P_n(z), \tag{2.17}$$

into (2.16) and using the orthogonality of the Legendre polynomials P_n we find

$$\int \mathbf{S}(\boldsymbol{x}, \boldsymbol{x}'; \boldsymbol{k})\, \mathrm{d}\Omega = 4\pi\, k_0^2 [\tfrac{2}{3} j_0(k_0 r)\, \mathbf{U} + \tfrac{1}{3} j_2(k_0 r)\, (3\hat{\boldsymbol{r}}\hat{\boldsymbol{r}} - \mathbf{U})]. \tag{2.18}$$

Equation (2.14) now follows by comparing (2.18) with the form (2.2*c*) of $\mathbf{F}$, by using the relation

$$h_n^{(1)}(z) = j_n(z) + \mathrm{i} y_n(z) \tag{2.19}$$

between the spherical Hankel function of the first kind and order n and the corresponding spherical Bessel and Neumann functions $j_n(z)$ and $y_n(z)$, which are real for z real. We note that (2.14) is valid even for $\boldsymbol{x} = \boldsymbol{x}'$, and that it is consistent with the definition (2.6).

The flux of radiation analysed for polarization may be simplified because the radiator (2.12*b*) can be written as a dyadic product

$$\mathbf{S}(\boldsymbol{x}, \boldsymbol{x}'; \boldsymbol{k}, \boldsymbol{v}) = k_0^2\, \boldsymbol{e}^*(\boldsymbol{x}; \boldsymbol{k}, \boldsymbol{v})\, \boldsymbol{e}(\boldsymbol{x}'; \boldsymbol{k}, \boldsymbol{v}) \tag{2.20a}$$

in which

$$\boldsymbol{e}(\boldsymbol{x}; \boldsymbol{k}, \boldsymbol{v}) \equiv \boldsymbol{v} \exp\,(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}). \tag{2.20b}$$

In terms of $\boldsymbol{e}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})$ the flux of radiation takes the form

$$I(\boldsymbol{k},\boldsymbol{v}) = \frac{ck_0^4}{8\pi}\Big|\sum_j \boldsymbol{e}(\boldsymbol{x}_j;\boldsymbol{k},\boldsymbol{v})\cdot\boldsymbol{P}_j\Big|^2. \tag{2.21}$$

To simplify the notation when we come to deal with averaged quantities as well as instantaneous ones, it is convenient to reformulate the results of this section in terms of distributions of molecules and dipoles, which formally are continuous. At the same time we shall change the notation slightly by introducing a superscript 'in' for quantities depending on the instantaneous configuration of molecules, whereas, henceforth, the same symbol without superscript will denote the corresponding averaged quantity.

We introduce the instantaneous density of molecules and the instantaneous polarization as

$$n^{\text{in}}(\boldsymbol{x}) = \sum_j \delta(\boldsymbol{x}-\boldsymbol{x}_j^{\text{in}}) \tag{2.22}$$

and

$$\boldsymbol{P}^{\text{in}}(\boldsymbol{x},\omega) = \sum_j \boldsymbol{P}_j^{\text{in}}(\omega)\,\delta(\boldsymbol{x}-\boldsymbol{x}_j^{\text{in}}) \tag{2.23}$$

for a given configuration $\boldsymbol{x}_j^{\text{in}}$. We may then write (2.1) as

$$\mathscr{E}^{\text{in}}(\boldsymbol{x},\omega) = \boldsymbol{E}(\boldsymbol{x},\omega) + \int_V \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{P}^{\text{in}}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}', \tag{2.24}$$

where the integration extends over the region V containing the molecules ($\mathscr{E}^{\text{in}}(\boldsymbol{x},\omega)$ here is the same as $\mathscr{E}(\boldsymbol{x},\omega)$ of (2.1)). Similarly (2.5) becomes

$$\boldsymbol{P}^{\text{in}}(\boldsymbol{x},\omega) = n^{\text{in}}(\boldsymbol{x})\,\alpha(\omega)\,\Big[\boldsymbol{E}(\boldsymbol{x},\omega) + \int_V \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{P}^{\text{in}}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}'\Big], \tag{2.25}$$

and the definition (2.6) is now written

$$\int \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\,\delta(\boldsymbol{x}-\boldsymbol{x}')\,\mathrm{d}\boldsymbol{x}' = \tfrac{2}{3}\mathrm{i}k_0^3\,\mathsf{U}. \tag{2.26}$$

Equation (2.25) is the fundamental equation of classical molecular optics.

In terms of densities the flux of radiation $I^{\text{in}}(\boldsymbol{k})$ takes the form

$$I^{\text{in}}(\boldsymbol{k}) = \frac{ck_0^2}{8\pi}\int_V\int_V \boldsymbol{P}^{\text{in}}(\boldsymbol{x},\omega)^*\cdot\mathsf{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k})\cdot\boldsymbol{P}^{\text{in}}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{x}', \tag{2.27a}$$

and $I^{\text{in}}(\boldsymbol{k},\boldsymbol{v})$ for radiation analysed for polarization takes the same form with $\mathsf{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k})$ replaced by $\mathsf{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})$. Alternatively, we may use the form (2.21) to get

$$I^{\text{in}}(\boldsymbol{k},\boldsymbol{v}) = \frac{ck_0^4}{8\pi}\left|\int_V \boldsymbol{e}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})\cdot\boldsymbol{P}^{\text{in}}(\boldsymbol{x},\omega)\,\mathrm{d}\boldsymbol{x}\right|^2. \tag{2.27b}$$

The molecular response relation (2.4) may be written most simply in terms of densities as

$$\boldsymbol{P}^{\text{in}}(\boldsymbol{x},\omega) = n^{\text{in}}(\boldsymbol{x})\,\alpha(\omega)\,\mathscr{E}^{\text{in}}(\boldsymbol{x},\omega). \tag{2.28}$$

It will prove convenient, however, to write it in a more elaborate form,

$$\boldsymbol{P}^{\text{in}}(\boldsymbol{x},\omega) = \int_V \boldsymbol{\Pi}^{\text{in}}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\mathscr{E}^{\text{in}}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}' \tag{2.29}$$

in terms of a tensor kernel defined as

$$\boldsymbol{\Pi}^{\mathrm{in}}(\boldsymbol{x},\boldsymbol{x}';\omega) = n^{\mathrm{in}}(\boldsymbol{x})\,\alpha(\omega)\,\delta(\boldsymbol{x}-\boldsymbol{x}')\,\mathsf{U}. \tag{2.30}$$

We shall also need a 'polarization propagator' $\mathbf{J\!I}^{\mathrm{in}}(\boldsymbol{x},\boldsymbol{x}';\omega)$, related to $\boldsymbol{\Pi}^{\mathrm{in}}$, which gives the polarization $\boldsymbol{P}^{\mathrm{in}}$ in response to the external field $\boldsymbol{E}$:

$$\boldsymbol{P}^{\mathrm{in}}(\boldsymbol{x},\omega) = \int_V \mathbf{J\!I}^{\mathrm{in}}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{E}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}'. \tag{2.31}$$

Equation (2.25) shows that $\mathbf{J\!I}^{\mathrm{in}}$ satisfies the integral equation

$$\mathbf{J\!I}^{\mathrm{in}}(\boldsymbol{x},\boldsymbol{x}';\omega) = \boldsymbol{\Pi}^{\mathrm{in}}(\boldsymbol{x},\boldsymbol{x}';\omega)+\int_V\int_V \boldsymbol{\Pi}^{\mathrm{in}}(\boldsymbol{x},\boldsymbol{x}'';\omega)\cdot\mathsf{F}(\boldsymbol{x}'',\boldsymbol{x}''';\omega)\cdot\mathbf{J\!I}^{\mathrm{in}}(\boldsymbol{x}''',\boldsymbol{x}';\omega)\,\mathrm{d}\boldsymbol{x}''\,\mathrm{d}\boldsymbol{x}''' \tag{2.32}$$

since $\boldsymbol{E}$ is arbitrary.

In the following section we shall work from (2.24), (2.27), and (2.29) and treat the problem of finding expressions for the average polarization, $\boldsymbol{P}$, the average field, $\mathscr{E}$, and the average flux of radiation, I.

3. Macroscopic kernels and integral equations

Macroscopic electrodynamical quantities are average values. They are obtained by averaging over microstates compatible with a given macroscopic state. We assume that the molecules are contained in a region V of volume $|V|$, and that the temperature is given together with either the number of molecules or the chemical potential. Conceptually, the case of a fixed number of molecules is most appropriate to the physical situation of a finite material system surrounded by empty space, and the averages are therefore taken according to the canonical probability distribution. For practical reasons we shall employ the grand canonical ensemble in some specific cases, however. Since we are dealing with fluctuation phenomena in the light scattering theory, the choice of statistical ensemble is not obviously immaterial; we shall comment on the problem in III, when the need for the grand ensemble arises.

Within linear response theory the field probes the state of the unperturbed fluid. It is therefore appropriate to use the statistical properties of the unperturbed fluid in equilibrium. We shall assume that the temperature is sufficiently low so that we may neglect thermal electronic excitations of the molecules.

We consider average values of $\boldsymbol{P}^{\mathrm{in}}$, $\mathscr{E}^{\mathrm{in}}$, and I^{in}. These average fields are mutually related by integral expressions involving kernels that are average values. It is these 'macroscopic kernels' that we are really interested in. For they are related directly to usual macroscopic parameters (dielectric constants, refractive indices, and differential scattering cross sections) that determine the response of the system according to macroscopic optics.

The purpose of this section is to obtain explicit series representations for the macroscopic kernels and to derive a number of relations between them that will prove useful in later stages of the theory.

From the set of coupled equations (2.24), (2.29) in $\boldsymbol{P}^{\mathrm{in}}$ and $\mathscr{E}^{\mathrm{in}}$ we obtain a set of coupled equations for the averaged polarization $\boldsymbol{P}$ and the averaged electric field $\mathscr{E}$. Equation (2.24) yields immediately

$$\mathscr{E}(\boldsymbol{x},\omega) = \boldsymbol{E}(\boldsymbol{x},\omega)+\int_V \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{P}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}'. \tag{3.1a}$$

When we take the average value of (2.29) we do not get an expression in $\boldsymbol{P}$ and $\mathscr{E}$ because the right side contains a product of functions depending on the instantaneous configuration. However, there must exist a relation between $\boldsymbol{P}$ and $\mathscr{E}$ of the form

$$\boldsymbol{P}(\boldsymbol{x},\omega) = \int_V \boldsymbol{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\mathscr{E}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}', \tag{3.1 b}$$

and we shall now find the kernel $\boldsymbol{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega)$ and show that it involves an infinite sequence of terms, which we can describe as 'microscopic multiple scattering' processes. All the macroscopic kernels have series expressions of this character and the work of this section is concerned to derive these and to obtain the different sets of intermolecular correlation functions that are associated with each of them.

First we derive an integral equation for $\boldsymbol{\Lambda}$. To do this note first that (3.1 *a*) and (3.1 *b*) combine in

$$\mathscr{E}(\boldsymbol{x},\omega) = \boldsymbol{E}(\boldsymbol{x},\omega)+\int_V\int_V \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{\Lambda}(\boldsymbol{x}',\boldsymbol{x}'';\omega)\cdot\mathscr{E}(\boldsymbol{x}'',\omega)\,\mathrm{d}\boldsymbol{x}'\,\mathrm{d}\boldsymbol{x}''. \tag{3.2}$$

But there is already a complication in (3.1 *a*) since the integrand is singular at $\boldsymbol{x}' = \boldsymbol{x}$. We define the integral in the spirit of the theory of generalized functions by

$$\int_V \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{P}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}' = \lim_{v\to 0}\int_{V-v} \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{P}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}' - \tfrac{4}{3}\pi\,\boldsymbol{P}(\boldsymbol{x},\omega). \tag{3.3}$$

The integral on the right side is a principal value integral obtained by excluding a vanishingly small spherical region about $\boldsymbol{x}$ from the domain of integration. Formally, (3.3) is equivalent to defining

$$\lim_{v\to 0}\int_v \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\,\mathrm{d}\boldsymbol{x}' = -\tfrac{4}{3}\pi\,\mathsf{U}, \tag{3.4}$$

and this seems natural since the left side must be an isotropic second rank tensor while

$$\tfrac{1}{3}\mathrm{Tr}\left\{\nabla\nabla\frac{1}{|\boldsymbol{x}-\boldsymbol{x}'|}\right\}\mathsf{U} = -\tfrac{4}{3}\pi\,\mathsf{U}\delta(\boldsymbol{x}-\boldsymbol{x}'). \tag{3.5}$$

However, this means that (3.1 *a*) and (3.3) together form the *definition* of the average electric field $\mathscr{E}(\boldsymbol{x},\omega)$. We shall find that it has all the properties of the usual macroscopic Maxwell electric field inside or outside a dielectric medium.

It is consistent with (2.24) and (2.29) to define a configurational dependent kernel $\boldsymbol{\Lambda}^{\mathrm{in}}(\boldsymbol{x},\boldsymbol{x}';\omega)$ such that

$$\boldsymbol{P}^{\mathrm{in}}(\boldsymbol{x},\omega) = \int_V \boldsymbol{\Lambda}^{\mathrm{in}}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\mathscr{E}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}'. \tag{3.6}$$

Then (3.1 *b*) means that

$$\boldsymbol{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega) = \langle\boldsymbol{\Lambda}^{\mathrm{in}}(\boldsymbol{x},\boldsymbol{x}';\omega)\rangle, \tag{3.7}$$

where angular brackets denote an ensemble average.

To find $\boldsymbol{\Lambda}^{\mathrm{in}}$ and $\boldsymbol{\Lambda}$ we derive integral equations for them. To reach these we eliminate $\boldsymbol{E}$ between equations (2.24) and (3.1 *a*) to obtain

$$\mathscr{E}^{\mathrm{in}}(\boldsymbol{x},\omega) = \mathscr{E}(\boldsymbol{x},\omega)+\int_V \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot[\boldsymbol{P}^{\mathrm{in}}(\boldsymbol{x}',\omega)-\boldsymbol{P}(\boldsymbol{x}',\omega)]\,\mathrm{d}\boldsymbol{x}'. \tag{3.8}$$

This result is substituted in (2.29), and (3.1b) and (3.6) for $\boldsymbol{P}$ and $\boldsymbol{P}^{\text{in}}$ are used to express the result solely in terms of $\mathscr{E}$ and the kernels. Since $\mathscr{E}$ must be arbitrary, because $\boldsymbol{E}$ is, we reach the integral equation for $\boldsymbol{\Lambda}^{\text{in}}$,

$$\boldsymbol{\Lambda}^{\text{in}}_{10} = \boldsymbol{\Pi}^{\text{in}}_{10} + \int_V\int_V \boldsymbol{\Pi}^{\text{in}}_{12}\cdot\mathsf{F}_{23}\cdot(\boldsymbol{\Lambda}^{\text{in}}_{30}-\boldsymbol{\Lambda}_{30})\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3. \tag{3.9}$$

We have adopted a subscript notation for positional variables; thus $\boldsymbol{\Lambda}_{30}$ means $\boldsymbol{\Lambda}(\boldsymbol{x}_3,\boldsymbol{x}_0;\omega)$ for example.

Equation (3.1b) shows that the kernel $\boldsymbol{\Lambda}$ is a (generalized) macroscopic susceptibility. To derive a series expression for it we first relate it to the polarization propagator $\mathbf{J\!I}$. By comparing (3.6) and (2.31) and expressing $\boldsymbol{E}$ in terms of $\mathscr{E}$ by means of (3.2) we find

$$\boldsymbol{\Lambda}^{\text{in}}_{10} = \mathbf{J\!I}^{\text{in}}_{10} - \int_V\int_V \mathbf{J\!I}^{\text{in}}_{12}\cdot\mathsf{F}_{23}\cdot\boldsymbol{\Lambda}_{30}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3 \tag{3.10}$$

so

$$\boldsymbol{\Lambda}_{10} = \mathbf{J\!I}_{10} - \int_V\int_V \mathbf{J\!I}_{12}\cdot\mathsf{F}_{23}\cdot\boldsymbol{\Lambda}_{30}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3. \tag{3.11}$$

This is the required integral equation for $\boldsymbol{\Lambda}$ itself but it depends on $\mathbf{J\!I}$.

Series expressions for $\mathbf{J\!I}^{\text{in}}$ and $\mathbf{J\!I}$ can be obtained by straightforward iteration of (2.32):

$$\mathbf{J\!I}^{\text{in}}_{10} = n^{\text{in}}_1\alpha\,\mathsf{U}\delta_{10} + \sum_{p=1}^{\infty}\alpha^{p+1}\int_V\cdots\int_V \mathsf{F}_{12}\cdot\mathsf{F}_{23}\cdots\mathsf{F}_{p0}\,n^{\text{in}}_1 n^{\text{in}}_2\cdots n^{\text{in}}_0\,\mathrm{d}\boldsymbol{x}_2\cdots\mathrm{d}\boldsymbol{x}_p, \tag{3.12}$$

$$\mathbf{J\!I}_{10} = n\alpha\,\mathsf{U}\delta_{10} + \sum_{p=1}^{\infty}(n\alpha)^{p+1}\int_V\cdots\int_V \mathsf{F}_{12}\cdot\mathsf{F}_{23}\cdots\mathsf{F}_{p0}\,G_{123\ldots p0}\,\mathrm{d}\boldsymbol{x}_2\cdots\mathrm{d}\boldsymbol{x}_p. \tag{3.13}$$

Here $n^{\text{in}}_j = n^{\text{in}}(\boldsymbol{x}_j)$ is the instantaneous density of molecules (2.22) (and observe $\boldsymbol{x}_j$ is a variable of integration, not a molecular site $\boldsymbol{x}^{\text{in}}_j$), $\delta_{10} = \delta(\boldsymbol{x}_1-\boldsymbol{x}_0)$ is a delta function, and

$$G_{123\ldots q} = n^{-q}\langle n^{\text{in}}(\boldsymbol{x}_1)\,n^{\text{in}}(\boldsymbol{x}_2)\ldots n^{\text{in}}(\boldsymbol{x}_q)\rangle \tag{3.14}$$

is a q-particle correlation function generalized to contain self-correlations (see, for example, Stell 1964)

$$\left.\begin{aligned} G_1 &= 1,\\ G_{12} &= g_{12}+n^{-1}\delta_{12},\\ G_{123} &= g_{123}+n^{-1}(\delta_{12}g_{23}+\delta_{23}g_{31}+\delta_{31}g_{12})+n^{-2}\delta_{12}\delta_{23};\end{aligned}\right\} \tag{3.15}$$

the terms g are the usual correlation functions (Hill 1956). Subsequently we call $G_{123\ldots q}$ as well as $\mathscr{G}_{123\ldots q} = n^q G_{123\ldots q}$ distribution functions to distinguish them from other correlation functions. Note that the first term in the sum in (3.13) (that involving $p=1$) is not integrated. This is to be understood similarly in all equations of the same structure we derive later.

The iterated solution of (3.11) is

$$\begin{aligned}\boldsymbol{\Lambda}_{10} = \mathbf{J\!I}_{10} &- \int_V\int_V \mathbf{J\!I}_{12}\cdot\mathsf{F}_{23}\cdot\mathbf{J\!I}_{30}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3\\ &+ \int_V\int_V\int_V\int_V \mathbf{J\!I}_{12}\cdot\mathsf{F}_{23}\cdot\mathbf{J\!I}_{34}\cdot\mathsf{F}_{45}\cdot\mathbf{J\!I}_{50}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3\,\mathrm{d}\boldsymbol{x}_4\,\mathrm{d}\boldsymbol{x}_5+\ldots.\end{aligned} \tag{3.16}$$

If the series (3.13) for $\mathbf{JI}$ is inserted and the terms in powers of $n\alpha$ are collected together at each order we readily find

$$\boldsymbol{\Lambda}_{10} = n\alpha\, \mathbf{\mathsf{U}}\delta_{10} + \sum_{p=1}^{\infty} (n\alpha)^{p+1} \int_V \cdots \int_V \mathbf{\mathsf{F}}_{12} \cdot \mathbf{\mathsf{F}}_{23} \ldots \mathbf{\mathsf{F}}_{p0}\, H_{123\ldots p0}\, \mathrm{d}\boldsymbol{x}_2 \ldots \mathrm{d}\boldsymbol{x}_p, \qquad (3.17)$$

and this is the series for $\boldsymbol{\Lambda}$ that involves an infinite series of microscopic multiple scattering processes. Later we shall introduce a diagrammatic notation for successive multiple scattering terms, but this is not necessary here.

