Macroscopic electromagnetic theory of resonant dielectrics[*]

J. E. Sipe and J. Van Kranendonk

Department of Physics, University of Toronto, Toronto, Ontario M5S 1A7, Canada

(Received 25 July 1973; revised manuscript received 28 January 1974)

The application of the macroscopic Maxwell equations to the resonant interaction of electromagnetic radiation and dielectric crystals consisting of molecules coupled via retarded dipole fields is investigated. The macroscopic fields are defined by space averaging over volume elements of linear dimensions Δ satisfying $a \ll \Delta \ll \lambda$, where a is the intermolecular separation and λ the wavelength *in vacuo*. The essential point of our method is the direct derivation from the microscopic equations of a constitutive relation for a finite dielectric, taking proper account of the radiation reaction terms and avoiding the use of an expansion in powers of the molecular polarizability. The results lead to a simple interpretation of the expressions for the internal fields derived by Vlieger along similar lines, and verify the validity of the standard equations of dispersion theory to all points inside the medium a distance Δ away from the surface. The transmission and scattering of radiation at or near a molecular resonance by media of over-all extent small and large compared to the wavelength are discussed for sphere and slab geometries, and the effective natural linewidths are calculated. The limits of validity of the constitutive relation are discussed, and the existence of frequency regions where the macroscopic description breaks down due to the appearance of large spatial variations in the dipole moments is pointed out. As an example of such "antiresonant" behavior and of the role played by the higher-order radiation-damping terms, the scattering of light from two interacting molecules is treated in detail. In the absence of sufficiently strong dissipative damping, the occurrence of antiresonance is predicted to be a general phenomenon giving rise to large oscillations in the scattering cross section even in the presence of spatial dispersion in a narrow region around the frequency where the expression for the macroscopic index of refraction diverges.

I. INTRODUCTION

The derivation of the Maxwell equations for the propagation of electromagnetic radiation in a macroscopic medium from the microscopic, or Lorentz, equations is a problem of long standing which over the years has been discussed in various stages of sophistication. For an account of the history of the subject and the present state of the art, we refer to the well-known books by Rosenfeld[1] and by de Groot.[2] The purpose of our paper is to analyze the special problems arising when the frequency of the incident radiation is equal, or close, to a resonance frequency of the molecules constituting the medium. We are interested in particular in the resonant electromagnetic properties of a dielectric crystal at low temperatures, which are governed by the radiative reaction forces. Under such conditions, the resonant scattering of radiation by large groups of molecules gives rise to "superradiant" effects and to a natural linewidth many orders of magnitude larger than for incoherent excitation, as first pointed out by Dicke.[3]

For systems containing N molecules with an over-all size small compared with the wavelength of the incident radiation, the N molecules behave as one big molecule with a "giant" dipole moment and a radiative-damping constant equal to N times that for a single molecule—although, as we shall see, the incident field can also excite modes of a quite different kind in spite of the fact that it is almost uniform over the system. The original motivation for the present work was to obtain an expression for the natural linewidth of a molecular resonance in a crystal as a function of the shape and the over-all size of the crystal, in particular for systems which are large compared with the wavelength, the case of practical interest for frequencies in the infrared and visible region. This problem was discussed previously for a linear chain of molecules[4] for which a complete solution can be obtained in terms of the normal modes of the system. For a chain small compared with the wavelength, the natural linewidth is proportional to the number of molecules in the chain (or, for a given spacing, to the length of the chain), whereas for a long chain the width tends to a constant value roughly equal to the number of molecules on a wavelength times the width for incoherent excitation. The problem of obtaining similar results for three-dimensional systems is more difficult because a treatment in terms of the normal modes of the system is not practical.

The study of this problem naturally led us to the investigation of the validity of the *macroscopic* equations in a dielectric for frequencies at or near a resonance frequency of the constituent molecules, and for points inside the medium a distance of the order of the wavelength or less from the boundary of the system. Zaidi[5] has recently discussed the natural linewidth, on the basis of the macroscopic equations, for a gaseous system of spherical external shape large compared with the wavelength. His work will be discussed further in Sec. VII.

Lorentz introduced the idea of obtaining the macroscopic fields by averaging the microscopic fields over "physically infinitesimal" volume elements. Three lengths enter into the problem: the average separation between the molecules, or the lattice spacing, a; the linear dimension of the volume elements over which averages are taken, Δ; and the wavelength *in vacuo* corresponding to the frequency of the incident radiation, λ. For the validity of a macroscopic description it is necessary that these quantities satisfy the inequalities

$$a \ll \Delta \ll \lambda. \tag{1}$$

A detailed exposition of the application of the Lorentz method of averaging to the theory of dispersion, based on Hoek's work,[6] can be found in Rosenfeld's book.[1] In addition to the conditions (1), this "rigorous theory of dispersion" also involves the assumption that each volume element of size Δ can be surrounded by a sphere with a radius of order λ which lies wholly within the medium. This condition limits Hoek's proof of the validity of the macroscopic equations to points inside the medium at least a distance of order λ away from the boundary of the system. For frequencies sufficiently far removed from resonances, this restriction poses no problem at infrared and visible frequencies, although it is clearly undesirable for microwave and radio frequencies. However, at or near a resonance, the macroscopic fields can vary appreciably over distances of the order of magnitude λ at the boundary, and the adequacy of a macroscopic description has therefore not been established for such problems by Hoek's analysis. Vlieger[7] has recently given an improved derivation of the macroscopic equations based only on the conditions (1) and avoiding the expansion in powers of the polarizability employed by Hoek, which is also questionable at or near a resonance. Vlieger's derivation is based on a transformation of certain lattice sums involving the retarded dipolar fields according to the method of Nyboer and de Wette.[8] Unfortunately, this method is rather cumbersome for the

present problem, and the physical interpretation of the resulting expressions (especially those involving sums over the reciprocal lattice), is obscure, but will be clarified in this paper. We present here an alternative derivation, employing Russakoff's method[9] of introducing a smooth weight function of range Δ to carry out the required averaging, but avoiding entirely the transformation of the lattice sums into strongly convergent ones. This goal is accomplished by deriving directly an expression for the constitutive relation between the macroscopic field $\vec{E}(\vec{R})$ and the polarization $\vec{P}(\vec{R})$, rather than first deriving an equation for $\vec{P}(\vec{R})$ alone, which is the standard method. The integral equation for $\vec{P}(\vec{R})$ is obtained by combining our constitutive relation with the macroscopic Maxwell equations which follow immediately on the basis of Russakoff's averaging procedure.[9] The expressions we derive admit of a very simple physical interpretation, and Vlieger's lattice sums are shown to reduce exactly to our simple expressions. Finally, it is apparent from our derivation that the constitutive relation is correct at all points within the dielectric except in a surface layer of thickness Δ, where Δ satisfies the inequalities (1), which is negligible on a macroscopic scale.

A different method of deriving the macroscopic equations was pioneered by Mazur and Nyboer,[10] who averaged the microscopic field at a given point in space with the help of a statistical distribution function. For a gaseous or liquid system the resulting average is a smooth function of position and time, which can be identified with the corresponding macroscopic quantity, and for such systems this method is appropriate. However, for a solid the statistical average of the microscopic field at a given point is still a strongly varying function of position within the unit cell, and to obtain the macroscopic field an additional space average over a unit cell must be performed. Thus for the problems of interest here the statistical method offers no advantages.

Fundamental to the concept of describing the electromagnetic properties of a macroscopic body by a macroscopic theory based on field averaging is, of course, the assumption that the dipole moments induced by the external field vary little over distances of the order of magnitude Δ. In the opposite case, the macroscopic polarization $\vec{P}(\vec{R})$ cannot be expected to give an adequate description of the properties of the system, just as the over-all magnetization $\vec{M}(\vec{R})$ does not adequately describe the properties of an antiferromagnetic system. We shall demonstrate the possibility that in a resonant dielectric, in the absence of sufficient real damping, the dipole moments attain a

staggered, or antiferromagneticlike, arrangement at certain frequencies. For want of a better term, we call this behavior, where the dipole moments vary greatly over a few lattice spacings, antiresonant. On the basis of a microscopic example, we predict that for pure radiative damping there always exist frequencies where such antiresonant behavior occurs and where the macroscopic description of the response of the system breaks down.

In Sec. II we discuss within the framework of semiclassical radiation theory the form of the molecular polarizability at frequencies where radiative damping is important. In Sec. III we present our derivation of the constitutive relation for a simple dielectric crystal. This is combined in Sec. IV with the macroscopic Maxwell equations to yield the dispersion integral equation and the Lorentz-Lorenz relation. In Sec. V the limits of validity of the macroscopic theory are discussed. The resonant and anitresonant scattering from a pair of interacting molecules is treated in Sec. VI. The scattering from macroscopic resonant dielectrics in the form of a sphere and a slab is discussed in Sec. VII. Finally, in Sec. VIII some concluding remarks are made.