In the series (3.17) the correlation functions H are defined by

$$H_{123\ldots q} = \sum_{j=0}^{q} (-1)^j \sum_{\{i\}} G_{123\ldots i_1} G_{(i_1+1)\ldots i_2} \cdots G_{(i_j+1)\ldots q}, \qquad (3.18a)$$

$$\{i\} = \{i_1, i_2, \ldots, i_j\}, \quad 1 \leqslant i_1 < \ldots < i_j < q, \quad q \geqslant 2. \qquad (3.18b)$$

In (3.18*a*) the sum is taken over all different sets of integers (3.18*b*). For $j = 0$ there is only the empty set, and the corresponding term is $G_{123\ldots q}$.

We have now determined the kernel $\boldsymbol{\Lambda}$ and hence the relation (3.1*b*) between $\boldsymbol{P}$ and $\boldsymbol{\mathcal{E}}$. This relation is evidently the appropriate one for obtaining a susceptibility or a dielectric constant ϵ. But it is not suited for obtaining the refractive index, m, despite the simple macroscopic relation $\epsilon = m^2$ that connects the two quantities. The reason is that while the susceptibility can be defined as a ratio of amplitudes of $\boldsymbol{P}$ and $\boldsymbol{\mathcal{E}}$, the refractive index is defined as a ratio of wavenumbers of fields in the medium and in empty space. The refractive index theory must therefore be developed separately, and the macroscopic relation $\epsilon = m^2$ will then emerge as a *result* of the microscopic theory.

In the argument involving the extinction theorem, which we shall give in §§5, 6 to obtain a refractive index it would be inconvenient to have the field $\boldsymbol{\mathcal{E}}$ inside an integral as in (3.1*b*). We therefore now introduce an alternative relation between $\boldsymbol{P}$ and $\boldsymbol{\mathcal{E}}$,

$$\boldsymbol{P}(\boldsymbol{x}, \omega) = n\alpha(\omega)\, \boldsymbol{\mathcal{E}}(\boldsymbol{x}, \omega) + \int_V \boldsymbol{\Gamma}(\boldsymbol{x}, \boldsymbol{x}'; \omega) \cdot \boldsymbol{P}(\boldsymbol{x}', \omega)\, \mathrm{d}\boldsymbol{x}' \qquad (3.19)$$

to replace (3.1*b*) in the refractive index theory. To derive this equation and obtain $\boldsymbol{\Gamma}$ we note that $\boldsymbol{P}$ satisfies an equation of the form

$$\boldsymbol{P}(\boldsymbol{x}, \omega) = n\alpha(\omega)\, \boldsymbol{E}(\boldsymbol{x}, \omega) + \int_V \mathbf{\mathsf{C}}(\boldsymbol{x}, \boldsymbol{x}'; \omega) \cdot \boldsymbol{P}(\boldsymbol{x}', \omega)\, \mathrm{d}\boldsymbol{x}', \qquad (3.20)$$

in which the auxilliary kernel $\mathbf{\mathsf{C}}$ is still to be determined. Equations (3.1*a*), (3.19) and (3.20) show that $\boldsymbol{\Gamma}$ is simply related to $\mathbf{\mathsf{C}}$:

$$\boldsymbol{\Gamma}(\boldsymbol{x}, \boldsymbol{x}'; \omega) = \mathbf{\mathsf{C}}(\boldsymbol{x}, \boldsymbol{x}'; \omega) - n\alpha(\omega)\, \mathbf{\mathsf{F}}(\boldsymbol{x}, \boldsymbol{x}'; \omega). \qquad (3.21)$$

On the other hand, equations (3.20) and the average of (2.31) show that $\mathbf{\mathsf{C}}$ is related to $\mathbf{JI}$ as

$$\mathbf{JI}_{10} = \boldsymbol{\Pi}_{10} + \int_V \mathbf{\mathsf{C}}_{12} \cdot \mathbf{JI}_{20}\, \mathrm{d}\boldsymbol{x}_2. \qquad (3.22)$$

This result can be rewritten

$$\mathbf{\mathsf{C}}_{10} = \mathbf{JI}'_{10} - \int_V \mathbf{\mathsf{C}}_{12} \cdot \mathbf{JI}'_{20}\, \mathrm{d}\boldsymbol{x}_2 \qquad (3.23)$$

in which the dimensionless kernel

$$\textbf{Л}'(\boldsymbol{x},\boldsymbol{x}';\omega) = (n\alpha)^{-1}[\textbf{Л}(\boldsymbol{x},\boldsymbol{x}';\omega)-\mathbf{\Pi}(\boldsymbol{x},\boldsymbol{x}';\omega)] \tag{3.24}$$

is given by the expansion (3.13) multiplied by $(n\alpha)^{-1}$, with the first term omitted. The iterative solution of (3.23), namely

$$\mathsf{C}_{10} = \textbf{Л}'_{10}-\int_V \textbf{Л}'_{12}\cdot\textbf{Л}'_{20}\,\mathrm{d}\boldsymbol{x}_2+\int_V\int_V \textbf{Л}'_{12}\cdot\textbf{Л}'_{23}\cdot\textbf{Л}'_{30}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3+\ldots \tag{3.25}$$

then immediately provides the series expansion of $\mathbf{\Gamma}$:

$$\mathbf{\Gamma}_{10} = \sum_{p=1}^{\infty}(n\alpha)^p\int_V\ldots\int_V \mathsf{F}_{12}\cdot\mathsf{F}_{23}\ldots\mathsf{F}_{p0}\,C_{123\ldots p0}\,\mathrm{d}\boldsymbol{x}_2\ldots\mathrm{d}\boldsymbol{x}_p, \tag{3.26}$$

in which the correlation functions C are defined as

$$\left.\begin{aligned} C_{123\ldots q} &= \sum_{j=0}^{q-1}(-1)^j\sum_{\{i\}}G_{123\ldots i_1}G_{i_1\ldots i_2}\ldots G_{i_j\ldots q},\\ \{i\} &= \{i_1,i_2,\ldots,i_j\},\quad 1<i_1<i_2<\ldots<i_j<q,\quad q\geqslant 3.\end{aligned}\right\} \tag{3.27}$$

The first few functions H and C are

$$\left.\begin{aligned} H_{12} &= G_{12}-1,\\ H_{123} &= G_{123}-G_{12}-G_{23}+1,\\ H_{1234} &= G_{1234}-G_{123}-G_{234}-G_{12}G_{34}+G_{12}+G_{23}+G_{34}-1\end{aligned}\right\} \tag{3.28}$$

and

$$\left.\begin{aligned} C_{12} &= G_{12}-1,\\ C_{123} &= G_{123}-G_{12}G_{23},\\ C_{1234} &= G_{1234}-G_{123}G_{34}-G_{12}G_{234}+G_{12}G_{23}G_{34}.\end{aligned}\right\} \tag{3.29}$$

The kernels $\mathbf{\Lambda}$ and $\mathbf{\Gamma}$ are related by

$$\mathbf{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega) = \mathbf{\Pi}(\boldsymbol{x},\boldsymbol{x}';\omega)+\int_V\mathbf{\Gamma}(\boldsymbol{x},\boldsymbol{x}'';\omega)\cdot\mathbf{\Lambda}(\boldsymbol{x}'',\boldsymbol{x}';\omega)\,\mathrm{d}\boldsymbol{x}'', \tag{3.30}$$

as can be seen by substituting (3.1*b*) into (3.19); $\mathscr{E}$ is considered arbitrary. The relation (3.30) connects the dielectric constant theory and the refractive index theory, as we shall see in §5.

We now consider scattering. From (2.27) we obtain the energy flux of incoherent scattering per unit solid angle in the direction of $\boldsymbol{k}$,

$$J(\boldsymbol{k},\boldsymbol{v}) = \frac{ck_0^2}{8\pi}\int_V\int_V\langle(\Delta\boldsymbol{P}^{\mathrm{in}}(\boldsymbol{x},\omega))^*\cdot\mathsf{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})\cdot\Delta\boldsymbol{P}^{\mathrm{in}}(\boldsymbol{x}',\omega)\rangle\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{x}'. \tag{3.31}$$

This is the average value of $I^{\mathrm{in}}(\boldsymbol{k},\boldsymbol{v})$ minus the spatially coherent scattering obtained by replacing $\boldsymbol{P}^{\mathrm{in}}(\boldsymbol{x},\omega)$ by $\boldsymbol{P}(\boldsymbol{x},\omega)$ in (2.27) ($\Delta\boldsymbol{P}^{\mathrm{in}}$ denotes $\boldsymbol{P}^{\mathrm{in}}-\boldsymbol{P}$).

We express $J(\boldsymbol{k},\boldsymbol{v})$ as a quadratic form in $\mathscr{E}$:

$$J(\boldsymbol{k},\boldsymbol{v}) = \frac{ck_0^2}{8\pi}\int_V\int_V\mathscr{E}^*(\boldsymbol{x},\omega)\cdot\boldsymbol{\sigma}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})\cdot\mathscr{E}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{x}', \tag{3.32}$$

in which we have used (3.1 *b*) and (3.6) and introduced the scattering kernels

$$\boldsymbol{\sigma}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}) = \int_V \int_V \langle (\Delta\boldsymbol{\Lambda}^{\mathrm{in}}(\boldsymbol{x},\boldsymbol{x}'';\omega))^{\dagger}\cdot\mathbf{S}(\boldsymbol{x}'',\boldsymbol{x}''';\boldsymbol{k},\boldsymbol{v})\cdot\Delta\boldsymbol{\Lambda}^{\mathrm{in}}(\boldsymbol{x}''',\boldsymbol{x}';\omega)\rangle\,\mathrm{d}\boldsymbol{x}''\,\mathrm{d}\boldsymbol{x}'''. \tag{3.33a}$$

$$\boldsymbol{\sigma}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k}) = \sum_{j=1,2} \boldsymbol{\sigma}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}_j), \tag{3.33b}$$

with $\Delta\boldsymbol{\Lambda}^{\mathrm{in}} \equiv \boldsymbol{\Lambda}^{\mathrm{in}}-\boldsymbol{\Lambda}$. The superscript † in the expression for $\boldsymbol{\sigma}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})$ is used to denote a hermitian conjugate and the same notation will be used for any tensor kernel throughout these papers. Thus, for any tensor kernel $\mathbf{T}(\boldsymbol{x},\boldsymbol{x}')$, $(T_{ij}(\boldsymbol{x},\boldsymbol{x}'))^{\dagger} = T^{*}_{ji}(\boldsymbol{x}',\boldsymbol{x})$ with $*$ the complex conjugate.

The form (3.33 *b*) applies to scattering not analysed for polarization. The kernels $\boldsymbol{\sigma}$ of (3.33 *a*, *b*) are closely related to the susceptibility kernel $\boldsymbol{\Lambda}$; $\boldsymbol{\sigma}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})$ has the series expansion

$$\boldsymbol{\sigma}_{10} = \sum_{p=1}^{\infty} (n\alpha)^{p+1} \int_V \cdots \int_V \mathfrak{S}\{\mathbf{F}_{12}\cdot\mathbf{F}_{23}\ldots\mathbf{F}_{p0}\}\, H_{123\ldots p0}\,\mathrm{d}\boldsymbol{x}_2\ldots\mathrm{d}\boldsymbol{x}_p, \tag{3.34}$$

where we have introduced the notation

$$\mathfrak{S}\{\mathbf{F}_{12}\cdot\mathbf{F}_{23}\ldots\mathbf{F}_{p0}\} = \sum_{q=1}^{p} \mathbf{F}^{*}_{12}\cdot\mathbf{F}^{*}_{23}\ldots\mathbf{F}^{*}_{(q-1)\,q}\cdot\mathbf{S}_{q(q+1)}\cdot\mathbf{F}_{(q+1)\,(q+2)}\ldots\mathbf{F}_{p0}. \tag{3.35}$$

In (3.35) index $p+1$ is to be interpreted as index 0. Thus, $\mathfrak{S}\{\mathbf{F}_{12}\cdot\mathbf{F}_{20}\} = \mathbf{S}_{12}\cdot\mathbf{F}_{20}+\mathbf{F}^{*}_{12}\cdot\mathbf{S}_{20}$, for example.

The structure of the series expansion (3.34) is evidently correct, and we need only establish the form of the correlation functions. We work from (3.33) and substitute the series for $\Delta\boldsymbol{\Lambda}^{\mathrm{in}}$ and $\Delta\boldsymbol{\Lambda}^{\mathrm{in}\dagger}$. The series representation of $\boldsymbol{\Lambda}^{\mathrm{in}}$ is (3.17) with the functions H replaced by configurational dependent functions H^{in} determined by the recurrence relation

$$H^{\mathrm{in}}_{123\ldots p} = n^{\mathrm{in}}_{1}(H^{\mathrm{in}}_{23\ldots p}-H_{23\ldots p}) = n^{\mathrm{in}}_{1}\Delta H^{\mathrm{in}}_{23\ldots p}, \tag{3.36}$$

with $H^{\mathrm{in}}_{1} = n^{\mathrm{in}}_{1}$. This is obtained from the integral equation (3.9). Similarly, the hermitian conjugate kernel $\boldsymbol{\Lambda}^{\mathrm{in}\dagger}$ has an expansion given by the complex conjugate of (3.17) with the functions H replaced by configurational dependent functions

$$H^{\mathrm{in}\dagger}_{123\ldots(p-1)\,p} \equiv H^{\mathrm{in}}_{p(p-1)\ldots 321}. \tag{3.37}$$

(The tensor kernel $\mathbf{F}$ is symmetrical, and the functions H^{in} are real.) Hence, the functions $H^{\mathrm{in}\dagger}$ satisfy the recurrence relation

$$H^{\mathrm{in}\dagger}_{123\ldots p} = \Delta H^{\mathrm{in}\dagger}_{123\ldots(p-1)}\, n^{\mathrm{in}}_{p}, \tag{3.38}$$

with $H^{\mathrm{in}\dagger}_{1} = n^{\mathrm{in}}_{1}$.

We now determine the combination of correlation functions appearing in the q'th term at order $p+1$ of the expansion of (3.33). It is

$$\begin{aligned}\langle \Delta H^{\mathrm{in}\dagger}_{1\ldots q}\,\Delta H^{\mathrm{in}}_{(q+1)\ldots p0}\rangle &= \langle H^{\mathrm{in}\dagger}_{1\ldots q}\,\Delta H^{\mathrm{in}}_{(q+1)\ldots p0}\rangle \\ &= \langle \Delta H^{\mathrm{in}\dagger}_{1\ldots(q-1)}\, n^{\mathrm{in}}_{q}\Delta H^{\mathrm{in}}_{(q+1)\ldots p0}\rangle = \langle \Delta H^{\mathrm{in}\dagger}_{1\ldots(q-1)}\, H^{\mathrm{in}}_{q\ldots p0}\rangle = \langle \Delta H^{\mathrm{in}\dagger}_{1\ldots(q-1)}\,\Delta H^{\mathrm{in}}_{q\ldots p0}\rangle \\ &= \ldots = \langle (n^{\mathrm{in}}_{1}-n)^{\dagger}\Delta H^{\mathrm{in}}_{23\ldots p0}\rangle = H_{123\ldots p0}.\end{aligned} \tag{3.39}$$

This completes the proof of (3.34).

Notice that the result (3.39) is independent of q: all terms of (3.34) at a given order in $n\alpha$ contain the same correlation function, an H function (3.18). Moreover, this correlation function is *identical* with the one in the term at the same order of the series expansion (3.17) of $\boldsymbol{\Lambda}$. This result suggests that the scattering kernel $\boldsymbol{\sigma}$ is related to the susceptibility kernel $\boldsymbol{\Lambda}$. We shall demonstrate what this means in physical terms once we have noted some properties of the H functions.

It is easy to verify that the recurrence relation (3.36) has indeed the averaged solution (3.18). We may formally write

$$H^{\text{in}}_{123\ldots p} = n^{\text{in}}_1(n^{\text{in}}_2 - \langle n^{\text{in}}_2)\,(n^{\text{in}}_3 - \langle n^{\text{in}}_3)\ldots(n^{\text{in}}_p - \langle n^{\text{in}}_p), \tag{3.40}$$

in terms of a linear averaging operator $\langle$, which acts on everything to the right. To obtain $H_{123\ldots p}$ explicitly, expand the product (3.40) and complete the angular brackets by adding the proper number of brackets $\rangle$ to the right of each term.

We note that $H_{123\ldots p}$ is invariant under reversal of the order of the variables, so $\boldsymbol{\Lambda}$ is symmetrical as a tensor kernel (i.e. in the variables and tensor indices combined). It therefore defines a self-adjoint integral operator as do $\mathbf{F}$, $\boldsymbol{\Pi}^{\text{in}}$, and $\mathfrak{J}^{\text{in}}$, but not $\boldsymbol{\Lambda}^{\text{in}}$. This means that the hermitian conjugate of $\boldsymbol{\Lambda}$ equals its complex conjugate, whereas $\boldsymbol{\Pi}^{\text{in}}$ is hermitian.

It is useful to generalize the notation (3.35) by treating $\mathfrak{S}$ as a linear operator. In this way it may be taken outside the integrations and the summation in (3.34), and this relation may then be written very compactly,

$$\boldsymbol{\sigma}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}) = \mathfrak{S}\{\boldsymbol{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega)\}. \tag{3.41}$$

The image under $\mathfrak{S}$ of a term without $\mathbf{F}$ tensors vanishes by definition. It is important in (3.41) that radiation reaction is retained as a result of self-correlations in $\boldsymbol{\Lambda}$: a self-correlation $\delta(\boldsymbol{x}_j - \boldsymbol{x}_{j+1})$ produces a scattering term in $\mathbf{S}_{jj}$ in the term $q = j$ of the sum (3.35).

The formal relation (3.41) implies the physically important relation

$$\int \boldsymbol{\sigma}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k})\,\mathrm{d}\Omega = 4\pi\,k_0^{-1}\,\mathrm{Im}\,\{\boldsymbol{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega)\}, \tag{3.42}$$

in which the integration is over all directions of $\boldsymbol{k}$. To prove (3.42) we need a generalization of the Bohr–Peierls–Placzek relation (2.14)

$$\int \sum_{v_1,\,v_2} \mathfrak{S}\{\mathbf{F}_{12}\cdot\mathbf{F}_{23}\ldots\mathbf{F}_{p0}\}\,\mathrm{d}\Omega = 4\pi\,k_0^{-1}\,\mathrm{Im}\,\{\mathbf{F}_{12}\cdot\mathbf{F}_{23}\ldots\mathbf{F}_{p0}\}. \tag{3.43}$$

The sum in (3.43) is taken over two orthogonal polarization vectors orthogonal to $\boldsymbol{k}$. Equation (3.43) is verified by direct evaluation of the left side by using (2.14) and (3.35):

$$4\pi\,k_0^{-1}\sum_{q=1}^{p}(\mathbf{F}'_{12} - \mathrm{i}\mathbf{F}''_{12})\ldots\mathbf{F}''_{q(q+1)}\ldots(\mathbf{F}'_{p0} + \mathrm{i}\mathbf{F}''_{p0}). \tag{3.44}$$

We have denoted the real and imaginary parts of $\mathbf{F}$ by $\mathbf{F}'$ and $\mathbf{F}''$ respectively. The sum in (3.44) contains j terms with j imaginary parts in given positions $s_1, s_2, \ldots, s_j$, since any of the factors $\mathbf{F}''$ can originate in $\mathbf{S}_{q(q+1)}$. The term with $q = s_r$ has a factor $(-\mathrm{i})^{r-1}\,\mathrm{i}^{j-r} = (-1)^{r-1}\,\mathrm{i}^{j-1}$, but otherwise the j terms are equal. The sum of the j terms therefore vanishes if j is even and equals the first term of the sum (with $q = s_1$) if j is odd. So we get precisely one term with imaginary parts in positions $s_1, s_2, \ldots, s_j$ (for j odd); it appears with sign $(-1)^{\frac{1}{2}(j-1)}$, and evidently, the sum in (3.44) contains all distributions $\{s\}$. This proves (3.43).