II. RADIATION DAMPING AND THE MOLECULAR POLARIZABILITY

For an isotropic harmonic oscillator of mass m, charge q, and resonance frequency ω_0, the equations of motion in the presence of a given external field $\vec{e}(t)$ are[1]

$$m(\ddot{\vec{r}} + \omega_0^2 \vec{r} - \gamma \dddot{\vec{r}}) = q\vec{e}(t) , \qquad (2)$$

where

$$\gamma = (2q^2/3mc^3) \qquad (3)$$

is the radiation-damping constant. Equation (2) can be interpreted in two ways. As written, the term $m\gamma\dddot{\vec{r}}$ in Eq. (2) is regarded as the radiative damping force, the nature of which, just as for the elastic force $-m\omega_0^2\vec{r}$, is not indicated explicitly. However, this damping force is, of course, always due to the electric field created by the charge q itself, the self-field, and Eq. (2) can therefore also be written in the equivalent form,[11]

$$m(\ddot{\vec{r}} + \omega_0^2\vec{r}) = q[\vec{e}(t) + \vec{e}_r] , \qquad (4)$$

where

$$\vec{e}_r = (2q/3c^3)\dddot{\vec{r}} \qquad (5)$$

is the radiative part of the self-field. The part of the self-field in phase with the oscillator gives rise to a self-energy which is assumed to be eliminated by renormalization. Thus in Eq. (4)

one regards the oscillator as undamped but acted upon by the total field equal to the sum of the external field and the self-field.

Corresponding to the two ways of writing the equation of motion, one can introduce two polarizabilities, α and α_0. For a harmonically varying external field of frequency ω,

$$\vec{e}(t) = \text{Re}[\vec{e}_0 e^{-i\omega t}] , \qquad (6)$$

the steady-state amplitude of the dipole moment obtained from Eq. (2) is given by

$$\vec{\mu}(\omega) = \alpha(\omega)\vec{e}_0 , \qquad (7)$$

where

$$\alpha(\omega) = \frac{\frac{3}{2}c^3\gamma}{\omega_0^2 - \omega^2 - i\gamma\omega^3} . \qquad (8)$$

When this same dipole moment is calculated from Eq. (4), one obtains

$$\vec{\mu}(\omega) = \alpha_0(\omega)(\vec{e}_0 + \vec{e}_r) , \qquad (9)$$

where

$$\alpha_0(\omega) = \frac{\frac{3}{2}c^3\gamma}{\omega_0^2 - \omega^2} . \qquad (10)$$

The expressions (7) and (9) for the induced dipole moment are identical, and the two polarizabilities are connected by the equation

$$\alpha(\omega)^{-1} = \alpha_0(\omega)^{-1} - \frac{2}{3}i(\omega/c)^3 . \qquad (11)$$

The validity of this relation is not restricted to a harmonic oscillator but is generally valid.

We now consider a molecule in its ground state $|a\rangle$ having excited states $|b\rangle$ with excitation energies $\hbar\omega_{ab} = E_b - E_a$ and interacting with the electromagnetic field through the electric dipole interaction. In the presence of an external field $\vec{e}(t)$, given by Eq. (6) and switched on adiabatically in the past, the state of the molecule at the time t, $|t\rangle$, can be obtained by standard perturbation theory from the Schrödinger equation

$$i\hbar \frac{d}{dt} |t\rangle = [H_0 - \vec{\mu} \cdot (\vec{e} + \vec{e}_r)] |t\rangle , \qquad (12)$$

where H_0 is the Hamiltonian of the free molecule and $\vec{e} + \vec{e}_r$ is the total field at the position of the molecule and is equal to the sum of the external field and the field produced by the molecule itself.[12] In the approximation of semiclassical radiation theory, we replace the self-field by the field created by the expectation value $\vec{\mu}(t) = \langle t|\vec{\mu}|t\rangle$ of the dipole moment in the state $|t\rangle$. This field contains a part in phase with $\vec{\mu}(t)$ which we assume to be eliminated by renormalization, and a radiative part which has the value

$$\vec{e}_r = (2/3c^3)\dddot{\vec{\mu}}(t) \qquad (13)$$

at the position of the molecule. Performing the perturbation calculation on Eq. (12), we obtain for the Fourier amplitude of $\vec{\mu}(t)$,

$$\vec{\mu}(\omega) = \alpha_0(\omega)[\vec{e}_0 + \tfrac{2}{3}ik^3\vec{\mu}(\omega)] \,, \tag{14}$$

where

$$\alpha_0(\omega) = \frac{e^2}{m_e} \sum_b{}' \frac{f_{ab}}{\omega_{ab}^2 - \omega^2} \,, \tag{15}$$

and f_{ab} is the oscillator strength of the resonance defined by

$$(e^2/m_e)f_{ab} = (2\omega_{ab}/\hbar)\,|\langle b\,|\,\vec{\mu}\,|\,a\rangle|^2 \,, \tag{16}$$

e and m_e being the charge and mass of an electron. We have assumed for simplicity that $\alpha_0(\omega)$ is isotropic. The result (14) can also be written in the form

$$\vec{\mu}(\omega) = \alpha(\omega)\vec{e}_0 \,, \tag{17}$$

where $\alpha(\omega)$ is related to $\alpha_0(\omega)$ by Eq. (11).