We now complete the proof of (3.42) by summing (3.41) over polarizations and integrating over all directions of $\boldsymbol{k}$: the relation (3.42) then follows from (3.43) by using the linearity of the operator $\mathfrak{S}$ and of the imaginary part operator. The result (3.42) itself evidently has the form of a Bohr–Peierls–Placzek relation. It provides a link between the theory of scattering (through $\boldsymbol{\sigma}$) and the theory of the complex refractive index (through $\mathrm{Im}\{\Lambda\}$). It is an exact result and demonstrates the internal consistency of the theory.

This completes the structural ground work of the ensemble averaged theory. But to handle the intricate surface effects with physical insight we need still more powerful machinery. This we develop in §4.

4. Screened propagators

The susceptibility kernel $\boldsymbol{\Lambda}$ and the scattering kernel $\boldsymbol{\sigma}$ both depend on the geometry of the region V, as scrutiny of (3.17) and (3.34) will show. Whereas $\boldsymbol{\Lambda}$ depends rather weakly on V, the dependence is quite strong for $\boldsymbol{\sigma}$: this fact expresses a surface dependence of the scattering, which we shall come to exhibit as refraction and reflection of the scattered light at the surface of the sample. It is therefore imperative to develop the kernels so as to isolate the surface dependence.

The processes that transform $\boldsymbol{E}$ into $\mathscr{E}$, $\boldsymbol{P}$ or J may be described as a series of microscopic multiple scattering processes, as we have already said. These involve alternating polarizations of molecules by fields and propagation of fields emitted from induced dipoles. In these processes, fields propagate in empty space and molecules are polarized as isolated molecules.

It is natural to ask if there exists a more economical description in terms of composite processes such as propagation of electromagnetic fields in the material medium. Such composite processes must themselves be describable in terms of microscopic multiple scattering processes taking place in vacuum. It is such a formulation we shall give in this section; it will provide the tools for the solution of the problem of the surface dependence of $\boldsymbol{\Lambda}$ and $\boldsymbol{\sigma}$.

Consider again the molecular system in a fixed configuration $\boldsymbol{x}_j^{\text{in}}$, and choose for the present argument the field from an oscillatory dipole $\boldsymbol{P}(\omega)$ at $\boldsymbol{x}'$ as the external field $\boldsymbol{E}(\boldsymbol{x},\omega)$ in (2.24). The dipole is not considered part of the molecular system; it is a dipole probe and admittedly somewhat unphysical. But it is used here merely to justify the introduction of certain propagators in the theory. These propagators, as well as the entire theory, are well defined and totally independent of dipole probes, and we can forget about these probes as soon as they have motivated the introduction of the propagators.

So consider (2.24) and let $\boldsymbol{E}(\boldsymbol{x},\omega) = \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{P}(\omega)$ temporarily. The total field from the dipole $\boldsymbol{P}(\omega)$ in the presence of all the molecules is then the $\mathscr{E}^{\text{in}}$ of (2.24). We express this field as $\mathscr{F}^{\text{in}}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{P}(\omega)$, which defines the propagator $\mathscr{F}^{\text{in}}$. From (2.24) we then find the equation for $\mathscr{F}^{\text{in}}$,

$$\mathscr{F}^{\text{in}}_{10} = \mathsf{F}_{10} + \int_V\int_V \mathsf{F}_{12}\cdot\boldsymbol{\Pi}^{\text{in}}_{23}\cdot\mathscr{F}^{\text{in}}_{30}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3 \tag{4.1}$$

by use of (2.29).

To find an integral equation for $\mathscr{F}$, the average of $\mathscr{F}^{\text{in}}$, we first note that $\mathscr{F}^{\text{in}}$ satisfies the equation

$$\mathscr{F}^{\text{in}}_{10} = \mathsf{F}_{10} + \int_V\int_V \mathsf{F}_{12}\cdot\boldsymbol{\Lambda}^{\text{in}}_{23}\cdot\mathscr{F}_{30}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3, \tag{4.2}$$

since this evidently has a solution and any solution of it satisfies (4.1). This can be seen by substituting (3.9) for $\boldsymbol{\Lambda}^{\text{in}}$ in (4.2) and by using (4.2) itself, and the average of it. Since $\mathscr{F}^{\text{in}}$

can be assumed to be uniquely determined by (4.1), it is uniquely determined by (4.2) as well, and by taking the average value we then obtain the integral equation for $\mathscr{F}$, the screened photon propagator.

$$\mathscr{F}_{10} = \mathbf{F}_{10} + \int_V \int_V \mathbf{F}_{12} \cdot \boldsymbol{\Lambda}_{23} \cdot \mathscr{F}_{30} \, \mathrm{d}\boldsymbol{x}_2 \, \mathrm{d}\boldsymbol{x}_3. \tag{4.3}$$

Now to derive an integral equation for $\boldsymbol{\Lambda}^{\mathrm{in}}$ in terms of $\mathscr{F}$ we first note the relations

$$\int_V \boldsymbol{\Lambda}^{\mathrm{in}}_{12} \cdot \mathscr{F}_{20} \, \mathrm{d}\boldsymbol{x}_2 = \int_V \boldsymbol{\Pi}^{\mathrm{in}}_{12} \cdot \mathscr{F}^{\mathrm{in}}_{20} \, \mathrm{d}\boldsymbol{x}_2 = \int_V \boldsymbol{\varPi}^{\mathrm{in}}_{12} \cdot \mathbf{F}_{20} \, \mathrm{d}\boldsymbol{x}_2. \tag{4.4}$$

The first one follows by multiplying (3.9) by $\mathscr{F}$ from the right, integrating, and using (4.2) and (4.3). The second relation is verified by noting that the two sides satisfy the same linear homogeneous integral equation: compare (4.1) and (2.32) after multiplication by $\boldsymbol{\Pi}^{\mathrm{in}}$ from the left, and by $\mathbf{F}$ from the right, respectively, followed by integration.

We rewrite (2.32) as

$$\boldsymbol{\varPi}^{\mathrm{in}}_{10} = \boldsymbol{\Pi}^{\mathrm{in}}_{10} + \int_V \int_V \boldsymbol{\varPi}^{\mathrm{in}}_{12} \cdot \mathbf{F}_{23} \cdot \boldsymbol{\Pi}^{\mathrm{in}}_{30} \, \mathrm{d}\boldsymbol{x}_2 \, \mathrm{d}\boldsymbol{x}_3 \tag{4.5}$$

and use (4.4) to rewrite it still further as

$$\boldsymbol{\varPi}^{\mathrm{in}}_{10} = \boldsymbol{\Pi}^{\mathrm{in}}_{10} + \int_V \int_V \boldsymbol{\Lambda}^{\mathrm{in}}_{12} \cdot \mathscr{F}_{23} \cdot \boldsymbol{\Pi}^{\mathrm{in}}_{30} \, \mathrm{d}\boldsymbol{x}_2 \, \mathrm{d}\boldsymbol{x}_3. \tag{4.6}$$

By using (4.4) again we may rewrite (3.10) as

$$\boldsymbol{\Lambda}^{\mathrm{in}}_{10} = \boldsymbol{\varPi}^{\mathrm{in}}_{10} - \int_V \int_V \boldsymbol{\Lambda}^{\mathrm{in}}_{12} \cdot \mathscr{F}_{23} \cdot \boldsymbol{\Lambda}_{30} \, \mathrm{d}\boldsymbol{x}_2 \, \mathrm{d}\boldsymbol{x}_3. \tag{4.7}$$

Substitution of (4.6) for $\boldsymbol{\varPi}^{\mathrm{in}}$ in (4.7) then yields the desired integral equation for $\boldsymbol{\Lambda}^{\mathrm{in}}$:

$$\boldsymbol{\Lambda}^{\mathrm{in}}_{10} = \boldsymbol{\Pi}^{\mathrm{in}}_{10} + \int_V \int_V \boldsymbol{\Lambda}^{\mathrm{in}}_{12} \cdot \mathscr{F}_{23} \cdot (\boldsymbol{\Pi}^{\mathrm{in}}_{30} - \boldsymbol{\Lambda}_{30}) \, \mathrm{d}\boldsymbol{x}_2 \, \mathrm{d}\boldsymbol{x}_3. \tag{4.8}$$

We also note the average of (4.7),

$$\boldsymbol{\Lambda}_{10} = \boldsymbol{\varPi}_{10} - \int_V \int_V \boldsymbol{\Lambda}_{12} \cdot \mathscr{F}_{23} \cdot \boldsymbol{\Lambda}_{30} \, \mathrm{d}\boldsymbol{x}_2 \, \mathrm{d}\boldsymbol{x}_3, \tag{4.9}$$

which we shall use in II.

The averaged solution to the nonlinear integral equations (4.8) has the form

$$\boldsymbol{\Lambda}_{10} = n\alpha \mathbf{U} \delta_{10} + \sum_{p=1}^{\infty} (n\alpha)^{p+1} \int_V \dots \int_V \mathscr{F}_{12} \cdot \mathscr{F}_{23} \dots \mathscr{F}_{p0} \, Y_{123\dots p0} \, \mathrm{d}\boldsymbol{x}_2 \dots \mathrm{d}\boldsymbol{x}_p. \tag{4.10}$$

We shall call a formulation of the theory in terms of $\mathscr{F}$ the 'screened' theory, and we refer to (4.10) as the 'screened series' in contradistinction to the corresponding unscreened formulation presented in §3. The functions $Y_{123\dots p0}$ can be expressed explicitly in terms of generalized Ursell functions (Hynne 1970, 1975),

$$Y_{123\dots p} = \sum_{\kappa \in \mathscr{C}_p} \prod_{C \in \kappa} U_C. \tag{4.11a}$$

In (4.11 a) the sum is taken over the class $\mathscr{C}_p$ of all 'connected' partitions κ of the ordered index set $[p] = [1, 2, 3, \dots, p]$ into subsets C, and the product is over all subsets C of κ, while U_C

is the generalized Ursell function with variables indicated by C. Mentally we use a diagrammatic notation to define a connected partition of $[p]$. The indices 1, 2, 3, ..., p are represented by consecutive vertices of a regular polygon of p sides. A partition of $[p]$ is represented by a collection of polygons, each having the representative points of a set of the partition as vertices. By definition a partition is connected if the representative diagram is connected as a point set. The first few Y functions are

$$\left.\begin{aligned} Y_{12} &= U_{12}, \\ Y_{123} &= U_{123}, \\ Y_{1234} &= U_{1234} + U_{13}\,U_{24}, \\ Y_{12345} &= U_{12345} + U_{13}\,U_{245} + U_{24}\,U_{135} + U_{35}\,U_{124} + U_{14}\,U_{235} + U_{25}\,U_{134}. \end{aligned}\right\} \qquad (4.11\,b)$$

The generalized Ursell functions are given in terms of the generalized distribution functions G by the recurrence relation (Lebowitz & Percus 1963; Stell 1964)

$$G_{123\dots p} = \sum_{\psi} \prod_{Q\in\psi} U_Q, \qquad (4.12\,a)$$

in which the sum is taken over all partitions ψ of the set $[p]$ and the product is over all subsets Q of ψ. The first few generalized Ursell functions are

$$\left.\begin{aligned} U_{12} &= G_{12} - 1, \\ U_{123} &= G_{123} - G_{12} - G_{23} - G_{31} + 2, \\ U_{1234} &= G_{1234} - \dots. \end{aligned}\right\} \qquad (4.12\,b)$$

(The one-body correlation functions of the theory are defined as $G_1 = H_1 = U_1 = Y_1 = 1$). The Ursell functions are useful in the theory because they have the cluster property of vanishing when any pair of points (molecules) is well separated.

The first functions Y can be derived directly from (4.8). The kernel $\mathbf{\Lambda}^{\text{in}}$ is given by the expansion (4.10) with the functions $Y_{123\dots p0}$ replaced by configuration dependent functions $Y^{\text{in}}_{123\dots p0}$ with averages $Y_{123\cdots p0}$. The first functions Y^{in} are then easily generated through a recurrence relation obtained from (4.8). For the general result (4.11 a) we must refer to Hynne (1975).

The propagator $\mathscr{F}$ is itself given by a series expansion in terms of F, obtained from the iterated solution of (4.1):

$$\mathscr{F}_{10} = \sum_{p=1}^{\infty} (n\alpha)^{p-1} \int_V \dots \int_V \mathsf{F}_{12}\cdot\mathsf{F}_{23}\dots\mathsf{F}_{p0}\,G_{23\dots p}\,\mathrm{d}\boldsymbol{x}_2\dots\mathrm{d}\boldsymbol{x}_p, \qquad (4.13)$$

in which the first term is F_{10} by definition. If the series (4.13) is substituted for $\mathscr{F}$ in (4.10) and the resulting series is rearranged as a power series in $n\alpha$ we get the unscreened solution (3.17) back, of course: the screened formulation is rigorously equivalent to the unscreened one, and we shall call it the rigorously screened theory when we need to distinguish it from approximations to be introduced in later papers of this series. Actually, the substitution of (4.13) in (4.10) generates a classification of terms of the unscreened series for $\mathbf{\Lambda}$, which identifies the surface-dependent terms. Still, the main virtue of a screened formulation (in terms of $\mathscr{F}$) is that it aids an interpretation of the results of the theory in terms of macroscopic concepts.

We now consider scattering. The field at a distant point $\boldsymbol{R}$ from a dipole probe $\boldsymbol{P}(\omega)$ at

$\boldsymbol{x}$ is $\mathscr{F}^{\text{in}}(\boldsymbol{R},\boldsymbol{x};\omega)\cdot\boldsymbol{P}(\omega)$, and the component in the direction $\boldsymbol{v}$ of a polarization analyser is then $\boldsymbol{v}\cdot\mathscr{F}^{\text{in}}\cdot\boldsymbol{P}$, or

$$R^{-1}\exp(\mathrm{i}k_0R)\,k_0^2\,\boldsymbol{\varepsilon}^{\text{in}}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})\cdot\boldsymbol{P}(\omega), \tag{4.14}$$

where $\boldsymbol{\varepsilon}^{\text{in}}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})$ is obtained from (4.1) or (4.2) with the asymptotic form (2.3*b*) as either of the two explicit expressions

$$\boldsymbol{\varepsilon}^{\text{in}}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v}) = \boldsymbol{e}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})+\int_V\int_V \boldsymbol{e}(\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})\cdot\boldsymbol{\Pi}^{\text{in}}(\boldsymbol{x}',\boldsymbol{x}'';\omega)\cdot\mathscr{F}^{\text{in}}(\boldsymbol{x}'',\boldsymbol{x};\omega)\,\mathrm{d}\boldsymbol{x}'\,\mathrm{d}\boldsymbol{x}'', \tag{4.15a}$$

or
$$\boldsymbol{\varepsilon}^{\text{in}}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v}) = \boldsymbol{e}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})+\int_V\int_V \boldsymbol{e}(\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})\cdot\boldsymbol{\Lambda}^{\text{in}}(\boldsymbol{x}',\boldsymbol{x}'';\omega)\cdot\mathscr{F}(\boldsymbol{x}'',\boldsymbol{x};\omega)\,\mathrm{d}\boldsymbol{x}'\,\mathrm{d}\boldsymbol{x}''. \tag{4.15b}$$

Thus, the flux per unit solid angle of radiation from a collection of dipole probes at sites $\boldsymbol{x}_j$ embedded in the molecular system in configuration $\boldsymbol{x}_j^{\text{in}}$ is given by (2.11) with $\mathbf{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})$ replaced by

$$\mathscr{S}^{\text{in}}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}) = k_0^2\,\boldsymbol{\varepsilon}^{\text{in}*}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})\,\boldsymbol{\varepsilon}^{\text{in}}(\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}); \tag{4.16}$$

and the average flux is given by the same expression with the average of $\mathscr{S}^{\text{in}}$, namely

$$\mathscr{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}) = k_0^2\langle\boldsymbol{\varepsilon}^{\text{in}*}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})\,\boldsymbol{\varepsilon}^{\text{in}}(\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})\rangle, \tag{4.17a}$$

which we call a screened dipole radiator. For radiation not analysed for polarization it takes the form

$$\mathscr{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k}) = \sum_{j=1,2}\mathscr{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}_j), \quad \boldsymbol{v}_1\cdot\boldsymbol{v}_2=0. \tag{4.17b}$$

The average field at $\boldsymbol{R}$ from a dipole probe at $\boldsymbol{x}$ is given by (4.14) with $\boldsymbol{\varepsilon}^{\text{in}}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})$ replaced by its average value,

$$\boldsymbol{\varepsilon}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v}) = \langle\boldsymbol{\varepsilon}^{\text{in}}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})\rangle. \tag{4.18}$$

Explicitly, $\boldsymbol{\varepsilon}$ is

$$\boldsymbol{\varepsilon}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v}) = \boldsymbol{e}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})+\int_V\int_V \boldsymbol{e}(\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})\cdot\boldsymbol{\Lambda}(\boldsymbol{x}',\boldsymbol{x}'';\omega)\cdot\mathscr{F}(\boldsymbol{x}'',\boldsymbol{x};\omega)\,\mathrm{d}\boldsymbol{x}'\,\mathrm{d}\boldsymbol{x}'', \tag{4.19}$$

the average of (4.15*b*). We shall refer to $\boldsymbol{\varepsilon}$ as the 'weight field'. It will play an important role when we come to analyse the behaviour of the scattered light at the surface of the medium. The reason for the designation 'weight field' will then become clear.

The flux calculated from the average field differs from the average flux: it is governed by radiators

$$\mathscr{S}'(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}) = k_0^2\,\boldsymbol{\varepsilon}^*(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})\,\boldsymbol{\varepsilon}(\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}), \tag{4.20a}$$

$$\mathscr{S}'(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k}) = \sum_{j=1,2}\mathscr{S}'(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}_j). \tag{4.20b}$$

Thus the radiators $\mathscr{S}$ and $\mathscr{S}'$ are distinct: from the expression (4.15*b*) and the definitions (4.17*a*) and (4.20*a*) we see that they are related by

$$\mathscr{S}_{10} = \mathscr{S}'_{10}+\int_V\int_V \mathscr{F}^*_{12}\cdot\boldsymbol{\sigma}_{23}\cdot\mathscr{F}_{30}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3, \tag{4.21}$$

where we have introduced the scattering kernel $\boldsymbol{\sigma}$ by the definition (3.33*a*). This relation applies as well to radiation not analysed for polarization.

The average flux of scattered light differs from the flux of the average scattered field by including the incoherent scattering of the average field propagating through the molecular system. This difference is described by the term in $\boldsymbol{\sigma}$ in (4.21). The relation (4.21) will come to play a central role in the development of macroscopic multiple scattering, which we will present in III.

We have now introduced all the screened propagators we shall need, $\mathscr{F}$, $\mathscr{S}$, and $\mathscr{S}'$, and from now on we shall work with these as objects defined, and well defined, in terms of the fundamental propagators $\mathbf{F}$ and $\mathbf{S}$. We understand their significance in terms of dipole probes, but there are actually no such probes in the theory.

Physically, the scattering theory is most naturally formulated in terms of the weight field $\boldsymbol{\varepsilon}$ (or through the dyadic combination $\mathscr{S}'$, which we shall call the simple screened radiator). But a screened formulation in terms of $\mathscr{F}$ and $\mathscr{S}$ is formally simpler than one in terms of $\mathscr{F}$ and $\mathscr{S}'$ because $\mathscr{S}$ is the natural counterpart of $\mathscr{F}$. We now show that $\mathscr{S}$ is related to $\mathscr{F}$ in the same way as $\mathbf{S}$ to $\mathbf{F}$. We first note the formal relation

$$\mathscr{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v}) = \mathfrak{S}\{\mathscr{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\}. \tag{4.22}$$

The right side of (4.22) is defined from the expression (4.13) for $\mathscr{F}$ by applying the operator $\mathfrak{S}$ to the integrand of each term by using the definition (3.35).

For the left side of (4.22) we use the definition (4.17) with (4.15a) and its adjoint, namely

$$\boldsymbol{\varepsilon}^{\text{in}*}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v}) = \boldsymbol{e}^*(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v}) + \int_V\int_V \mathscr{F}^{\text{in}*}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\mathbf{\Pi}^{\text{in}*}(\boldsymbol{x}',\boldsymbol{x}'';\omega)\cdot\boldsymbol{e}^*(\boldsymbol{x}'';\boldsymbol{k},\boldsymbol{v})\,\mathrm{d}\boldsymbol{x}'\,\mathrm{d}\boldsymbol{x}''. \tag{4.23}$$

For the $\mathscr{F}^{\text{in}}$ and $\mathscr{F}^{\text{in}*}$ in (4.15a) and (4.22) we substitute the iterated solution of (4.1) to obtain an explicit series representation of $\mathscr{S}$, which may be simplified by use of (2.30). The correlation functions that arise are evidently the distribution functions (3.14). In all terms we get a dyadic product of $\boldsymbol{e}^*$ and $\boldsymbol{e}$, which together with the factor k_0^2 gives the kernel $\mathbf{S}$ by the definition (2.20a). By collecting the terms according to the total number of propagators $\mathbf{F}^*$, $\mathbf{F}$, and $\mathbf{S}$, and by comparing the result with the right side, the identity (4.22) then follows. Note that (4.22) may be viewed as a series representation of $\mathscr{S}$, in terms of $\mathbf{F}$ and $\mathbf{S}$, in condensed form.

A screened expansion of the scattering kernel $\boldsymbol{\sigma}$ (in terms of $\mathscr{F}$ and $\mathscr{S}$) is now easily derived. We first note a straightforward generalization of (4.22)

$$\mathfrak{S}\{\mathscr{F}_{12}\mathscr{F}_{23}\dots\mathscr{F}_{(p-1)\,p}\} = \sum_{q=1}^{p-1}\mathscr{F}^*_{12}\cdot\mathscr{F}^*_{23}\dots\mathscr{S}_{q(q+1)}\dots\mathscr{F}_{(p-1)\,p}. \tag{4.24}$$

This result (together with the linearity of the operator $\mathfrak{S}$) allows us to interpret the relation (3.41) between the scattering kernel and the susceptibility kernel in terms of screened expansions. This means that we can take the screened expansion of $\boldsymbol{\sigma}$ directly from (4.10) to get

$$\boldsymbol{\sigma}_{10} = \sum_{p=1}^{\infty}(n\alpha)^{p+1}\int_V\int_V \mathfrak{S}\{\mathscr{F}_{12}\mathscr{F}_{23}\dots\mathscr{F}_{p0}\}\,Y_{123\dots p0}\,\mathrm{d}\boldsymbol{x}_2\dots\mathrm{d}\boldsymbol{x}_p, \tag{4.25}$$

in which the factor in $\mathfrak{S}$ is a shorthand notation for the sum defined through (4.24). We also note that the Bohr–Peierls–Placzek relation between $\mathscr{S}$ and $\mathscr{F}$

$$\int\mathscr{S}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k})\,\mathrm{d}\Omega = 4\pi\,k_0^{-1}\,\mathrm{Im}\,\{\mathscr{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\} \tag{4.26}$$

is an immediate consequence of equations (4.22) and (3.43) with the expansion (4.13) of $\mathscr{F}$.

The expansion (4.25) with (4.24) is particularly simple in that all terms of the same order p contain the same correlation function, Y, independently of the index q (which determines the position of the radiator $\mathscr{S}$ in the string of propagators $\mathscr{F}$). This form lends itself to a comparison between the refractive index theory and the scattering theory.

Unfortunately, we must ultimately express the scattered flux in terms of the weight field $\boldsymbol{\varepsilon}$ (or of the simple radiator $\mathscr{S}'$) because $\boldsymbol{\varepsilon}$ describes essentially the scattered wave in the medium and its behaviour at the surface. This can be achieved through an iterated solution of (4.21) for $\mathscr{S}$ in terms of $\mathscr{S}'$, and this solution generates an expansion of the scattering in terms of *macroscopic* multiple scattering to all orders, which we shall derive in III. This multiple scattering expansion builds directly on the solution (4.25) and becomes expressed in terms of the Y functions.

Still, we shall also need more explicit expressions for the scattering in terms of the weight field together with either $\mathscr{F}$ or F. These we derive now. We use the factorization (2.20a) of S to write the scattered flux (3.33a) as

$$J(\boldsymbol{k},\boldsymbol{v}) = \frac{ck_0^4}{8\pi}\left\langle\left|\int_V\int_V \boldsymbol{e}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})\cdot\Delta\boldsymbol{\Lambda}^{\text{in}}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})\cdot\mathscr{E}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{x}'\right|^2\right\rangle. \tag{4.27}$$

We wish to obtain a similar expression in terms of the weight field $\boldsymbol{\varepsilon}$. We first note that (4.19) is equivalent to the integral equation in $\boldsymbol{\varepsilon}$

$$\boldsymbol{\varepsilon}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v}) = \boldsymbol{e}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})+\int_V\int_V \boldsymbol{\varepsilon}(\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})\cdot\boldsymbol{\Lambda}(\boldsymbol{x}',\boldsymbol{x}'';\omega)\cdot\mathsf{F}(\boldsymbol{x}'',\boldsymbol{x};\omega)\,\mathrm{d}\boldsymbol{x}'\,\mathrm{d}\boldsymbol{x}''. \tag{4.28}$$

This can be seen by comparing the iterated solution of (4.28) with the iterated solution of (4.3) substituted in (4.19).

We now obtain the scattering in terms of $\boldsymbol{\varepsilon}$ as

$$J(\boldsymbol{k},\boldsymbol{v}) = \frac{ck_0^4}{8\pi}\left\langle\left|\int_V\int_V \boldsymbol{\varepsilon}(\boldsymbol{x};\boldsymbol{k},\boldsymbol{v})\cdot\boldsymbol{\Delta}^{\text{in}}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\mathscr{E}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{x}'\right|^2\right\rangle \tag{4.29}$$

by substituting the expression for $\boldsymbol{e}$ in terms of $\boldsymbol{\varepsilon}$, obtained from (4.28), into (4.27). The kernel $\boldsymbol{\Delta}^{\text{in}}$ is defined by

$$\boldsymbol{\Delta}^{\text{in}}_{10} = \Delta\boldsymbol{\Lambda}^{\text{in}}_{10}-\int_V\int_V \boldsymbol{\Lambda}_{12}\cdot\mathsf{F}_{23}\cdot\Delta\boldsymbol{\Lambda}^{\text{in}}_{30}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3. \tag{4.30}$$

We shall derive equations for $\boldsymbol{\Delta}^{\text{in}}$ in terms of $\mathscr{F}$ and prove that the tensor kernel $\boldsymbol{\Delta}^{\text{in}}$ is symmetrical. From the fact that F and $\boldsymbol{\Lambda}$ are symmetrical it follows that $\mathscr{F}$ satisfies the real adjoint of (4.3), namely

$$\mathscr{F}_{10} = \mathsf{F}_{10}+\int_V\int_V \mathscr{F}_{12}\cdot\boldsymbol{\Lambda}_{23}\cdot\mathsf{F}_{30}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3. \tag{4.31}$$

By moving the integral in (4.31) to the left side of the equation and substituting the resulting expression for F into (4.30) we find by use of (4.30) itself that

$$\Delta\boldsymbol{\Lambda}^{\text{in}}_{10} = \boldsymbol{\Delta}^{\text{in}}_{10}+\int_V\int_V \boldsymbol{\Lambda}_{12}\cdot\mathscr{F}_{23}\cdot\boldsymbol{\Delta}^{\text{in}}_{30}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3. \tag{4.32}$$

Comparison of (4.30) and (4.32) demonstrates the identity

$$\int_V \mathsf{F}_{12}\cdot\Delta\boldsymbol{\Lambda}^{\text{in}}_{20}\,\mathrm{d}\boldsymbol{x}_2 = \int_V \mathscr{F}_{12}\cdot\boldsymbol{\Delta}^{\text{in}}_{20}\,\mathrm{d}\boldsymbol{x}_2. \tag{4.33}$$

By use of (4.33) in (3.9) we then find

$$\mathbf{\Lambda}_{10}^{\mathrm{in}} = \mathbf{\Pi}_{10}^{\mathrm{in}} + \int_V \int_V \mathbf{\Pi}_{12}^{\mathrm{in}} \cdot \mathscr{F}_{23} \cdot \mathbf{\Lambda}_{30}^{\mathrm{in}} \, \mathrm{d}\boldsymbol{x}_2 \, \mathrm{d}\boldsymbol{x}_3 \tag{4.34}$$

and subtraction of (4.32) from (4.34) yields

$$\mathbf{\Lambda}_{10}^{\mathrm{in}} = \mathbf{\Pi}_{10}^{\mathrm{in}} - \mathbf{\Lambda}_{10} + \int_V \int_V (\mathbf{\Pi}_{12}^{\mathrm{in}} - \mathbf{\Lambda}_{12}) \cdot \mathscr{F}_{23} \cdot \mathbf{\Lambda}_{30}^{\mathrm{in}} \, \mathrm{d}\boldsymbol{x}_2 \, \mathrm{d}\boldsymbol{x}_3. \tag{4.35}$$

This is a linear integral equation in $\mathbf{\Lambda}^{\mathrm{in}}$ with $\mathbf{\Pi}^{\mathrm{in}} - \mathbf{\Lambda}$ as a source. The iterated solution of (4.35) together with the fact that $\mathbf{\Pi}^{\mathrm{in}}$, $\mathbf{\Lambda}$, and $\mathscr{F}$ are each symmetrical then shows that $\mathbf{\Lambda}^{\mathrm{in}}$ is a symmetrical kernel.

We close this section by considering the development of the scattering (4.29) in terms of F. We may write

$$J(\boldsymbol{k}, \boldsymbol{v}) = \sum_{p=2}^{\infty} J_p(\boldsymbol{k}, \boldsymbol{v}); \quad J_p(\boldsymbol{k}, \boldsymbol{v}) = \sum_{q=1}^{p-1} J_{pq}(\boldsymbol{k}, \boldsymbol{v}), \tag{4.36a}$$

$$J_{pq}(\boldsymbol{k}, \boldsymbol{v}) = \frac{ck_0^4}{8\pi} (n\alpha)^p \int_V \mathrm{d}\boldsymbol{x}_1 \ldots \int_V \mathrm{d}\boldsymbol{x}_p (\mathscr{E}_1 \cdot \mathsf{F}_{12} \ldots \mathsf{F}_{(q-1)\,q} \cdot \boldsymbol{\varepsilon}_q)^* \\ \times (\boldsymbol{\varepsilon}_{q+1} \cdot \mathsf{F}_{(q+1)\,(q+2)} \ldots \mathsf{F}_{(p-1)\,p} \cdot \mathscr{E}_p) \, K_{123\ldots p}^{(q)}. \tag{4.36b}$$

By use of (3.39), (4.29), and (4.30) we find the functions $K_{123\ldots p}^{(q)}$ explicitly in terms of the H functions

$$K_{123\ldots p}^{(q)} = H_{123\ldots p} - \sum_{j=q+1}^{p-1} H_{(q+1)\ldots j} H_{1\ldots q(j+1)\ldots p} \\ - \sum_{j=1}^{q-1} H_{(j+1)\ldots q} H_{1\ldots j(q+1)\ldots p} + \sum_{j=1}^{q-1} \sum_{l=q+1}^{p-1} H_{(j+1)\ldots q} H_{(q+1)\ldots l} H_{12\ldots j(l+1)\ldots p} \tag{4.37}$$

with $H_1 = 1$. The first few K functions are

$$\left.\begin{aligned} K_{12}^{(1)} &= H_{12} = U_{12}, \\ K_{123}^{(1)} &= K_{123}^{(2)} = H_{123} - H_{13} = U_{123}, \\ K_{1234}^{(1)} &= H_{1234} - H_{134} - H_{23} H_{14} = U_{1234} + U_{13} U_{24} + U_{124}, \\ K_{1234}^{(2)} &= H_{1234} - H_{124} - H_{134} + H_{14} = U_{1234} + U_{13} U_{24} + U_{14} U_{23}, \\ K_{1234}^{(3)} &= H_{1234} - H_{124} - H_{23} H_{14} = U_{1234} + U_{13} U_{24} + U_{134}. \end{aligned}\right\} \tag{4.38}$$

Recall that the unscreened or screened expressions contain $H_{123\ldots p}$ or $Y_{123\ldots p}$ respectively at order p independently of q (the position of the dipole radiator). In contrast, the form of the function $K_{123\ldots p}^{(q)}$ depends on q, and it is not possible to express the scattering (4.36) compactly in terms of an operator like $\mathfrak{S}$.

We have now derived explicit expressions for the susceptibility kernel $\mathbf{\Lambda}$ and the scattering kernel $\boldsymbol{\sigma}$ in the form of screened and unscreened series expansions. We have also established a number of relations between them. These results have been mathematical ones, each of which is formally exact. Because they are available we can now return to the physical problems they have been designed to describe. The analysis of these physical problems becomes that much simpler if we can draw at will on the relations established in this section and the preceding one.

5. Optical parameters

In this section we obtain expressions for wave vector and frequency dependent dielectric constants, for the refractive index, for the total scattering cross section and for the extinction coefficient, and we derive certain relations between these optical parameters.

We first look at (3.1 *b*) and regard it as a relation determined by the kernel (3.17); thus $\boldsymbol{P}$ is a functional of $\mathscr{E}$, with $\mathscr{E}$ essentially arbitrary. We choose for V a parallel-sided box, and Fourier resolve $\boldsymbol{P}(\boldsymbol{x},\omega)$ and $\mathscr{E}(\boldsymbol{x},\omega)$ in V in terms of a set of orthogonal running vector waves. We find the equivalent relation

$$\boldsymbol{P}(\boldsymbol{h},\omega) = \sum_{\boldsymbol{h}'} \boldsymbol{\Lambda}(\boldsymbol{h},\boldsymbol{h}';\omega)\cdot\mathscr{E}(\boldsymbol{h}',\omega) \tag{5.1}$$

with the Fourier coefficients defined by

$$\boldsymbol{P}(\boldsymbol{h},\omega) = \int_V \boldsymbol{P}(\boldsymbol{x},\omega)\exp(-\mathrm{i}\boldsymbol{h}\cdot\boldsymbol{x})\,\mathrm{d}\boldsymbol{x}, \tag{5.2a}$$

$$\begin{aligned}\boldsymbol{\Lambda}(\boldsymbol{h},\boldsymbol{h}';\omega) &= |V|^{-1}\int_V\int_V \boldsymbol{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega)\exp(\mathrm{i}\boldsymbol{h}'\cdot\boldsymbol{x}'-\mathrm{i}\boldsymbol{h}\cdot\boldsymbol{x})\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{x}'\\ &= |V|^{-1}\int_V \mathrm{d}\boldsymbol{x}\exp[\mathrm{i}(\boldsymbol{h}'-\boldsymbol{h})\cdot\boldsymbol{x}]\int_V \boldsymbol{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega)\exp[\mathrm{i}\boldsymbol{h}'\cdot(\boldsymbol{x}'-\boldsymbol{x})]\,\mathrm{d}\boldsymbol{x}'\end{aligned} \tag{5.2b}$$

and similarly for $\mathscr{E}(\boldsymbol{x},\omega)$. Note that in general $\boldsymbol{\Lambda}(\boldsymbol{h},\boldsymbol{h}';\omega)$ depends on $\boldsymbol{h}$ and $\boldsymbol{h}'$ separately.

The kernel $\boldsymbol{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega)$ can be written as a sum of two terms, a short-range function of $\boldsymbol{x}-\boldsymbol{x}'$, which we call the local part of $\boldsymbol{\Lambda}$, and a correction term. 'Short-range' characterizes a function that is negligible when $|\boldsymbol{x}-\boldsymbol{x}'| \gg l$, where l is a typical intermolecular correlation length. The non-local correction term is either not short range or it depends on $\boldsymbol{x}$ and $\boldsymbol{x}'$ separately. We assume for the present that the correction term can be neglected to a good approximation. We return to this question in §6 when we look at the $\boldsymbol{x}$ and $\boldsymbol{x}'$ dependence of $\boldsymbol{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega)$ again. Until then we also assume that the kernel $\boldsymbol{\Gamma}(\boldsymbol{x},\boldsymbol{x}';\omega)$ is local in the sense just assumed for $\boldsymbol{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega)$.

If $\boldsymbol{\Lambda}$ is local then the final form of (5.2 *b*) shows that $\boldsymbol{\Lambda}(\boldsymbol{h},\boldsymbol{h}';\omega)$ is diagonal to a very good approximation, so

$$\boldsymbol{\Lambda}(\boldsymbol{h},\boldsymbol{h}';\omega) \simeq \boldsymbol{\Lambda}(\boldsymbol{h},\omega)\,\delta_{\boldsymbol{h},\boldsymbol{h}'}. \tag{5.3}$$

Here $\delta_{\boldsymbol{h},\boldsymbol{h}'}$ is a Kronecker delta and $\boldsymbol{\Lambda}(\boldsymbol{h},\omega)$ is defined by

$$\boldsymbol{\Lambda}(\boldsymbol{h},\omega) = \boldsymbol{\Lambda}(\boldsymbol{h},\boldsymbol{h};\omega) = |V|^{-1}\int_V\int_V \boldsymbol{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega)\exp[\mathrm{i}\boldsymbol{h}\cdot(\boldsymbol{x}'-\boldsymbol{x})]\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{x}'. \tag{5.4}$$

In the approximation (5.3), the relation (5.1) takes the simple form

$$\boldsymbol{P}(\boldsymbol{h},\omega) = \boldsymbol{\Lambda}(\boldsymbol{h},\omega)\cdot\mathscr{E}(\boldsymbol{h},\omega), \tag{5.5}$$

Since $\boldsymbol{P}$ is the average polarization, and $\mathscr{E}$ is given by equation (3.1 *a*) and interpreted as the average electric field in the medium for $\boldsymbol{x}\in V$, (5.5) exhibits $\boldsymbol{\Lambda}(\boldsymbol{h},\omega)$ as the dielectric susceptibility. In the particular case where the system is excited by light, $\boldsymbol{h}$ and ω are connected by a dispersion relation, as we show below. But in the general case $\boldsymbol{h}$ and ω are both free variables and $\boldsymbol{\Lambda}(\boldsymbol{h},\omega)$ determines $\boldsymbol{h}$ and ω dependent dielectric constants. For short correlation lengths

$\mathbf{\Lambda}(\boldsymbol{h}, \omega)$ depends only on one direction, that of $\boldsymbol{h}$, and it can then be split into longitudinal and transverse parts:

$$\mathbf{\Lambda}(\boldsymbol{h},\omega) = \mathit{\Lambda}_{\parallel}(h,\omega)\,\hat{\boldsymbol{h}}\hat{\boldsymbol{h}} + \mathit{\Lambda}_{\perp}(h,\omega)\,(\mathbf{U} - \hat{\boldsymbol{h}}\hat{\boldsymbol{h}}). \tag{5.6}$$

This form depends on the approximate local property of $\mathbf{\Lambda}$, for it neglects any dependence of $\mathbf{\Lambda}(\boldsymbol{h}, \omega)$ on the geometry and it assumes the symmetry

$$\mathbf{\Lambda}(\boldsymbol{h},\omega) = \mathbf{\Lambda}^{\mathrm{T}}(-\boldsymbol{h},\omega) = \mathbf{\Lambda}^{\mathrm{T}}(\boldsymbol{h},\omega) \tag{5.7}$$

in which T denotes transposition of the tensor (cf. Bullough (1968), the footnote to p. 420). The first part of (5.7) follows rigorously from the symmetry of $\mathbf{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega)$ as a tensor kernel. To prove the second equality of (5.7) we assume that for the local part of $\mathbf{\Lambda}$ the integrations in each term of the series (3.17) for $\mathbf{\Lambda}$ can effectively be extended to all space. Since the integrands in (3.17) are invariant under reflections in the point $\frac{1}{2}(\boldsymbol{x}+\boldsymbol{x}')$, it then follows that the local part of $\mathbf{\Lambda}$ is symmetrical in the variables $\boldsymbol{x}$ and $\boldsymbol{x}'$ and in the tensor indices separately. The last equality of (5.7) then follows when the non-local part of $\mathbf{\Lambda}$ is neglected.