For a two-level system there is only one resonance at $\omega_0 = \omega_{ab}$. From Eqs. (11) and (15) we get for such a system

$$\alpha(\omega) = \frac{e^2}{m_e} \frac{f_0}{\omega_0^2 - \omega^2 - i\gamma\omega^3} \,, \tag{18}$$

where γ is given by Eq. (3) with $(q^2/m) = (e^2/m_e)f_0$,

$$\gamma = (2e^2/3m_ec^3)f_0 \,. \tag{19}$$

We note that for a multilevel system the polarizability $\alpha(\omega)$ is not equal to a sum of terms of the form (18), but is given by Eqs. (11) and (15). For such a system it is often a good approximation to assume that near a resonance the quantity $\alpha_0(\omega)$ is equal to

$$\alpha_0(\omega) = \alpha_\infty + \frac{e^2}{m_e} \frac{f_0}{\omega_0^2 - \omega^2} \,, \tag{20}$$

where α_∞ is the contribution from the high-frequency resonances, which may be assumed to be constant. The corresponding polarizability $\alpha(\omega)$ is given by Eqs. (11) and (20) and is not equal to a constant term plus a resonance term of the form (18). Finally, we remark that it is, of course, possible to introduce in a phenomenological way the effect of dissipative processes, such as phonon damping, by including a term $-i\omega\Gamma$ in the resonance denominators of $\alpha_0(\omega)$.

The expression (19) for γ is appropriate for a single molecule located in empty space, which can freely radiate. It is also correct for a system of molecules in empty space, provided one calculates the dipole moment induced in a given molecule by multiplying the polarizability α by the local field at the molecule, which is equal to the external field plus the field due to all the other molecules.

In general the value of γ depends on the boundary conditions at large distances from the molecule. We will always assume boundary conditions appropriate for free space.

III. DERIVATION OF THE CONSTITUTIVE RELATION

We consider a finite, three-dimensional crystal of arbitrary shape, consisting of N identical molecules fixed at the sites $\vec{R}_i$ $(i = 1, \ldots, N)$ of a simple Bravais lattice. The volume of a unit cell is denoted by v and the number of molecules per unit volume by ρ, so that $\rho v = 1$. We also define a length a of the order of magnitude of the lattice spacing, by the relation $v = a^3$. The molecules are characterized by an isotropic polarizability $\alpha(\omega)$, as discussed in Sec. II, and interact with each other only via the retarded dipole-dipole interaction. The effect of interactions of shorter range will be briefly discussed later.

In the presence of an external field of definite frequency ω,

$$\vec{E}_0(\vec{R}, t) = \mathrm{Re}[\vec{E}_0(\vec{R})e^{-i\omega t}] \,, \tag{21}$$

the amplitudes $\vec{\mu}_i(\omega)$ of the dipole moments induced in the molecules in the stationary state corresponding to the presence of the field (21) satisfy the "molecular" equations[1]

$$\vec{\mu}_i(\omega) = \alpha(\omega)\left(\vec{E}_0(\vec{R}_i) + \sum_j{}' \vec{F}(\vec{R}_i - \vec{R}_j) \cdot \vec{\mu}_j(\omega)\right) \,, \tag{22}$$

where the prime indicates $j \neq i$, and

$$\vec{F}(\vec{R}_i - \vec{R}_j) \cdot \vec{\mu}_j = \vec{\nabla}_i \times \vec{\nabla}_i \times (\vec{\mu}_j e^{ikR_{ij}}/R_{ij}) \,, \tag{23}$$

is the total electric field at $\vec{R}_i$ due to the dipole $\vec{\mu}_j$ and $\vec{R}_j$. We have set $R_{ij} = |\vec{R}_{ij}|$, $\vec{R}_{ij} = \vec{R}_i - \vec{R}_j$, and $k = (\omega/c)$. Following Russakoff[9] and Vlieger,[7] we define the macroscopic polarization $\vec{P}(\vec{R})$ by