If $\mathscr{E}(\boldsymbol{h},\omega)$ is split into longitudinal and transverse parts, (5.5) splits into two independent equations that naturally define longitudinal and transverse dielectric constants, $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ by

$$[\epsilon_{\parallel,\perp}(h,\omega) - 1]/4\pi = \mathit{\Lambda}_{\parallel,\perp}(h,\omega). \tag{5.8}$$

We now turn to a solution of the set of equations (3.1). The field $\boldsymbol{E}$ is a coherent field satisfying the time Fourier transformed wave equation,

$$(\nabla^2 + k_0^2)\,\boldsymbol{E}(\boldsymbol{x},\omega) = \mathbf{0}, \quad k_0 = \omega/c \tag{5.9}$$

and the transversality condition

$$\nabla\cdot\boldsymbol{E}(\boldsymbol{x},\omega) = 0. \tag{5.10}$$

The objective is to find an expression for the refractive index. We base the definition of the refractive index on the average polarization: we suppose $\boldsymbol{P}(\boldsymbol{x},\omega)$ satisfies the (Fourier transformed) wave equation

$$[\nabla^2 + m^2(\omega)\,k_0^2]\,\boldsymbol{P}(\boldsymbol{x},\omega) = \mathbf{0}, \quad \boldsymbol{x}\in V, \tag{5.11}$$

and then, by definition, $m(\omega)$ is the refractive index of the fluid.

We choose to solve the equations for $\boldsymbol{P}$ in the form (3.1*a*), (3.19), and we rewrite $\mathscr{E}$ as (cf. Rosenfeld 1951)

$$\mathscr{E}(\boldsymbol{x},\omega) = \boldsymbol{E}(\boldsymbol{x},\omega) - \tfrac{4}{3}\pi\,\boldsymbol{P}(\boldsymbol{x},\omega) + \int_{V-v} \mathbf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{P}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}' \tag{5.12a}$$

$$= \boldsymbol{E}(\boldsymbol{x},\omega) + (\nabla\nabla + k_0^2\,\mathbf{U})\cdot\int_V G(|\boldsymbol{x}-\boldsymbol{x}'|)\,\boldsymbol{P}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}'. \tag{5.12b}$$

In integrals over v, or $V-v$, a limit $v\to 0$ as the radius of the small sphere goes to zero is always understood. In (5.12*b*)

$$G(r) = \exp(\mathrm{i}k_0 r)/r \tag{5.13a}$$

and satisfies the equation

$$(\nabla^2 + k_0^2)\,G(|\boldsymbol{x}-\boldsymbol{x}'|) = -4\pi\,\delta(\boldsymbol{x}-\boldsymbol{x}'). \tag{5.13b}$$

The step from (5.12*a*) to (5.12*b*) involves an interchange of the order of differentiation and integration; and since the region of integration depends on $\boldsymbol{x}$ through v, a surface integral evaluated over the surface of v arises as the operator is taken outside (see also Rosenfeld (1951)). The contribution of this exactly cancels the term arising from the definition of the integral over v in (3.4). Notice now that the principal value prescription on the integral in (5.12a) becomes unnecessary in (5.12b) because the singularity from G is integrable. Accordingly, $V-v$ is replaced by V as the region of integration. This form (5.12b) for $\mathscr{E}$ means that $\mathscr{E}$ cannot depend on v, while it also agrees with macroscopic electrodynamics written in terms of the Hertz vector. Our definition of $\mathscr{E}$ nevertheless remains as it was introduced at (3.1a), in which the integral is interpreted by (3.3). The physical justification for this is implicit in what follows.

By use of the Green theorem and (5.11) and (5.13) we may rewrite (5.12b) as

$$\mathscr{E}(\boldsymbol{x},\omega) = \boldsymbol{E}(\boldsymbol{x},\omega)+\boldsymbol{\Sigma}(\boldsymbol{x};\boldsymbol{P})+\frac{4\pi\, k_0^{-2}}{m^2-1}(\nabla\nabla+k_0^2\,\mathsf{U})\cdot\boldsymbol{P}(\boldsymbol{x},\omega) \tag{5.14}$$

in which

$$\boldsymbol{\Sigma}(\boldsymbol{x};\boldsymbol{P}) = (m^2-1)^{-1}\,k_0^{-2}(\nabla\nabla+k_0^2\,\mathsf{U})\cdot\int_{\partial V}\mathrm{d}\boldsymbol{A}'\cdot\{[\nabla' G(r,\omega)]\,\boldsymbol{P}(\boldsymbol{x}',\omega)$$
$$-[\nabla'\boldsymbol{P}(\boldsymbol{x}',\omega)]\,G(r,\omega)\}. \tag{5.15}$$

Here $r=|\boldsymbol{x}-\boldsymbol{x}'|$, ∇' denotes differentiation with respect to $\boldsymbol{x}'$ and ∂V denotes the surface of V.

We now reduce the set of equations (3.1a), (3.19) to a single equation by substituting the result (5.14) for $\mathscr{E}$ in (3.19) to get

$$\boldsymbol{P}(\boldsymbol{x},\omega) = n\alpha\boldsymbol{E}(\boldsymbol{x},\omega)+n\alpha\boldsymbol{\Sigma}(\boldsymbol{x};\boldsymbol{P})+\frac{4\pi\, n\alpha}{(m^2-1)\,k_0^2}(\nabla\nabla+k_0^2\,\mathsf{U})\cdot\boldsymbol{P}(\boldsymbol{x},\omega)$$
$$+\int_V \boldsymbol{\Gamma}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{P}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}'. \tag{5.16}$$

Fourier resolution of the last term yields

$$\int_V \boldsymbol{\Gamma}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{P}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}' \simeq |V|^{-1}\sum_{\boldsymbol{h}}\exp(\mathrm{i}\boldsymbol{h}\cdot\boldsymbol{x})\,\boldsymbol{\Gamma}(\boldsymbol{h},\omega)\cdot\boldsymbol{P}(\boldsymbol{h},\omega), \tag{5.17}$$

in which we have used

$$|V|^{-1}\int_V\int_V \boldsymbol{\Gamma}(\boldsymbol{x},\boldsymbol{x}';\omega)\exp(\mathrm{i}\boldsymbol{h}'\cdot\boldsymbol{x}'-\mathrm{i}\boldsymbol{h}\cdot\boldsymbol{x})\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{x}' \simeq \boldsymbol{\Gamma}(\boldsymbol{h},\omega)\,\delta_{\boldsymbol{h},\boldsymbol{h}'}, \tag{5.18a}$$

$$\boldsymbol{\Gamma}(\boldsymbol{h},\omega) = |V|^{-1}\int_V\int_V \boldsymbol{\Gamma}(\boldsymbol{x},\boldsymbol{x}';\omega)\exp[\mathrm{i}\boldsymbol{h}\cdot(\boldsymbol{x}'-\boldsymbol{x})]\,\mathrm{d}\boldsymbol{x}', \tag{5.18b}$$

by arguments similar to those leading to (5.4).

Because of (5.11) only terms with $h=|\boldsymbol{h}|=mk_0$ contribute to the sum in (5.17). The last term of (5.16) therefore satisfies the wave equation (5.11) and so does the term in $\boldsymbol{P}(\boldsymbol{x},\omega)$. On the other hand the first two terms in (5.16) satisfy the wave equation (5.9). Consequently the equation (5.16) must split into two equations, each of which must be satisfied separately. The one satisfying (5.9) is

$$\boldsymbol{E}(\boldsymbol{x},\omega)+\boldsymbol{\Sigma}(\boldsymbol{x};\boldsymbol{P}) = \boldsymbol{0}, \quad \boldsymbol{x}\in V, \tag{5.19}$$

and this is the optical extinction theorem due to Ewald (1912, 1916) and Oseen (1915). It expresses the extinction of the free field satisfying (5.9) at all points inside V.

The second equation from (5.16) applies to terms of wavenumber mk_0. It can be split still further because the localization assumption (5.18a) means that there is no coupling between longitudinal and transverse parts of $\boldsymbol{P}$. Consequently

$$\mathbf{\Gamma}(\boldsymbol{h},\omega) = \Gamma_{\parallel}(h,\omega)\,\hat{\boldsymbol{h}}\hat{\boldsymbol{h}} + \Gamma_{\perp}(h,\omega)\,(\mathbf{U}-\hat{\boldsymbol{h}}\hat{\boldsymbol{h}}), \tag{5.20}$$

and the resulting equations are homogeneous in $P_{\parallel}$ and $P_{\perp}$. Then they imply the two dispersion relations (cf. Bullough 1968)

$$1+4\pi n\alpha(\omega) = \Gamma_{\parallel}(mk_0,\omega) \tag{5.21}$$

and

$$\frac{m^2-1}{4\pi} = \frac{n\alpha}{1-\Gamma_{\perp}(mk_0,\omega)}. \tag{5.22}$$

Actually, $\boldsymbol{P}$ must be split into longitudinal and transverse parts satisfying two distinct wave equations of the form (5.11). These define longitudinal and transverse refractive indices, which are then determined by each of the two dispersion relations (5.21), (5.22). We concentrate on the transverse dispersion relation (5.22) and refer to Bullough (1968, 1970) for a discussion of the longitudinal relation. We continue to denote the solution to (5.22) by $m(\omega)$.

Equation (3.30) lets us relate the refractive index and the dielectric constant. Fourier transformation over the region V yields a relation for the Fourier coefficients that can be split into separate equations for longitudinal and transverse parts. These can be solved for $\Lambda_{\parallel,\perp}$:

$$\Lambda_{\parallel,\perp}(h,\omega) = \frac{n\alpha(\omega)}{1-\Gamma_{\parallel,\perp}(h,\omega)}. \tag{5.23}$$

This result immediately gives the relations

$$\Lambda_{\parallel}(mk_0,\omega) = -(4\pi)^{-1} \tag{5.24}$$

$$(m^2-1)/4\pi = \Lambda_{\perp}(mk_0,\omega) = |V|^{-1}\,\mathrm{Tr}\int_V\int_V \mathbf{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\tilde{\mathbf{I}}(\boldsymbol{x}',\boldsymbol{x})\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{x}'. \tag{5.25}$$

The notation in (5.25) is that $\tilde{\mathbf{I}}(\boldsymbol{x}',\boldsymbol{x})$ denotes either of the two forms

$$\tilde{\mathbf{I}}(\boldsymbol{x}',\boldsymbol{x};mk_0,\boldsymbol{u}) = \boldsymbol{u}\boldsymbol{u}\exp[\mathrm{i}m\boldsymbol{k}_0\cdot(\boldsymbol{x}'-\boldsymbol{x})], \tag{5.26a}$$

$$\tilde{\mathbf{I}}(\boldsymbol{x}',\boldsymbol{x};mk_0) = \tfrac{1}{2}(\mathbf{U}-\hat{\boldsymbol{k}}_0\hat{\boldsymbol{k}}_0)\exp[\mathrm{i}m\boldsymbol{k}_0\cdot(\boldsymbol{x}'-\boldsymbol{x})]. \tag{5.26b}$$

Then Tr means the trace of the tensor, $\boldsymbol{u}$ is a unit vector orthogonal to the wave vector $m(\omega)\,\boldsymbol{k}_0$, and $|\boldsymbol{k}_0| = \omega/c$; otherwise $\boldsymbol{u}$ and $\boldsymbol{k}_0$ have arbitrary directions.

We have introduced the kernels $\tilde{\mathbf{I}}$ to emphasize a formal similarity with kernels related to the screened radiator $\mathscr{S}'$, which we shall consider in III. The two forms (5.26a, b) correspond to polarized and unpolarized waves in the medium, respectively, but in (5.25) it makes no difference whether (5.26a) or (5.26b) is used. In (5.26), m is really to be understood as Re (m), and the same applies to the m that appears in the arguments of $\mathbf{\Gamma}$ and $\mathbf{\Lambda}$ in (5.22) and (5.25).

Equation (5.24) implies $\mathscr{E}_{\parallel} = -4\pi\boldsymbol{P}_{\parallel}$. Because (5.15) means that $\nabla\cdot\boldsymbol{\Sigma}(\boldsymbol{x};\boldsymbol{P}) = 0$ we can expect that $\boldsymbol{P}_{\parallel}$ does not couple to the external field $\boldsymbol{E}$ through (5.19) so that $\mathscr{E}_{\parallel}$ and $\boldsymbol{P}_{\parallel}$ are free: this is already discussed elsewhere (Bullough 1968, 1970). On the other hand $\boldsymbol{P}_{\perp}$ and $\mathscr{E}_{\perp}$ are also solutions of homogeneous equations but are certainly not free: they are fixed by the constraint of the optical extinction theorem (5.19), and we show in §6 what this means for the particular geometry chosen for V there. Certainly it means that $\boldsymbol{P}_{\perp}$ is excited by light that satisfies the free field equation (5.9) with wavenumber k_0, while $|\boldsymbol{h}|$ in (5.5) takes on the value mk_0. This then defines a frequency dependent dielectric constant $\epsilon(\omega)$, and comparison of (5.8) with (5.25) shows that

$$\epsilon(\omega) = \epsilon_{\perp}(m(\omega)\, k_0, \omega) = m^2(\omega). \tag{5.27}$$

The relation (5.27) agrees with macroscopic electrodynamics and so expresses consistency between the dielectric constant theory based on (5.5) and the refractive index theory based on (5.11). Thus it justifies our introduction of $\mathscr{E}(\boldsymbol{x}, \omega)$ and our interpretation of it as a Maxwell type electric field for points $\boldsymbol{x}$ inside V. However, the definition (3.1 *a*) of $\mathscr{E}(\boldsymbol{x}, \omega)$ involves the further definitions, which are (3.3) and (3.4), and since these definitions may seem arbitrary we must understand the reasons for them more completely.

The key point is that the physics does *not* depend on the definitions (3.3) or (3.4). To see this, first note that the dielectric constant $\epsilon_{\perp}(h, \omega)$ in (5.8) depends on both (3.1 *a*) and (3.3) in so far as (5.5) relates $\boldsymbol{P}(\boldsymbol{h}, \omega)$ to the field $\mathscr{E}(\boldsymbol{h}, \omega)$. (Its relation to the *external* field $\boldsymbol{E}(\boldsymbol{x}, \omega)$ is more complicated as we show in §6.) Against this we have defined the observable, the refractive index, in terms of the wave vector of the average polarization, and this is entirely independent of any physical interpretation of the right side of (3.1 *a*), or of the definitions (3.3) or (3.4), as we now demonstrate.

For the moment we go back to (3.19), the origin of (5.16). In this equation we take the integral expression for $\mathscr{E}$ (namely (3.1 *a*)) together with the first term arising from substituting the expansion (3.26) into (3.19). Together these quantities contribute

$$n\alpha \int_V \mathsf{F}(\boldsymbol{x}, \boldsymbol{x}'; \omega) \cdot \boldsymbol{P}(\boldsymbol{x}', \omega)\, \mathrm{d}\boldsymbol{x}' + n\alpha \int_V \mathsf{F}(\boldsymbol{x}, \boldsymbol{x}'; \omega) \cdot \boldsymbol{P}(\boldsymbol{x}', \omega)\, C_2(\boldsymbol{x}, \boldsymbol{x}')\, \mathrm{d}\boldsymbol{x}'$$

$$= n\alpha \int_V \mathsf{F}(\boldsymbol{x}, \boldsymbol{x}'; \omega) \cdot \boldsymbol{P}(\boldsymbol{x}', \omega)\, g_2(\boldsymbol{x}, \boldsymbol{x}')\, \mathrm{d}\boldsymbol{x}' + \tfrac{2}{3}\mathrm{i}k_0^3\, \boldsymbol{P}(\boldsymbol{x}, \omega). \tag{5.28}$$

The two-body correlation function $C_2(\boldsymbol{x}, \boldsymbol{x}')$ is given by (3.29), (3.15). We see that the two terms combine into a *convergent* integral once the self-interaction has been evaluated by the rule of (2.26). The integral of the right side of (5.28) is convergent where $\boldsymbol{x}' = \boldsymbol{x}$, since $g_2(\boldsymbol{x}, \boldsymbol{x}') \to 0$ for $\boldsymbol{x}' \to \boldsymbol{x}$, and no special interpretation of the integral is needed.

On the other hand, in the derivation of (3.19) we have implicitly made the step backwards from the right of (5.28) to the left. This has meant replacing $g_2(\boldsymbol{x}, \boldsymbol{x}')$ by its asymptotic value for large $|\boldsymbol{x} - \boldsymbol{x}'|$, namely 1; and this number 1 gives the contribution of distant dipoles through the first integral of the left side of (5.28). This must now be corrected for the effect of close dipoles and this is done through the second integral, which contains $C_2(\boldsymbol{x}, \boldsymbol{x}')$ in which the 1 is now subtracted off again. These formal steps introduce what was the Lorentz *local* field correction via the second integral and, as we shall see, the Lorentz field term $(4\pi/3)\, \boldsymbol{P}(\boldsymbol{x}, \omega)$ from distant dipoles via the first integral.

Note first of all, however, that both the integrands in the left side of (5.28) are singular even though the integrand in the right side is non-singular. Thus the effects of the two singularities necessary cancel exactly and so they must cancel exactly in (3.19) and (5.16). This means that as far as the refractive index theory goes we can make any interpretation whatsoever of the two singularities.

The natural choice is to make a principal value interpretation of both integrals by abstracting a small sphere v about $\boldsymbol{x}$ in the regions of integration of both integrals. This choice is consistent with the physical fact that $g_2(\boldsymbol{x}, \boldsymbol{x}') \to 0$ as $\boldsymbol{x}' \to \boldsymbol{x}$, since the reference molecule at $\boldsymbol{x}$ excludes the possibility of a second molecule being there. For almost all $\boldsymbol{x}$ in V, g_2-1 is then spherically symmetric about $\boldsymbol{x}$ since, despite the boundary to V, $g_2 \rightarrow 1$ rapidly for all such $\boldsymbol{x}$. It then follows from the form of $\mathbf{F}$ that the contribution of the term in g_2-1 in the second integral in the left of (5.28) is *small*; and it is really this that motivates the principle value integral interpretation. From this we see that the usual Lorentz term, $\frac{4}{3}\pi\boldsymbol{P}(\boldsymbol{x},\omega)$, arising from distant dipoles, appears now when the integral operator is taken outside the integral, as in the step from (5.12a) to (5.12b). These mathematical steps thus implement the Lorentz's original physical intuition and do not appeal to (3.4).

However, in actual practice we have adopted a point of view that does involve (3.4): we chose to conceal a Lorentz term $\frac{4}{3}\pi\boldsymbol{P}(\boldsymbol{x},\omega)$ in each of the integrals by including the small spheres v in the regions of integration. The principal value interpretation can be regained by abstracting both small spheres: then, in the interpretation of (3.4), terms $\mp\frac{4}{3}\pi\boldsymbol{P}(\boldsymbol{x},\omega)$ arise from the first and second integrals, respectively, and mutually cancel. However, if the small spheres v are retained the term $-\frac{4}{3}\pi\boldsymbol{P}(\boldsymbol{x},\omega)$ from the first integral can be used to cancel the Lorentz term from the conditionally convergent part as it arises in the step from (5.12a) to (5.12b). Consequently the net effect is to transfer the $\frac{4}{3}\pi\boldsymbol{P}(\boldsymbol{x},\omega)$ term arising from distant dipoles to the second integeral of the left side of (5.28), now to be interpreted through the definition (3.4).

We now see that the way the Lorentz term appears to emerge in the refractive index theory through the action of (3.4) is actually misleading. But formulated in this fashion the theory offers several manipulative advantages. For it is certainly necessary to isolate the '1' and make up the first integral on the left side of (5.28) to apply the argument involving the optical extinction theorem of §6, which leads to the result (5.19). By making the interpretation (3.4) we can then draw the connection between the dielectric constant and refractive index theories.

Furthermore, the delta functions in the correlation functions (the self-correlations) cannot act in the principal value integral, but by including the integration over v these self-correlations can be handled together with interparticle correlations, a feature that greatly simplifies the calculation. The 'book-keeping' for the Lorentz terms is also simplified: this is desirable because although there is only one such term in $\Gamma_{\perp}(mk_0,\omega)$ of (5.22) (as we show below), the kernel $\Lambda_{\perp}(mk_0,\omega)$ of (5.25) contains an infinity of such terms. Finally, the definition (3.4) suggests an analogous interpretation in the screened theory (in terms of $\mathscr{F}$) developed in II and this has far reaching physical consequences.