$$\vec{P}(\vec{R}) = \int \Delta(\vec{R}' - \vec{R}) \sum_i \vec{\mu}_i \delta(\vec{R}' - \vec{R}_i)\, d\vec{R}'$$

$$= \sum_i \Delta(\vec{R}_i - \vec{R})\vec{\mu}_i \,, \tag{24}$$

where $\Delta(\vec{R}' - \vec{R})$ is a suitable weight function satisfying the normalization condition

$$\int \Delta(\vec{R}' - \vec{R})\, d\vec{R}' = 1 \tag{25}$$

and having a width Δ satisfying the inequalities (1). Our derivation is independent of the exact shape of the function $\Delta(\vec{R}' - \vec{R})$ and it is not necessary to assume a specific analytic form for this function. From Eqs. (22) and (24), we obtain for

interior points $\vec{R}$ at least a distance Δ inside the surface,

$$\alpha^{-1}\vec{P}(\vec{R}) = \rho\vec{E}_0(\vec{R})$$
$$+ \sum_i \Delta(\vec{R}_i - \vec{R}) \sum_j{}' \vec{F}(\vec{R}_i - \vec{R}_j) \cdot \vec{\mu}_j ,$$
(26)

where we have used the condition $k\Delta \ll 1$ in the first term.

The essential point of our method is not to evaluate the right-hand side of Eq. (26) directly, but to consider first the corresponding expression for the macroscopic $\vec{E}$ field in terms of the appropriate molecular quantities. Let $\vec{e}(\vec{R})$ be the microscopic (Lorentz) field at the point $\vec{R}$ due to all the molecules. The field $\vec{e}(\vec{R})$ is defined both outside and inside the molecular charge distributions. The limit to point molecules will be taken at the appropriate stages of the derivation. In terms of the field $\vec{e}(\vec{R})$, the macroscopic (Maxwell) field is given by

$$\vec{E}(\vec{R}) = \vec{E}_0(\vec{R}) + \int \Delta(\vec{R}' - \vec{R})e(\vec{R}')\, d\vec{R}' .$$
(27)

One may also average the incident field and regard the first term in Eq. (27) as an approximation which is then exactly equal to the first term in Eq. (26). However, we prefer to regard the incident field as a macroscopic field and to define the Maxwell field $\vec{E}$ as in Eq. (27). Since $a \ll \Delta$, we may write Eq. (27) in the form

$$\vec{E}(\vec{R}) = \vec{E}_0(\vec{R}) + v \sum_i \Delta(\vec{R}_i - \vec{R})\vec{e}_{av}(\vec{R}_i) ,$$
(28)

where $\vec{e}_{av}(\vec{R}_i)$ is the unweighted average of $\vec{e}(\vec{R})$ over a cell of volume v surrounding the point $\vec{R}_i$. The cells are chosen in such a way that in an infinite crystal they would fill out all of space. For convenience we choose Wigner-Seitz cells centered at the points $\vec{R}_i$, and we write

$$v\vec{e}_{av}(\vec{R}_i) = \int_0^v \vec{e}(\vec{R}_i + \vec{r}_i)\, d\vec{r}_i ,$$
(29)

where $\vec{r}_i$ is a position vector relative to $\vec{R}_i$ as origin, and the integral extends over the ith cell. Let $\vec{e}_i(\vec{r}_i)$ be the field in cell i due to the charge distribution of the molecule i in that cell, the "self-field". Then we can write

$$v\vec{e}_{av}(\vec{R}_i) = \int_0^v \vec{e}_i(\vec{r}_i)\, d\vec{r}_i$$
$$+ \sum_j{}' \int_0^v \vec{F}(\vec{R}_i + \vec{r}_i - \vec{R}_j) \cdot \vec{\mu}_j\, d\vec{r}_i , \quad (30)$$

where in the second term we have taken the limit

to point dipoles. Our main problem is the evaluation of the terms in the right-hand side of Eq. (30), which can be done in a straightforward way using only the conditions (1).

The evaluation of the self-field term in Eq. (30) is facilitated by introducing the Hertz vector of the field produced by the molecule. For a general charge-current distribution, we introduce the polarization potential $\vec{p}(\vec{r})$ by writing

$$\rho(\vec{r}) = -\vec{\nabla} \cdot \vec{p}(\vec{r}), \quad \vec{j}(\vec{r}) = \dot{\vec{p}}(\vec{r}) .$$
(31)

The Hertz vector produced by this charge-current distribution is

$$\vec{\Pi}(\vec{r}) = \int \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|}\, \vec{p}(\vec{r}')\, d\vec{r}' ,$$
(32)

and the electric component of the field is given by

$$\vec{e}(\vec{r}) = \vec{\nabla} \times \vec{\nabla} \times \vec{\Pi}(\vec{r}) - 4\pi\vec{p}(\vec{r}) .$$
(33)

For the total dipole moment $\vec{\mu}$ of the charge distribution $\rho(\vec{r})$, we obtain by partial integration

$$\vec{\mu} = \int \vec{r}\rho(\vec{r})\, d\vec{r} = \int \vec{p}(\vec{r})\, d\vec{r} .$$
(34)

The Hertz vector outside the charge distribution of a source having only an electric dipole moment is given by the point-dipole approximation

$$\vec{\Pi}(\vec{r}) = (e^{ikr}/r)\vec{\mu} .$$
(35)

To calculate the integral of the self-field over the Wigner-Seitz cell, we inscribe a sphere in cell i with $\vec{R}_i$ as center and touching the nearest faces of the cell. When the limit to point molecules is taken, the radius of this sphere may be taken arbitrarily small, the only condition being that the molecule lies wholly inside the sphere, so that Eq. (34) can be used. For finite molecules it is least restrictive and hence preferable to choose as large a sphere as possible and this we will do. The volume of this sphere is denoted by v_s. We split the integral over the cell appearing in the first term in Eq. (30) into an integral over the sphere and an integral over the remainder of the cell,

$$\int_0^v \vec{e}_i(\vec{r})\, d\vec{r} = \int_0^{v_s} \vec{e}_i(\vec{r})\, d\vec{r} + \int_{v_s}^v \vec{e}_i(\vec{r})\, d\vec{r} ,$$
(36)

where we have replaced $\vec{r}_i$ by $\vec{r}$ for notational convenience. Using Eq. (33) for $\vec{e}_i(\vec{r})$, and assuming that the central molecule lies wholly within the sphere, we obtain

$$\int_0^{v_s} \vec{e}_i(\vec{r})\, d\vec{r} = \int_{v_s} d\vec{S} \times (\vec{\nabla} \times \vec{\Pi}) - 4\pi\vec{\mu}_i .$$
(37)

where $d\vec{S}$ is an outwardly directly surface element on the sphere. Using the point-dipole expression (35) for the Hertz vector on the surface of the sphere, we get

$$\int_0^{v_s} \vec{e}_i(\vec{r})\, d\vec{r} = \tfrac{8}{3}\pi e^{ikr_s}(1 - ikr_s)\vec{\mu}_i - 4\pi\vec{\mu}_i , \qquad (38)$$

where r_s is the radius of the sphere. Since $kr_s \lesssim ka \ll 1$, it is normally sufficient to retain only the first nonvanishing terms in the real and imaginary parts in Eq. (38) in an expansion in powers of kr_s, giving

$$\int_0^{v_s} \vec{e}_i(\vec{r})\, d\vec{r} = -\tfrac{4}{3}\pi\vec{\mu}_i + \tfrac{2}{3}ik^3 v_s\vec{\mu}_i . \qquad (39)$$

Under exceptional circumstances the approximation (39) is not adequate and one must then go back to the full expression (38), as will be discussed in Sec. VI.

The second term in Eq. (36) in the limit of a point dipole is equal to

$$\int_{v_s}^{v} \vec{e}_i(\vec{r})\, d\vec{r} = \int_{v_s}^{v} \vec{F}(\vec{r}) \cdot \vec{\mu}_i\, d\vec{r} . \qquad (40)$$

To first nonvanishing order in an expansion in powers of kr of the real and imaginary parts, we have

$$\vec{F}(\vec{r}) \cdot \vec{\mu} = \vec{T}(\vec{r}) \cdot \vec{\mu} + \tfrac{2}{3}ik^3\vec{\mu} + \ldots , \qquad (41)$$

where

$$\vec{T}(\vec{r}) \cdot \vec{\mu} = \vec{\nabla} \times \vec{\nabla} \times r^{-1}\vec{\mu} , \qquad (42)$$

is the unretarded dipole field. This field can be expressed in terms of the dipole potential ϕ_d,

$$\vec{T}(\vec{r}) \cdot \vec{\mu} = -\vec{\nabla}\phi_d = -\vec{\nabla}(r^{-3}\vec{\mu} \cdot \vec{r}) . \qquad (43)$$

Using Eqs. (41) and (43) in (40), we obtain

$$\int_{v_s}^{v} \vec{e}_i(\vec{r})\, d\vec{r} = \tfrac{2}{3}ik^3(v - v_s) - \int_v \phi_d\, d\vec{S} + \int_{v_s} \phi_d\, d\vec{S} . \qquad (44)$$