All these features suggest that we use the rule (3.4) in the refractive index theory. In using it we must simply bear in mind that the Lorentz terms arise for sound physical reasons, and that the small sphere interpretation is in principle unnecessary for the refractive index theory, although it is essential for the dielectric constant theory.

We still have to check that the remaining terms of (3.19), which arise from the expansion (3.26) are well defined without any special interpretation other than (2.26). However, this can be seen immediately from the form of the higher correlation functions (3.27): all propagators $\mathbf{F}$ in $\mathbf{\Gamma}$ are covered by distribution functions G, which, apart from the self-correlations, vanish as pairs of points approach each other. Consequently there is a Lorentz contribution only from the first term of the expansion of $\mathbf{\Gamma}$, and we can write the Fourier integral (5.18b) as

$$\mathbf{\Gamma}(\boldsymbol{h},\omega) = \mathbf{\Gamma}^0(\boldsymbol{h},\omega)+\tfrac{4}{3}\pi\, n\alpha\, \mathbf{U}, \tag{5.29}$$

where $\mathbf{\Gamma}^0(\boldsymbol{h},\omega)$ is a series in which all integrals are convergent without the interpretation (3.4).

We now use the result (5.29) to bring the dispersion relation (5.22) and (5.25) to the conventional form exhibiting the Lorentz field correction. We split (5.29) into longitudinal and transverse parts and substitute into (5.23) to get

$$A_{\parallel,\perp}(h,\omega) = \frac{n\alpha(\omega)}{1-\frac{4}{3}\pi\, n\alpha(\omega)-\Gamma^{0}_{\parallel,\perp}(h,\omega)}. \tag{5.30a}$$

This may also be transformed to

$$\frac{A_{\parallel,\perp}(h,\omega)}{1+\frac{4}{3}\pi\, A_{\parallel,\perp}(h,\omega)} = \frac{n\alpha(\omega)}{1-\Gamma^{0}_{\parallel,\perp}(h,\omega)}, \tag{5.30b}$$

in which $\Gamma^{0}_{\parallel,\perp}(h,\omega)$ are the longitudinal and transverse parts. Equation (5.25) in particular then yields

$$\left(\frac{m^2-1}{4\pi}\right)\left(\frac{3}{m^2+2}\right) = \frac{n\alpha(\omega)}{1-\Gamma^{0}_{\perp}(mk_0,\omega)}, \tag{5.31}$$

which is the generalized Lorentz–Lorenz relation. Plainly the $\frac{4}{3}\pi\, n\alpha\, \mathbf{U}$ term in (5.29) determines the characteristic Lorentz form on the left side. As we have seen this is exactly the effect of distant dipoles, as Lorentz described, and its appearance does not depend on the definition (3.4).

The result (5.31) contains an infinite series in the denominator. Expansion yields a formal series in $n\alpha$ for the Lorentz–Lorenz ratio. However, the coefficients depend explicitly on n and (weakly) on m. Comparisons with (5.29) and (5.30) show that the result is simply

$$\left(\frac{m^2-1}{4\pi}\right)\left(\frac{3}{m^2+2}\right) = A^{0}_{\perp}(mk_0,\omega), \tag{5.32}$$

in which $A^{0}_{\perp}(mk_0,\omega)$ denotes the unscreened series $A_{\perp}(mk_0,\omega)$ with, however, all contributions from small spheres arising through the definition (3.4) now simply omitted. In practice the series (5.32) can be obtained by redefining the integral (3.4) as zero, or alternatively by placing V by $V-v$ after all delta functions (representing self-correlations) have been integrated. We shall develop the result (5.32) further in II. Note in passing that if the left side is replaced by $(m^2-1)/4\pi$, simply the definition (3.4) for the integrals must be retained: in effect the $\frac{4}{3}\pi\, n\alpha$ term in the denominator (5.30a) gets developed in the expansion and this indicates very well the mathematical validity of (3.4) within generalized function theory.

We now proceed to derive an expression for the total scattering cross section. From the Fourier resolution

$$\mathscr{E}(\boldsymbol{x},\omega) = |V|^{-1}\sum_{\boldsymbol{h}}\mathscr{E}(\boldsymbol{h},\omega)\exp(\mathrm{i}\boldsymbol{h}\cdot\boldsymbol{x}), \tag{5.33}$$

the quadratic form (3.32) in $\mathscr{E}$ is obtained as a sum over modes

$$J(\boldsymbol{k},v) = \frac{ck_0^2}{8\pi}\sum_{\boldsymbol{h},\boldsymbol{h}'}\mathscr{E}^{*}(\boldsymbol{h},\omega)\cdot\boldsymbol{\sigma}(\boldsymbol{h},\boldsymbol{h}';\boldsymbol{k},v)\cdot\mathscr{E}(\boldsymbol{h}',\omega), \tag{5.34}$$

in which

$$\boldsymbol{\sigma}(\boldsymbol{h},\boldsymbol{h}';\boldsymbol{k},v) = |V|^{-1}\int_V\int_V\boldsymbol{\sigma}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},v)\exp(\mathrm{i}\boldsymbol{h}'\cdot\boldsymbol{x}'-\mathrm{i}\boldsymbol{h}\cdot\boldsymbol{x})\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{x}'. \tag{5.35}$$

The terms in (5.34) with $\boldsymbol{h}'\neq\boldsymbol{h}$ evidently describe interference between scattering from different modes of $\mathscr{E}$. The diagonal terms of $\boldsymbol{\sigma}$, namely

$$\boldsymbol{\sigma}(\boldsymbol{h};\boldsymbol{k},v) \equiv \boldsymbol{\sigma}(\boldsymbol{h},\boldsymbol{h};\boldsymbol{k},v) = |V|^{-1}\int_V\int_V\boldsymbol{\sigma}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},v)\exp[\mathrm{i}\boldsymbol{h}\cdot(\boldsymbol{x}'-\boldsymbol{x})]\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{x}' \tag{5.36}$$

have some of the character of a scattering cross section, as we shall now see.

To define a scattering cross section in these terms, consider a single transverse mode for $\mathscr{E}(\boldsymbol{x},\omega)$ inside V, excited by light,

$$\mathscr{E}(\boldsymbol{x},\omega) = |V|^{-1}\tilde{\boldsymbol{E}}_0 \exp\left[\mathrm{i}m(\omega)\,\boldsymbol{k}_0\cdot\boldsymbol{x}\right]. \tag{5.37}$$

The wave vector is determined in magnitude by (5.5) and the fact that $\boldsymbol{P}$ has wavenumber mk_0; its direction is arbitrary except that $\tilde{\boldsymbol{E}}_0$ and $\boldsymbol{k}_0$ are perpendicular. The intensity of the single mode running wave in the medium is

$$I_0(\boldsymbol{x},\omega) = c\,\mathrm{Re}\,\{m(\omega)\}\,|V|^{-2}\,|\tilde{\boldsymbol{E}}_0|^2 \exp\left[-\tau(\omega)\,\hat{\boldsymbol{k}}_0\cdot\boldsymbol{x}\right]/8\pi, \tag{5.38}$$

in which

$$\tau(\omega) = 2k_0\,\mathrm{Im}\,\{m(\omega)\} \tag{5.39a}$$

is the extinction coefficient. The expression (5.38) can be obtained from the Poynting theorem by using a homogeneous Maxwell equation on the assumption that the relative magnetic permeability of the fluid is unity. The extinction coefficient, which appears in (5.38), may be obtained directly from the result (5.25) since (5.39*a*) may be rewritten as

$$\tau = \frac{4\pi\,k_0}{\mathrm{Re}\,(m)}\,\mathrm{Im}\left\{\frac{m^2-1}{4\pi}\right\}. \tag{5.39b}$$

We propose to obtain a differential scattering cross section per unit volume by normalizing the energy flux of light scattered in direction $\boldsymbol{k}$ from an undamped field corresponding to (5.37), against the intensity (5.38) of the same undamped single mode incident wave in the medium, namely (5.38) without the exponential damping factor, thus

$$n\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{k_0^2}{\mathrm{Re}\,(m)}\,|V|^{-1}\,\mathrm{Tr}\int_V\int_V \boldsymbol{\sigma}(\boldsymbol{x},\boldsymbol{x}';\boldsymbol{k},\boldsymbol{v})\cdot\tilde{\mathbf{I}}(\boldsymbol{x}',\boldsymbol{x};m\boldsymbol{k}_0,\boldsymbol{u})\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{x}'. \tag{5.40}$$

The form (5.26*b*) of $\tilde{\mathbf{I}}$ is used for scattering from an unpolarized incident wave. Notice that the scattering cross section defined by (5.40) has a global rather than local character through the integrations of $\boldsymbol{x}$ and $\boldsymbol{x}'$ over the entire region V. This feature is actually necessary because the integral over $\boldsymbol{x}'$ is not independent of $\boldsymbol{x}$ and proves to depend in a non-trivial way on the position $\boldsymbol{x}$ in relation to the boundary of V.

We shall show nevertheless that the total scattering cross section per unit volume obtained from (5.40), $n\sigma(\omega)$, is equal to the extinction coefficient; that is

$$n\sigma(\omega) = \tau(\omega), \tag{5.41a}$$

or in more detail

$$n\int\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\,\mathrm{d}\Omega = 2k_0\,\mathrm{Im}\,\{m(\omega)\}. \tag{5.41b}$$

This result expresses a local requirement of conservation of energy flow. But as we have seen it is obtained only in a global sense.

The relation (5.41) is nevertheless an exact result derived by direct transformation of the expression for $n\sigma$ into the one for τ by using the integral equations satisfied by the macroscopic kernels. By integration over all directions of $\boldsymbol{k}$ we obtain from (5.40), by use of the Bohr–Peierls–Placzek relation (2.14),

$$n\sigma = \frac{4\pi\,k_0}{\mathrm{Re}\,(m)\,|V|}\,\mathrm{Tr}\int_V\cdots\int_V \langle(\Delta\boldsymbol{\Lambda}_{12}^{\mathrm{in}})^{\dagger}\cdot\mathrm{Im}\,\{\mathbf{F}_{23}\}\cdot\Delta\boldsymbol{\Lambda}_{30}^{\mathrm{in}}\rangle\cdot\tilde{\mathbf{I}}_{01}\,\mathrm{d}\boldsymbol{x}_1\ldots\mathrm{d}\boldsymbol{x}_0. \tag{5.42}$$

In (5.42), the imaginary part operator can be taken outside the integrations because the right side of (5.42) is real and remains real if Im ($\mathbf{F}$) is replaced by Re ($\mathbf{F}$). To see this, perform a complex conjugation, which for a scalar equals hermitian conjugation; then use the fact that Re($\mathbf{F}$) and Im ($\mathbf{F}$) are hermitian kernels.

We may now replace $(\Delta\mathbf{\Lambda}^{\text{in}}_{12})^{\dagger}$ by $\mathbf{\Lambda}^{\text{in}\dagger}_{12}$ since the contribution of $\mathbf{\Lambda}^{\dagger}_{12}$ vanishes because $\langle\Delta\mathbf{\Lambda}^{\text{in}}_{30}\rangle = \mathbf{0}$. We then obtain

$$n\sigma = \frac{4\pi\, k_0}{\operatorname{Re}(m)\,|V|}\operatorname{Im}\left\{\operatorname{Tr}\int_V \dots \int_V \langle\mathbf{\Lambda}^{\text{in}\dagger}_{12}\cdot\mathbf{F}_{23}\cdot\Delta\mathbf{\Lambda}^{\text{in}}_{30}\rangle\cdot\tilde{\mathbf{I}}_{01}\,\mathrm{d}\boldsymbol{x}_1\dots\mathrm{d}\boldsymbol{x}_0\right\}. \tag{5.43}$$

Now substitute the right side of the hermitian conjugate of (3.9),

$$\mathbf{\Lambda}^{\text{in}\dagger}_{12} = \mathbf{\Pi}^{\text{in}}_{12} + \int_V\int_V (\Delta\mathbf{\Lambda}^{\text{in}}_{14})^{\dagger}\cdot\mathbf{F}^{\dagger}_{45}\cdot\mathbf{\Pi}^{\text{in}}_{52}\,\mathrm{d}\boldsymbol{x}_4\,\mathrm{d}\boldsymbol{x}_5 \tag{5.44}$$

for $\mathbf{\Lambda}^{\text{in}\dagger}_{12}$ in (5.43). The second term of (5.44) results in a real integral that vanishes when the imaginary part is taken. (Note that $\mathbf{\Pi}^{\text{in}}$ is a hermitian kernel.) We are then left with

$$n\sigma = \frac{4\pi\, k_0}{\operatorname{Re}(m)\,|V|}\operatorname{Im}\left\{\operatorname{Tr}\int_V\int_V \left\langle\int_V\int_V \mathbf{\Pi}^{\text{in}}_{12}\cdot\mathbf{F}_{23}\cdot\Delta\mathbf{\Lambda}^{\text{in}}_{30}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3\right\rangle\cdot\tilde{\mathbf{I}}_{01}\,\mathrm{d}\boldsymbol{x}_1\,\mathrm{d}\boldsymbol{x}_0\right\}. \tag{5.45}$$

From (3.9) we see that the quantity inside the angular brackets is just $\mathbf{\Lambda}^{\text{in}}_{10}-\mathbf{\Pi}^{\text{in}}_{10}$; but the contribution from $\mathbf{\Pi}^{\text{in}}_{10}$ is the imaginary part of a real quantity, which vanishes. We therefore reach the result (5.41) by use of (5.25) and (5.39*b*).

This proof of (5.41) is entirely independent of series representations of the macroscopic kernels given in §5. It is straightforward to confirm the relation (5.42) by use of the result (3.42), which is based on the series representations (3.17) and (3.34); one has only to remember that the real and imaginary parts of the kernel $\mathbf{\Lambda}$ are each hermitian.

We emphasize that the differential scattering cross section, as defined by (5.40), is not physically satisfactory because it proves to depend strongly on the geometry of the region V, as we shall see in III. In contrast, the *integrated* cross section σ scarcely depends on the scattering geometry, and the refractive index given by (5.25) fortunately also has this same property. The result (5.41) is therefore physically meaningful despite the formal character of the differential scattering cross section (5.40).

This paradoxical difference of status of the differential and total scattering cross sections can be understood roughly as follows (this anticipates results to be given in III): an essentially local differential scattering cross section can be defined for the scattering of an incoming wave in the medium to an outgoing wave in the medium. But (5.40) describes scattering detected in vacuum and it contains surface terms that account for the transformation of a scattered wave in the medium into one in vacuum: the transformation can be interpreted in terms of refraction and reflection of the scattered wave at the surface and 'macroscopic' multiple scattering (Hynne 1980, Hynne & Bullough 1982). Thus the effect of the surface terms of $\boldsymbol{\sigma}$ is to change the angular distribution of the scattering, and this redistribution prevents a sensible definition of a differential cross section directly from $\boldsymbol{\sigma}$. But since scattering in the medium in one direction appears ultimately in some other direction, the total scattering detected in vacuum outside the material system is not expected to differ from the total scattering as it emerges from local scattering processes in the medium.

This explanation removes any paradox that might appear when the exact result (5.41) is contrasted with the difficulties with the definition of a differential cross section through (5.40). We have given the explanation in macroscopic terms, but it will be substantiated in III, where we shall show that the macroscopic features are indeed contained in the microscopic theory. There we shall reach a more acceptable definition of a differential scattering cross section.

The purpose of the preliminary discussion we have just given has been to obtain the result (5.41), which shows that the unified theory of dielectric properties and scattering that we are developing is internally consistent and firmly based in physics. Because of that internal consistency reference to the refractive index theory will therefore help in the interpretation of the scattering theory and vice versa. Paper III, in particular, will exploit that relation.

6. THE OPTICAL EXTINCTION THEOREM

In this section we complete the solution of the set of equations (3.1 a) and (3.19) for $\mathscr{E}$ and $\boldsymbol{P}$. We have already shown that if these fields satisfy a wave equation of the form (5.11), then the wavenumber mk_0 is determined by (5.25) for the refractive index. It remains to be shown that solutions $\mathscr{E}$, $\boldsymbol{P}$ of the proposed form actually exist. This means demonstrating that the extinction theorem (5.19) can be satisfied for some solution $\boldsymbol{P}$ to the wave equation (5.11). And we are also obliged to justify the neglect of possible non-local parts of the kernels $\boldsymbol{\Lambda}$ and $\boldsymbol{\Gamma}$, which was assumed in the derivation.

We first consider (5.19), which is a peculiar set of inhomogeneous integral equations for $\boldsymbol{P}$ and its normal derivative at the surface ∂V of V, depending on the parameter $\boldsymbol{x}$ and with the source $\boldsymbol{E}(\boldsymbol{x}, \omega)$ depending on $\boldsymbol{x}$. The set of equations has an infinity of solutions $\boldsymbol{P}$, $\boldsymbol{P}'_{\mathrm{n}}$ ($\boldsymbol{P}'_{\mathrm{n}}$ denotes the normal derivative of $\boldsymbol{P}$) at the surface, from which $\boldsymbol{P}$ is obtained throughout V as the solution to a well posed boundary value problem; thus a set of compatible boundary conditions for (5.11) is selected.

The solution $\boldsymbol{P}$ depends, of course, on the geometry of the region V and on the incident field $\boldsymbol{E}$. We shall only consider a parallel-sided slab and an obliquely incident plane wave $\boldsymbol{E}$. By actually finding a solution $\boldsymbol{P}$ we demonstrate that, for this particular case at least, there exists a solution to the wave equation (5.11), which satisfies the surface integral equations (5.19). The problem has been treated by Darwin (1924); Hoek (1939); Bullough (1962); Born & Wolf (1970); Lalor & Wolf (1972) and others. The extinction theorem has been placed in a broader context by Sein (1969, 1970) and has been discussed by many authors (Agerwal *et al.* 1971; Birman & Sein 1972; De Goede & Mazur 1972; Pattanayak & Wolf 1972; De Goede 1973; Wolf 1973, 1976).

In the present context, the extinction theorem arises as one part of the set of equations that determine the induced polarization. It appears here on the assumption that $\boldsymbol{P}(\boldsymbol{x}, \omega)$ satisfies (5.11) throughout the region V. Thus the question is whether there exists a function $\boldsymbol{P}(\boldsymbol{x}, \omega)$ satisfying *both* (5.11) *and* (5.16) including the condition (5.19) (the extinction theorem), and hence whether a refractive index exists in the simple sense of continuum optics.

We chose a coordinate system with z-axis normal to the surface of the slab in such a way that the wave vector $\boldsymbol{k}$ of the incident field

$$\boldsymbol{E}(\boldsymbol{x}, \omega) = \boldsymbol{E} \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) \tag{6.1}$$

has coordinates

$$\boldsymbol{k} = (k_{\mathrm{t}}, 0, k_{\mathrm{n}}), \quad k_{\mathrm{t}} \geqslant 0, \quad k_{\mathrm{n}} = \boldsymbol{n}\cdot\boldsymbol{k} > 0. \tag{6.2}$$

Subscripts t and n refer to components that are tangential and normal with respect to the surface, and $\boldsymbol{n}$ is a normal unit vector, $\boldsymbol{n} = (0, 0, 1)$.

We take the sides of the slab at $z = z^-$ and $z = z^+$ with $z^+ > z^-$ and take the slab infinite in all directions perpendicular to the z-axis. We shall ignore finite oscillatory contributions from surface integrals at infinity, which represent the diffraction pattern of a surface at infinity. Such contributions are unimportant to the present problem. The essential feature is that although the system is infinite in volume, it has a well defined surface and is finite in all directions not perpendicular to the slab axis.