The surface integrals depend only on the shape of the surfaces and not on their size. For the sphere we have

$$\int_{v_s} \phi_d\, d\vec{S} = \tfrac{4}{3}\pi\vec{\mu} , \qquad (45)$$

and for the cell we define a tensor $\vec{s}$ such that

$$\int_v \phi_d\, d\vec{S} = \tfrac{4}{3}\pi\vec{\mu} + \tfrac{4}{3}\pi\vec{s} \cdot \vec{\mu} . \qquad (46)$$

The tensor $\vec{s}$ depends on the shape of the Wigner-Seitz cell of the crystal but need not be evaluated, since it will be cancelled by a similar contribution coming from another source [cf. Eq. (62)]. Collecting the above results, we obtain the following expression for the integral of the self-field over the Wigner-Seitz cell:

$$\int_0^{v} \vec{e}_i(\vec{r}_i)\, d\vec{r}_i = -\tfrac{4}{3}\pi\vec{\mu}_i + \tfrac{2}{3}ik^3 v\vec{\mu}_i - \tfrac{4}{3}\pi\vec{s} \cdot \vec{\mu}_i . \qquad (47)$$

The imaginary term in Eq. (47) represents the retarded component of the average field in the cell and gives a significant contribution to the macroscopic field, as will be shown presently. In general, it is therefore not sufficient to consider only the contribution of the "near" or "static" field from the oscillating dipole in its own cell to the macroscopic field.

We now turn to the evaluation of the second term in Eq. (30). The quantity

$$\vec{d}(\vec{r}_i) = \sum_j {}' \vec{F}(\vec{R}_i + \vec{r}_i - \vec{R}_j) \cdot \vec{\mu}_j \qquad (48)$$

is the field in cell i due to the dipoles $\vec{\mu}_j$ lying outside this cell. We introduce a sphere S with $\vec{R}_i$ as center and a radius of the order of magnitude Δ satisfying Eq. (1), and we split the sum over j in Eq. (48) into two parts, corresponding to the dipoles inside and those outside of S:

$$\sum_j {}' = \sum_{j<S} {}' + \sum_{j>S} .$$

For the dipoles outside of S, we have

$$|\vec{r}_i/R_{ij}| \lesssim a/\Delta \ll 1 ,$$

and one may therefore assume that the field due to these dipoles is uniform over cell i, so that

$$\sum_{j>S} \vec{F}(\vec{R}_i + \vec{r}_i - \vec{R}_j) \cdot \vec{\mu}_j = \sum_{j>S} \vec{F}(\vec{R}_i - \vec{R}_j) \cdot \vec{\mu}_j \qquad (49)$$

in the limit $ka \ll 1$. We note that the retardation of the field due to these dipoles is fully taken into account in this limit. For the dipoles inside S we have

$$k|\vec{R}_i + \vec{r}_i - \vec{R}_j| \lesssim k\Delta \ll 1$$

for all values of $\vec{r}_i$ within cell i. For the fields due to these dipoles we may therefore use the approximation (41) for $\vec{F}(\vec{R}_i + \vec{r}_i - \vec{R}_j)$. For convenience we first split-off a term $\vec{F}(\vec{R}_i - \vec{R}_j)$, and we obtain

$$\sum_{j<S}{}' \vec{F}(\vec{R}_i +\vec{r}_i - \vec{R}_j) \cdot \vec{\mu}_j = \sum_{j<S}{}' \vec{F}(\vec{R}_i - \vec{R}_j) \cdot \vec{\mu}_j + \sum_{j<S} [\vec{T}(\vec{R}_i +\vec{r}_i - \vec{R}_j) - \vec{T}(\vec{R}_i - \vec{R}_j)] \cdot \vec{\mu}_j$$

$$= \sum_{j<S}{}' \vec{F}(\vec{R}_i - \vec{R}_j) \cdot \vec{\mu}_j + \sum_{j<S} \vec{\nabla}_{R_{ij}} \times \vec{\nabla}_{R_{ij}} \times \left(\frac{\vec{\mu}_j}{|\vec{r} +\vec{R}_{ij}|} - \frac{\vec{\mu}_j}{R_{ij}} \right). \quad (50)$$