To find a solution to (5.19), we evaluate the functional $\boldsymbol{\Sigma}(\boldsymbol{x};\boldsymbol{P})$ (equation (5.15)) when $\boldsymbol{P}$ is a transverse plane wave of wave vector $\tilde{\boldsymbol{k}}$,

$$\boldsymbol{P}(\boldsymbol{x},\omega) = \boldsymbol{P}_0 \exp(\mathrm{i}\tilde{\boldsymbol{k}}\cdot\boldsymbol{x}). \tag{6.3}$$

Quite generally, we may write

$$\boldsymbol{\Sigma}(\boldsymbol{x};\boldsymbol{P}) = \boldsymbol{\Sigma}^+(\boldsymbol{x};\boldsymbol{P}) + \boldsymbol{\Sigma}^-(\boldsymbol{x};\boldsymbol{P}) \tag{6.4}$$

as a sum of contributions from the right and left surfaces. We then find for $\boldsymbol{P}$, given by (6.3),

$$\boldsymbol{\Sigma}^{\pm}(\boldsymbol{x};\boldsymbol{P}) = \mp(m^2-1)^{-1}k_0^{-2}(\nabla\nabla + k_0^2\,\mathbf{U})\,[\boldsymbol{n}\cdot(\nabla + \mathrm{i}\tilde{\boldsymbol{k}})\,\zeta^{\pm}(\boldsymbol{x},\tilde{\boldsymbol{k}})]\cdot\boldsymbol{P}_0, \tag{6.5}$$

in which $\zeta^{\pm}$ is the surface integral

$$\zeta^{\pm}(\boldsymbol{x},\boldsymbol{k}) = \int_{z=z^{\pm}} \frac{\exp(\mathrm{i}k_0|\boldsymbol{x}-\boldsymbol{x}'|)}{|\boldsymbol{x}-\boldsymbol{x}'|}\exp(\mathrm{i}\tilde{\boldsymbol{k}}\cdot\boldsymbol{x}')\,\mathrm{d}A'. \tag{6.6}$$

Integration over the polar angle first yields a single integral containing a Bessel function that is known (see Erdelyi *et al.* (1954), vol. I, formulae 1.13 (48) and 2.13 (47) and their errata on p. xvi). The result is

$$\zeta^{\pm}(\boldsymbol{x},\tilde{\boldsymbol{k}}) = 2\pi\mathrm{i}\,h^{-1}\exp[\mathrm{i}(\tilde{k}_x x + \tilde{k}_y y) + h|z-z^{\pm}| + \tilde{k}_z z^{\pm}], \quad \tilde{k}_{\mathrm{t}} < k_0, \tag{6.7a}$$

$$\zeta^{\pm}(\boldsymbol{x},\tilde{\boldsymbol{k}}) = 2\pi\,h^{-1}\exp[\mathrm{i}(\tilde{k}_x x + \tilde{k}_y y) - h|z-z^{\pm}| + \mathrm{i}\tilde{k}_z z^{\pm}], \quad \tilde{k}_{\mathrm{t}} > k_0, \tag{6.7b}$$

in which

$$\tilde{k}_{\mathrm{t}} = (\tilde{k}_x^2 + \tilde{k}_y^2)^{\frac{1}{2}}, \quad h = |k_0^2 - \tilde{k}_{\mathrm{t}}^2|^{\frac{1}{2}}. \tag{6.8}$$

To satisfy (5.19) it is clearly necessary that $\tilde{k}_{\mathrm{t}} < k_0$, and the fields $\boldsymbol{\Sigma}^+$ and $\boldsymbol{\Sigma}^-$ are then waves with wave vectors $(k_x, k_y, \pm h)$. The upper (lower) sign of $\pm h$ applies in the region to the right (left) of the relevant surface. With proper choice of $\boldsymbol{P}_0$, $\boldsymbol{E}$ may be eliminated in V by $\boldsymbol{\Sigma}^-$ provided

$$\tilde{\boldsymbol{k}} = \tilde{\boldsymbol{k}}_1 = (k_{\mathrm{t}}, 0, \tilde{k}_{\mathrm{n}}) \tag{6.9a}$$

or

$$\tilde{\boldsymbol{k}} = \tilde{\boldsymbol{k}}_2 = (k_{\mathrm{t}}, 0, -\tilde{k}_{\mathrm{n}}). \tag{6.9b}$$

Here

$$\tilde{k}_{\mathrm{n}} = (m^2k_0^2 - k_{\mathrm{t}}^2)^{\frac{1}{2}} \tag{6.9c}$$

since $\boldsymbol{P}$ is supposed to satisfy (5.11).

However, the right surface *creates* a wave $\boldsymbol{\Sigma}^+$ in V with wave vector

$$\boldsymbol{k}' = (k_{\mathrm{t}}, 0, -k_{\mathrm{n}}). \tag{6.10}$$

But this can be avoided by using for $\boldsymbol{P}$, a linear combination of two waves with the two wave vectors (6.9),

$$\boldsymbol{P}(\boldsymbol{x},\omega) = \boldsymbol{P}^{(1)}\exp(\mathrm{i}\tilde{\boldsymbol{k}}_1\cdot\boldsymbol{x}) + \boldsymbol{P}^{(2)}\exp(\mathrm{i}\tilde{\boldsymbol{k}}_2\cdot\boldsymbol{x}) \tag{6.11}$$

with an appropriate linear relation between the two vector amplitudes $\boldsymbol{P}^{(1)}$ and $\boldsymbol{P}^{(2)}$.

Anticipating the proportionality between $\boldsymbol{\mathscr{E}}$ and $\boldsymbol{P}$ (to be derived at (6.15*b*) below), we note here that (6.9*a*) expresses the Snell law of refraction

$$k_{\mathrm{t}} = \tilde{k}_{\mathrm{t}} \quad \text{or} \quad \sin\theta = m\sin\tilde{\theta}, \tag{6.12a}$$

with
$$\sin\theta = k_{\mathrm{t}}/|\boldsymbol{k}|, \quad \sin\tilde{\theta} = \tilde{k}_{\mathrm{t}}/|\tilde{\boldsymbol{k}}| \tag{6.12b}$$

for the transformation of $\boldsymbol{E}$ (wave vector $\boldsymbol{k}$) into a wave of wave vector $\tilde{\boldsymbol{k}}_1$ at the surface $z = z^-$. Below, $\theta, \tilde{\theta}$ always denote the acute angles between the normal to a surface and the wave vectors of a pair of waves in vacuum and in the medium, respectively. We may think of these waves as a pair of corresponding incident and transmitted waves, whether the incident wave is in vacuum (as here) or in the medium. Similarly, (6.9*a, b*) express the law of reflection

$$\boldsymbol{n}\cdot\tilde{\boldsymbol{k}}_1 = -\boldsymbol{n}\cdot\tilde{\boldsymbol{k}}_2 \tag{6.12c}$$

at either of the two surfaces $z = z^{\pm}$.

We may now summarize the situation. The field $\boldsymbol{E}$ must be eliminated by $\boldsymbol{\Sigma}^-$ in V and hence everywhere to the right of the surface $z = z^-$. Similarly, $\boldsymbol{\Sigma}^+$ must vanish in V and hence everywhere to the left of the surface $z = z^+$:

$$\boldsymbol{E}(\boldsymbol{x},\omega) + \boldsymbol{\Sigma}^-(\boldsymbol{x};\boldsymbol{P}) = \boldsymbol{0}, \quad z > z^-, \tag{6.13a}$$

$$\boldsymbol{\Sigma}^+(\boldsymbol{x};\boldsymbol{P}) = \boldsymbol{0}, \quad z < z^+. \tag{6.13b}$$

Plainly, we also have
$$\boldsymbol{P}(\boldsymbol{x},\omega) = \boldsymbol{0}, \quad z < z^- \quad \text{or} \quad z > z^+. \tag{6.13c}$$

Hence, by (5.14) the average field $\boldsymbol{\mathscr{E}}$ may be written as a sum of three parts

$$\boldsymbol{\mathscr{E}}(\boldsymbol{x},\omega) = [\boldsymbol{E}(\boldsymbol{x},\omega) + \boldsymbol{\Sigma}^-(\boldsymbol{x};\boldsymbol{P})] + \boldsymbol{\Sigma}^+(\boldsymbol{x};\boldsymbol{P}) + 4\pi(m^2-1)^{-1}\boldsymbol{P}(\boldsymbol{x},\omega), \tag{6.14}$$

of which precisely one is non-vanishing in either of the three regions bounded by the surfaces:

$$\boldsymbol{\mathscr{E}}(\boldsymbol{x},\omega) = \begin{cases} \boldsymbol{E}(\boldsymbol{x},\omega) + \boldsymbol{\Sigma}^-(\boldsymbol{x};\boldsymbol{P}), \quad z < z^-, & (6.15a) \\ \dfrac{4\pi}{m^2-1}\boldsymbol{P}(\boldsymbol{x},\omega), \quad z^- < z < z^+, & (6.15b) \\ \boldsymbol{\Sigma}^+(\boldsymbol{x};\boldsymbol{P}), \quad z > z^+. & (6.15c) \end{cases}$$

Figure 1 displays the relations (6.12) and (6.15) and the various wave vectors and associated fields.

The relations (6.13*a, b*) again express the extinction theorem of Ewald (1912, 1916) and Oseen (1915): the polarization induced in a uniform material dielectric by a field $\boldsymbol{E}(\boldsymbol{x},\omega)$ of wavenumber $\boldsymbol{k}$ is such that the functional $\boldsymbol{\Sigma}(\boldsymbol{x};\boldsymbol{P})$ of $\boldsymbol{P}$ and its normal derivative at the surface equals $-\boldsymbol{E}(\boldsymbol{x},\omega)$. The functional exactly compensates the incident field throughout V. It creates no other field of wavenumber k_0 inside V but gives rise to reflected and transmitted waves outside V.

We now find vector amplitudes $\boldsymbol{P}^{(1)}$, $\boldsymbol{P}^{(2)}$ such that $\boldsymbol{P}$ (equation (6.11)) satisfies equations (6.13). For $z < z^+$ we find from (6.13*b*)

$$(\tilde{k}_{\mathrm{n}} - k_{\mathrm{n}})\exp(\mathrm{i}\tilde{k}_{\mathrm{n}}z^+)(\mathbf{U} - \hat{\boldsymbol{k}}'\hat{\boldsymbol{k}}')\cdot\boldsymbol{P}^{(1)} - (\tilde{k}_{\mathrm{n}} + k_{\mathrm{n}})\exp(-\mathrm{i}\tilde{k}_{\mathrm{n}}z^+)(\mathbf{U} - \hat{\boldsymbol{k}}'\hat{\boldsymbol{k}}')\cdot\boldsymbol{P}^{(2)} = \boldsymbol{0}. \tag{6.16}$$

For a wave with wave vector in the direction $\hat{\boldsymbol{h}}$, we choose an orthogonal basis for polarization vectors $\boldsymbol{u}_{\parallel}(\hat{\boldsymbol{h}}), \boldsymbol{u}_{\perp}(\hat{\boldsymbol{h}})$ in such a way that $\boldsymbol{u}_{\perp}(\boldsymbol{h})$ is always along the positive y-axis and $\boldsymbol{u}_{\parallel}(\hat{\boldsymbol{h}})$,

$\boldsymbol{u}_\perp(\hat{\boldsymbol{h}})$, and $\hat{\boldsymbol{h}}$ form a right-handed system. The subscripts $\|$ and $\perp$ now refer to vectors in the plane of incidence and vectors perpendicular to that plane respectively: (6.16) splits into two independent equations for the two types of components, and we find the linear relations

$$P^{(2)}_{\|,\perp} = R_{\|,\perp} \exp(\mathrm{i}2\tilde{k}_\mathrm{n} z^+)\, P^{(1)}_{\|,\perp}, \tag{6.17a}$$

in which

$$R_\perp = \frac{\tilde{k}_\mathrm{n} - k_\mathrm{n}}{\tilde{k}_\mathrm{n} + k_\mathrm{n}} = -\frac{\sin(\tilde{\theta}-\theta)}{\sin(\tilde{\theta}+\theta)}, \tag{6.17b}$$

$$R_\| = -R_\perp \frac{\cos(\tilde{\theta}+\theta)}{\cos(\tilde{\theta}-\theta)} = \frac{\tan(\tilde{\theta}-\theta)}{\tan(\tilde{\theta}+\theta)}. \tag{6.17c}$$

The relation (6.17*a*) agrees with macroscopic optics and the coefficients (6.17*b*, *c*) have the form of the appropriate Fresnel reflection coefficients (see, for example, Born & Wolf 1970 or Jackson 1975).

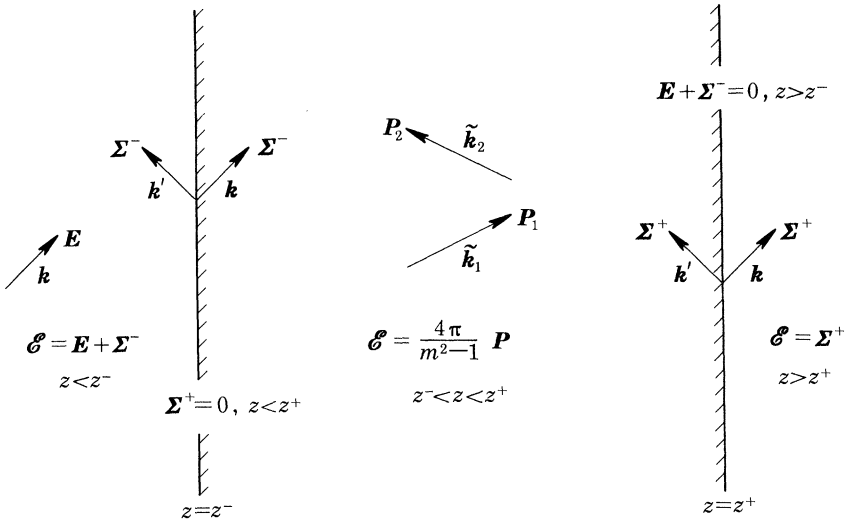

FIGURE 1. Wave vectors and fields associated with the extinction theorem for a parallel-sided slab and a plane incident wave.

From (6.13*a*), we similarly find the equation

$$\boldsymbol{E} - \frac{4\pi}{m^2-1}\frac{k_\mathrm{n}+\tilde{k}_\mathrm{n}}{2k_\mathrm{n}} \exp[\mathrm{i}(\tilde{k}_\mathrm{n}-k_\mathrm{n})z^-]\,(\mathbf{U} - \hat{\boldsymbol{k}}\hat{\boldsymbol{k}})\cdot \boldsymbol{P}^{(1)} - \frac{4\pi}{m^2-1}\frac{k_\mathrm{n}-\tilde{k}_\mathrm{n}}{2k_\mathrm{n}} \exp[-\mathrm{i}(\tilde{k}_\mathrm{n}+k_\mathrm{n})z^-]\,(\mathbf{U} - \hat{\boldsymbol{k}}\hat{\boldsymbol{k}})\cdot \boldsymbol{P}^{(2)} = \mathbf{0}. \tag{6.18}$$

By splitting into independent equations for components in the plane of incidence and perpendicular to that plane and by using the result (6.17) we then find linear relations fixing the amplitudes $P^{(1)}_{\|,\perp}$ in relation to the amplitudes $E_{\|,\perp}$ of the external field,

$$P^{(1)}_{\|,\perp} = \frac{m^2-1}{4\pi}\left\{\frac{T_{\|,\perp}\exp[\mathrm{i}(k_\mathrm{n}-\tilde{k}_\mathrm{n})z^-]}{1-R^2_{\|,\perp}\exp[\mathrm{i}2\tilde{k}_\mathrm{n}(z^+-z^-)]}E_{\|,\perp}\right\}. \tag{6.19a}$$

Here,

$$T_\perp = \frac{2k_\mathrm{n}}{k_\mathrm{n}+\tilde{k}_\mathrm{n}} = \frac{2\cos\theta\sin\tilde{\theta}}{\sin(\theta+\tilde{\theta})}, \tag{6.19b}$$

$$T_\| = T_\perp/\cos(\theta-\tilde{\theta}), \tag{6.19c}$$

have the form of Fresnel transmission coefficients for waves passing from vacuum into the medium.

Comparison of (6.15*b*) and (6.19*a*) shows that the term in curly brackets in (6.19*a*) can be identified with the amplitudes $\mathscr{E}^{(1)}_{\|,\perp}$ of the mode of the electric field in the medium with wave vector $\tilde{\boldsymbol{k}}_1$,

$$\mathscr{E}^{(1)}_{\|,\perp} = \frac{T_{\|,\perp}\exp\left[\mathrm{i}(k_\mathrm{n}-\tilde{k}_\mathrm{n})\,z^-\right]}{1-R^2_{\|,\perp}\exp\left[\mathrm{i}2\tilde{k}_\mathrm{n}(z^+-z^-)\right]}\,E_{\|,\perp}. \tag{6.20}$$

The amplitudes of the other mode (of wave vector $\tilde{\boldsymbol{k}}_2$), $\mathscr{E}^{(2)}_{\|,\perp}$, are obviously related to $\mathscr{E}^{(1)}_{\|,\perp}$ by a relation of the form (6.17*a*). The results (6.17), (6.19), and (6.20) are in complete agreement with macroscopic optics: they show that the slab acts as a Fabry–Perot interferometer in the usual way.

It is easy to confirm also that $\boldsymbol{\Sigma}^{\pm}(\boldsymbol{x};\boldsymbol{P})$ agree with the expressions of macroscopic optics for the transmitted wave ($\boldsymbol{\Sigma}^{+}$ for $z > z^+$) and for the reflected wave ($\boldsymbol{\Sigma}^{-}$ for $z < z^-$). The wave vectors are right, and we find for the amplitudes

$$\Sigma^{+}_{\|,\perp} = \frac{1}{T_{\|,\perp}}\exp\left[\mathrm{i}(\tilde{k}_\mathrm{n}-k_\mathrm{n})\,z^+\right]\mathscr{E}^{(1)}_{\|,\perp} - \frac{R_{\|,\perp}}{T_{\|,\perp}}\exp\left[\mathrm{i}(k_\mathrm{n}-\tilde{k}_\mathrm{n})\,z^+\right]\mathscr{E}^{(2)}_{\|,\perp}, \tag{6.21}$$

or by use of the equivalent of (6.17*a*)

$$\Sigma^{+}_{\|,\perp} = T^{\mathrm{out}}_{\|,\perp}\exp\left[\mathrm{i}(\tilde{k}_\mathrm{n}-k_\mathrm{n})\,z^+\right]\mathscr{E}^{(1)}_{\|,\perp} \tag{6.22a}$$

in which

$$T^{\mathrm{out}}_{\|,\perp} = \frac{1-R^2_{\|,\perp}}{T_{\|,\perp}} = \frac{\tilde{k}_\mathrm{n}}{k_\mathrm{n}}\,T_{\|,\perp} \tag{6.22b}$$

is a transmission coefficient for waves passing the surface from the medium into the vacuum outside V. Hence, $\boldsymbol{\Sigma}^{+}$ represents the transmitted wave for $z > z^+$.

For the amplitudes $\Sigma^{-}_{\|,\perp}$ we find

$$\Sigma^{-}_{\|,\perp} = -\frac{R_{\|,\perp}}{T_{\|,\perp}}\exp\left[\mathrm{i}(\tilde{k}_\mathrm{n}+k_\mathrm{n})\,z^-\right]\mathscr{E}^{(1)}_{\|,\perp} + \frac{1}{T_{\|,\perp}}\exp\left[-\mathrm{i}(\tilde{k}_\mathrm{n}+k_\mathrm{n})\,z^-\right]\mathscr{E}^{(2)}_{\|,\perp}. \tag{6.23}$$

By using (6.18) in the form

$$E_{\|,\perp} - \frac{1}{T_{\|,\perp}}\exp\left[\mathrm{i}(\tilde{k}_\mathrm{n}-k_\mathrm{n})\,z^-\right]\mathscr{E}^{(1)}_{\|,\perp} + \frac{R_{\|,\perp}}{T_{\|,\perp}}\exp\left[-\mathrm{i}(\tilde{k}_\mathrm{n}+k_\mathrm{n})\,z^-\right]\mathscr{E}^{(2)}_{\|,\perp} = 0, \tag{6.24}$$

we may eliminate $\mathscr{E}^{(1)}_{\|,\perp}$ between (6.23) and (6.24). We then find, by use of (6.22*b*),

$$\Sigma^{-}_{\|,\perp} = T^{\mathrm{out}}_{\|,\perp}\exp\left[\mathrm{i}(k_\mathrm{n}-\tilde{k}_\mathrm{n})\,z^-\right]\mathscr{E}^{(2)}_{\|,\perp} - R_{\|,\perp}\exp\left[\mathrm{i}2k_\mathrm{n}\,z^-\right]E_{\|,\perp}. \tag{6.25}$$

Thus, for $z < z^-$, $\boldsymbol{\Sigma}^{-}(\boldsymbol{x};\boldsymbol{P})$ is a sum of two contributions that can be interpreted as the wave $\boldsymbol{\mathscr{E}}^{(2)}\exp(\mathrm{i}\tilde{\boldsymbol{k}}_2\cdot\boldsymbol{x})$ transmitted through the surface $z = z^-$ and the wave $\boldsymbol{E}(\boldsymbol{x},\omega)$ reflected in the surface $z = z^-$. Note that $R_{\|,\perp}$ applies to internal reflections and $-R_{\|,\perp}$ is therefore the appropriate reflection coefficient here.

Let us review the argument that led to these results. The coupled equations for the induced polarization break into two equations for terms satisfying either of two distinct wave equations. One equation is homogeneous in $\boldsymbol{P}$ and is independent of the geometry of the system (on the assumption that the non-local parts of $\boldsymbol{\Lambda}$ and $\boldsymbol{\Gamma}$ are negligible); it fixes the wavenumber of $\boldsymbol{P}$ to mk_0. The other equation has $\boldsymbol{E}$ as a source and depends strongly on the geometry; it guarantees that no mode of wavenumber k_0 propagates in the medium, and it fixes the amplitudes of the various modes of wavenumber mk_0.

The argument through the assumption (5.11) breaks down if $\mathbf{\Lambda}$ and $\mathbf{\Gamma}$ have non-negligible non-local parts, because the coupled equations then do not split. In the following discussion we shall work in terms of $\mathbf{\Lambda}$, and we shall show that it has a non-local part that is small, but not obviously negligible: it appears at third and all higher orders in $n\alpha$ of the series expansion of $\mathbf{\Lambda}$. By generalization from the third order term (which we analyse in detail), we indicate how it is possible to carry the argument through in terms of a modified condition (5.11) and yet define a unique refractive index.

Consider the representation (3.17) of $\mathbf{\Lambda}$; this is formally a power series in $n\alpha$. The coefficients are tensor kernels given as products of propagators F integrated with a correlation function H as a weight. To isolate possible non-local parts of $\mathbf{\Lambda}$, it is convenient to express the H functions in terms of (generalized) Ursell functions, defined by the recurrence relation (4.12*a*); the first few functions are

$$\left.\begin{aligned} H_{10} &= U_{10}, \\ H_{120} &= U_{120}+U_{10}, \\ H_{1230} &= U_{1230}+U_{13}\,U_{20}+U_{10}\,U_{23}+U_{120}+U_{130}+U_{10}. \end{aligned}\right\} \tag{6.26}$$

As previously noted the Ursell functions have the useful cluster property that they tend rapidly to zero whenever the distance between any two of their variables tends to infinity. The two first terms of the expansion (3.17) are therefore short-range functions of $\boldsymbol{x}_1-\boldsymbol{x}_0$ and hence local in the sense used here. Equation (6.26) splits the third order term in two. The term in U_{120} is local because all the variables $\boldsymbol{x}_1$, $\boldsymbol{x}_2$ and $\boldsymbol{x}_0$ are 'covered' by the Ursell function. The integration with respect to $\boldsymbol{x}_2$ can then be extended to all space and the result depends only on $\boldsymbol{x}_1-\boldsymbol{x}_0$; furthermore, the term is evidently short range.

The part of the third order contribution to $\mathbf{\Lambda}$ from the term U_{10} of H_{120} (equation (6.26)) is

$$(n\alpha)^3\,U_2(\boldsymbol{x}_1,\boldsymbol{x}_0)\int_V \mathsf{F}(\boldsymbol{x}_1\,\boldsymbol{x}_2;\omega)\cdot\mathsf{F}(\boldsymbol{x}_2,\boldsymbol{x}_0;\omega)\,\mathrm{d}\boldsymbol{x}_2. \tag{6.27}$$

Here the integration cannot be extended to all space because F behaves asymptotically as given by (2.3*b*) namely

$$\mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\sim k_0^2\,(\boldsymbol{U}-\hat{\boldsymbol{r}}\hat{\boldsymbol{r}})\exp{(\mathrm{i}k_0\,r)}/r, \quad k_0\,r\gg 1 \tag{6.28}$$

(in the notation defined below (2.2*c*)), so the integral over all space diverges.

Because of the factor U_{10} we need only consider the case in which $|\boldsymbol{x}_1-\boldsymbol{x}_0|$ is not large compared to a correlation length l, which we may define as

$$l^2 = \int |x-x'|^2\,U_2(\boldsymbol{x},\boldsymbol{x}')\,\mathrm{d}\boldsymbol{x}'\bigg/\int U_2(\boldsymbol{x},\boldsymbol{x}')\,\mathrm{d}\boldsymbol{x}'. \tag{6.29}$$

Apart from finitely oscillating contributions at infinity, which we ignore, the integral (6.27) converges for the infinite parallel-sided slab, and for $\boldsymbol{x}_1$ well inside the slab we find

$$\begin{aligned}\int_V \mathsf{F}(\boldsymbol{x}_1,\boldsymbol{x}_2;\omega)\cdot\mathsf{F}(\boldsymbol{x}_2,\boldsymbol{x}_0;\omega)\,\mathrm{d}\boldsymbol{x}_2 &= 2\pi[\mathsf{F}(\boldsymbol{x}_1,\boldsymbol{x}_0;\,\omega)+(\boldsymbol{x}_1-\boldsymbol{x}_0)\cdot\nabla_1\,\mathsf{F}(\boldsymbol{x}_1,\boldsymbol{x}_0;\,\omega)] \\ &\quad+\frac{\pi}{2}k_0^3\left\{\frac{\exp{[\mathrm{i}2k_0(z_1-z^-)]}}{k_0(z_1-z^-)}+\frac{\exp{[\mathrm{i}2k_0(z^+-z_1)]}}{k_0(z^+-z_1)}\right\} \\ &\quad\times[1+O(k_0^2\,|x_1-x_0|^2)]+O((k_0^{-2}(z_1-z^-)^{-2})+O(k_0^{-2}(z^+-z_1)^{-2}).\end{aligned} \tag{6.30}$$

Equation (6.30) has been pieced together from a surface independent part obtained by all-space Fourier transformation, and a surface dependent part obtained by evaluation of the relevant integrals. The result has been checked by direct calculation of the imaginary part of the complete integral. The surface independent part is the term in F, which depends on $\boldsymbol{x}_1$ and $\boldsymbol{x}_0$ only through the difference $\boldsymbol{x}_1-\boldsymbol{x}_0$. The rest of (6.30) is surface dependent. It depends on the distances of $\boldsymbol{x}_1$ to the left and right surfaces of the slab, and hence it depends on $\boldsymbol{x}_1$ and $\boldsymbol{x}_0$ separately (z_1 denotes the coordinate of $\boldsymbol{x}_1$ along the slab axis).

The surface dependent part of the integral (6.30) is shown as the leading term of an expansion in the reciprocal distances to the surfaces. The contribution to $\boldsymbol{\Lambda}$ of the surface dependent part of the term (6.27) (which already may be relatively small on account of the factor $(n\alpha)^3$) is therefore completely negligible provided the point $\boldsymbol{x}_1$ is many wavelengths away from any part of the surface. When this condition is met the term (6.27) is indeed local since the Ursell function that multiplies the integral ensures the short range.

Generalization from this observation suggests that the non-local part of $\boldsymbol{\Lambda}(\boldsymbol{x}_1,\boldsymbol{x}_0;\omega)$ is negligible provided $\boldsymbol{x}_1$ is well inside the material system. We shall assume the validity of this generalization with a minor amendment. We defined 'locality' with reference to a correlation length l; but we must admit also small contributions to $\boldsymbol{\Lambda}$, which are 'local' only with reference to a wavelength. This is the case with the term at fourth order in $n\alpha$ arising from the second term on the right side of the last equation of (6.26), namely

$$(n\alpha)^4\int_V\int_V \mathsf{F}_{12}\cdot\mathsf{F}_{23}\cdot\mathsf{F}_{30}\,U_{13}\,U_{20}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3. \tag{6.31}$$

This term is not short range in the original sense because the points $\boldsymbol{x}_1$ and $\boldsymbol{x}_0$ are not connected by Ursell functions. Nevertheless, a subsequent integration with respect to $\boldsymbol{x}_0$ to obtain $\Lambda_\perp(mk_0,\omega)$ converges through the photon propagators, since the term (6.31) is approximately

$$(n\alpha)^4(\kappa_{\mathrm{T}}\,k_{\mathrm{B}}\,T)^2(\mathsf{U}-\hat{\boldsymbol{r}}\hat{\boldsymbol{r}})\,k_0^6\exp{(\mathrm{i}3k_0\,r)}/r^3,\quad k_0\,r\gg 1, \tag{6.32}$$

for separations $r=|\boldsymbol{x}_1-\boldsymbol{x}_0|$ large compared to a wavelength $2\pi\,k_0^{-1}$. In (6.32) we have used the fact that the integral of the two-body generalized Ursell function U_{12} is $n^{-1}\kappa_{\mathrm{T}}\,k_{\mathrm{B}}\,T$ for the grand ensemble; κ_{T} is the isothermal compressibility. (The grand ensemble is chosen only for simplicity; but it is interesting to note that precise choice of statistical ensemble may be important for the particular term (6.31) because of the combination of phase factors and Ursell functions. However, we shall not pursue this question.)

Even though the non-local part of $\boldsymbol{\Lambda}(\boldsymbol{x},\boldsymbol{x};\omega)$ is negligible when $\boldsymbol{x}$ is well inside the material system, it is not obvious that a non-vanishing contribution near the surface would not damage the argument in terms of the extinction theorem. This is because that argument rests on a global property of $\boldsymbol{P}$, namely the satisfaction of the wave equation (5.11) in the entire region V. We believe, however, that the situation is the following.

The average polarization can be split into a 'bulk part' $\boldsymbol{P}_{\mathrm{b}}$, which satisfies the wave equation (5.11) throughout V, and a 'surface part' $\boldsymbol{P}_{\mathrm{s}}$, which vanishes well inside the system;

$$\boldsymbol{P}(\boldsymbol{x},\omega)=\boldsymbol{P}_{\mathrm{b}}(\boldsymbol{x},\omega)+\boldsymbol{P}_{\mathrm{s}}(\boldsymbol{x},\omega). \tag{6.33}$$

For simplicity we assume that $\boldsymbol{P}_{\mathrm{b}}$ is transverse. We then obtain for the average electric field

$$\mathscr{E}(\boldsymbol{x},\omega)=\boldsymbol{E}(\boldsymbol{x},\omega)+\boldsymbol{\Sigma}(\boldsymbol{x};\boldsymbol{P}_{\mathrm{b}})+4\pi(m^2-1)^{-1}\boldsymbol{P}_{\mathrm{b}}(\boldsymbol{x},\omega)+\int_V \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{P}_{\mathrm{s}}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}'. \tag{6.34}$$

The original condition (5.19), which states that the field $\boldsymbol{E}(\boldsymbol{x},\omega)+\boldsymbol{\Sigma}(\boldsymbol{x};\boldsymbol{P})$ vanishes identically (for all $\boldsymbol{x}$ in V) is now replaced by the asymptotic relation

$$\boldsymbol{E}(\boldsymbol{x},\omega)+\boldsymbol{\Sigma}(\boldsymbol{x};\boldsymbol{P}_{\mathrm{b}})+\int_V \mathbf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{P}_{\mathrm{s}}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}'\sim \mathbf{0} \tag{6.35}$$

valid for $\boldsymbol{x}$ well inside V. When this condition on $\boldsymbol{x}$ is fulfilled, we expect the integral in $\boldsymbol{P}_{\mathrm{s}}$ to satisfy a wave equation of the form (5.9) rather than vanish. However, it satisfies neither (5.9) nor (5.11) when $\boldsymbol{x}$ is close to the surface; hence, $\boldsymbol{\mathscr{E}}$ also consists of bulk and surface parts. In the simple case of a parallel-sided slab, equations (6.13*a*) and (6.13*b*) now include the additional integral of $\boldsymbol{P}_{\mathrm{s}}$ from regions near the right and left surfaces respectively, and $\boldsymbol{P}_{\mathrm{s}}$ similarly modifies the transmitted and reflected fields, respectively.

We have now completed the solution of the set of equations (3.1) (or the equivalent set (3.1*a*), (3.19)), which was initiated in §5. The most important conclusion is that (3.1) has indeed a solution $\boldsymbol{P}(\boldsymbol{x},\omega)$ satisfying the wave equation (5.11) for $\boldsymbol{x}$ well inside the material medium. Thus (3.1) defines a refractive index. This means that all the expressions for the optical parameters derived in §5 have now been substantiated. In particular we have demonstrated that the refractive index is given by (5.25), and that this expression is essentially independent of the geometry of the region V.

7. CONCLUSION

We have solved the problem of finding the response of a molecular fluid to light. The molecular system is finite and the electromagnetic field is incident upon the system from the outside. We have calculated the average polarization, $\boldsymbol{P}$, the average electric field, $\boldsymbol{\mathscr{E}}$, inside and outside the system, and the flux of scattered light, J, induced in response to the external field $\boldsymbol{E}$.

The theory is completely general; but we have also treated one particular choice of geometry in detail: we have exhibited the polarization and the field induced in a molecular fluid contained in a parallel-sided slab in response to a plane incident wave $\boldsymbol{E}$. With $\boldsymbol{E}$ given by (6.1), (6.2) we found for the slab $z^- < z < z^+$ that the polarization is a sum of two modes (equation (6.11)) with amplitudes fixed by the external field as given by (6.17) and (6.19). Inside the medium the field $\boldsymbol{\mathscr{E}}$ similarly consists of two modes with amplitudes determined by (6.20) and a relation similar to (6.17). The field outside the medium is given by (6.15*a*, *c*) with (6.22) and (6.25). These fields agree with macroscopic optics. However, they apply only for points well away from the surface. In addition there are small contributions to both polarization and field at points near the surface, as we have demonstrated through analysis of one surface term, equation (6.27).

The theory is nowhere phenomenological and the transmission and reflection coefficients T and R in the relations between the amplitudes are derived through the constraint of the extinction theorem: this condition is one of two equations into which the response equation splits; the other equation fixes the parameter m, the refractive index. The result for m is the expression (5.25) in terms of the susceptibility kernel $\boldsymbol{\Lambda}$, which itself is given by the unscreened expansion (3.17), (3.18), or alternatively by the screened expansion (4.10), (4.11).

Actually, $\boldsymbol{\Lambda}$ determines wavenumber and frequency dependent dielectric constants (5.8), while the refractive index is initially obtained through the argument involving the extinction theorem in the different form (5.22) in terms of a kernel $\boldsymbol{\Gamma}$, equations (3.26), (3.27). But we have established the relation (3.30) between the kernels $\mathbf{\Lambda}$ and $\mathbf{\Gamma}$, and this allows us to derive the identity (5.27) between the frequency dependent dielectric constant and the refractive index. As a consequence we need only consider the refractive index and we may express it in terms of the susceptibility kernel, as in (5.25).

The flux of scattered light, collected at a distant detector outside the molecular system, is found as the quadratic form (3.32) in the average electromagnetic field, $\mathscr{E}$, which itself is determined by the external field (for the special geometry by (6.20) etc., as we have just mentioned). So J is obtained as the response to the external field $\boldsymbol{E}$. The kernel of the quadratic form, the scattering kernel $\boldsymbol{\sigma}$, is obtained in the form of series expansions to all orders, the unscreened expansion (3.34) with the definition (3.35), and the screened expansion (4.25) with the definition (4.24). The remarkable fact is that these expansions are governed by the *same* correlation functions as the corresponding expansions of the susceptibility kernel, namely the H and Y functions, respectively. These functions are defined in (3.18) and (4.11*a*), respectively, and the first few functions are displayed in (3.28) and (4.11*b*). The definitions are in terms of the generalized distribution functions G and Ursell functions U defined in (3.14) and (4.12*a*) and displayed in (3.15) and (4.12*b*).

Indeed, the similarity between the susceptibility kernel $\mathbf{\Lambda}$ and the scattering kernel $\boldsymbol{\sigma}$ is striking and applies in either unscreened or screened formulations. Thus a term with p propagators in the expansion of $\mathbf{\Lambda}$ corresponds to a sum of p terms with p propagators in the expansion of $\boldsymbol{\sigma}$. Each term contains a product of one special propagator, which we have called a 'radiator', together with $p-1$ ordinary propagators, and the sum is over all positions of the radiator in the chain of propagators; see (3.34) with (3.35) in the unscreened formulation and (4.25) with (4.24) in the screened one. Every term in the sum of p terms contains the same correlation function H or Y (which is identical with the one that appears in the corresponding term in the expansion of $\mathbf{\Lambda}$, as we have already said).

The radiators are defined by (2.12) (unscreened) and (4.17) (screened), and they qualify as 'propagators' not only because they formally appear as such in $\boldsymbol{\sigma}$, but also because Bohr–Peierls–Placzek relations connect S with F and $\mathscr{S}$ with $\mathscr{F}$; (2.14) and (4.26). We view the highly uniform structure of $\boldsymbol{\sigma}$ and $\mathbf{\Lambda}$ (expressed in condensed form in the relation (3.41)) as an important feature of the present formulation. The physically important Bohr–Peierls–Placzek relation (3.42) between the kernels $\boldsymbol{\sigma}$ and $\mathbf{\Lambda}$ is an immediate consequence, and this again implies the conservation relation (5.41) between the total scattering cross section and the extinction coefficient (although (5.41) was actually derived directly from the integral equations of §3).

The refractive index was transformed to a series (5.32), which generalizes the Lorentz–Lorenz relation; but beyond this we did not develop the theory of the refractive index. That development will be the subject of the second paper in this series. From (5.32) with the unscreened expansion (3.17) of the susceptibility kernel $\mathbf{\Lambda}$, we shall compute the correction to the Lorentz–Lorenz relation valid at low densities. We shall use the screened expansion (4.10) as basis for a discussion of the physical meaning of the corrections to the Lorentz–Lorenz relation, and for a comparison of two models of the local field. In this discussion we use the formulation in terms of generalized correlation functions with the definition (2.26) and the practice of concealing Lorentz terms as contributions from vanishingly small spheres through the definition (3.4). Through the formulation in these terms a generalization of the radiation reaction (2.26) to an Onsager type reaction field suggests itself; and as a result the complex polarizability (2.7) is generalized to a Böttcher type effective polarizability for a molecule in the many-body system. Thus, the alternative formulations and the several technical devices introduced in this paper will come into practical use in due course.

For the scattering of light, we calculated the flux of scattering in a given direction with a given polarization. We also found an expression for the total scattering cross section, which we used for the proof of the relation (5.41) as a sign of the internal consistency of the unified theory. But we were unable, at this stage of the development, to define a differential scattering cross section, and we indicated the reasons for this paradox. There remains a number of problems, primarily associated with the effect of the surface, which require a separate paper for their solution. The third and last paper in this series will deal with all of these problems.

Again, the solution of these difficult problems depends on some rather technical devices introduced in this paper, in this case the screened radiators $\mathscr{S}$ and $\mathscr{S}'$. It will turn out in III that the weight field $\boldsymbol{\varepsilon}$ (equation (4.19)) contained in $\mathscr{S}'$ (equation (4.20)) plays much the same role for the scattered wave as $\boldsymbol{\mathscr{E}}$ does for the incoming wave; and from the form of the scattering in terms of the weight field we shall demonstrate that the theory describes refraction and reflection of the scattered light. We shall also see that the subtle difference between the radiators $\mathscr{S}$ and $\mathscr{S}'$ contains the key to a complete solution of the intriguing problem of macroscopic multiple scattering: the solution is based on the screened expansion (4.25) of the scattering kernel. Working from the alternative expansion (4.36) we shall compute the scattering at low densities. We shall also analyse the Einstein (1910) light scattering equation: we simply calculate the expressions on each side of his formula from the microscopic result (5.25) with (3.17) and compare them.

So the forthcoming papers II and III will provide the elaboration, the computations, and the comparisons that this paper largely lacks. We have been concerned with presenting the foundation of the theory, establishing its internal consistency, and obtaining explicit expressions for the basic objects of the theory, the susceptibility kernel, $\mathbf{A}$, the scattering kernel, $\boldsymbol{\sigma}$, and various propagators. This work will lighten the papers II and III so that they may concentrate on physical ideas.

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