By expanding the quantity $|\vec{r} +\vec{R}_{ij}|^{-1}$ in powers of $\vec{r}$, we see that the last term in Eq. (50) falls off at large values of R_{ij} as R_{ij}^{-4}. We may therefore replace the sum over the dipoles inside S by an unrestricted sum, giving

$$\sum_{j<S}{}' \vec{F}(\vec{R}_i +\vec{r}_i - \vec{R}_j) \cdot \vec{\mu}_j$$

$$= \sum_{j<S}{}' \vec{F}(\vec{R}_i - \vec{R}_j) \cdot \vec{\mu}_j + \sum_j{}' [\vec{T}(\vec{R}_i +\vec{r}_i - \vec{R}_j)$$

$$- \vec{T}(\vec{R}_i - \vec{R}_j)] \cdot \vec{\mu}_j. \quad (51)$$

It should be noted that the imaginary terms coming from using Eq. (41) in Eq. (50) have not been neglected but cancel out. Substituting the results (47), (49), and (51) into Eq. (30), we obtain the following expression for the average of the microscopic field over cell i:

$$\vec{e}_{av}(\vec{R}_i) = -\tfrac{4}{3}\pi\rho\vec{\mu}_i +\tfrac{2}{3}ik^3\vec{\mu}_i -\tfrac{4}{3}\pi\rho\vec{s} \cdot \vec{\mu}$$

$$+ \sum_j{}' [\vec{F}(\vec{R}_i - \vec{R}_j) +\vec{G}(\vec{R}_i - \vec{R}_j)] \cdot \vec{\mu}_j, \quad (52)$$

where the quantity $\vec{G}(\vec{R}_i - \vec{R}_j)$ is defined as

$$\vec{G}(\vec{R}_i - \vec{R}_j) = v^{-1} \int_0^v [\vec{T}(\vec{R}_i +\vec{r}_i - \vec{R}_j)$$

$$- \vec{T}(\vec{R}_i - \vec{R}_j)] d\vec{r}_i, \quad (53)$$

which is clearly a function of $\vec{R}_{ij} = \vec{R}_i - \vec{R}_j$ falling off at large values of R_{ij} as R_{ij}^{-4}.

We now substitute the result (52) into the Eq. (28) for the macroscopic field, giving

$$\vec{E}(\vec{R}) = \vec{E}_0(\vec{R}) +(-\tfrac{4}{3}\pi +\tfrac{2}{3}ik^3v -\tfrac{4}{3}\pi\vec{s} \cdot)\vec{P}(\vec{R})$$

$$+v \sum_i \Delta(\vec{R}_i - \vec{R}) \sum_j{}' [\vec{F}(\vec{R}_i - \vec{R}_j)$$

$$+\vec{G}(\vec{R}_i - \vec{R}_j)] \cdot \vec{\mu}_j. \quad (54)$$

In the last term, we interchange the order of the two summations,

$$\sum_i \Delta(\vec{R}_i - \vec{R}) \sum_j{}' \vec{G}(\vec{R}_i - \vec{R}_j) \cdot \vec{\mu}_j$$

$$= \sum_j \vec{\mu}_j \cdot \sum_i{}' \Delta(\vec{R}_i - \vec{R})\vec{G}(\vec{R}_i - \vec{R}_j). \quad (55)$$

Since $\vec{G}(\vec{R}_i - \vec{R}_j)$ is short ranged, the function $\Delta(\vec{R}_i - \vec{R})$ is essentially constant in the sum over i and may hence be replaced by $\Delta(\vec{R}_j - \vec{R})$. It can then be combined with $\vec{\mu}_j$ to give $\vec{P}(\vec{R})$, so that

$$\sum_i \Delta(\vec{R}_i - \vec{R}) \sum_j{}' \vec{G}(\vec{R}_i - \vec{R}_j) \cdot \vec{\mu}_j$$

$$= \sum_j \vec{\mu}_j\Delta(\vec{R}_j - \vec{R}) \sum_i{}' \vec{G}(\vec{R}_i - \vec{R}_j) = \vec{s} \cdot \vec{P}(\vec{R}), \quad (56)$$

where $\vec{s}$ is defined as

$$\vec{s} = \sum_i{}' \vec{G}(\vec{R}_i - \vec{R}_j) = \sum_j{}' \vec{G}(\vec{R}_i - \vec{R}_j)$$

$$= v^{-1} \int_0^v \sum_j{}' [\vec{T}(\vec{R}_i +\vec{r}_i - \vec{R}_j) - \vec{T}(\vec{R}_i - \vec{R}_j)] d\vec{r}_i, \quad (57)$$

and is independent of $\vec{R}_j$ for points within the medium at least a distance Δ from the surface. The step involved in Eq. (56) is an essential one in making possible a description in terms of the macroscopic polarization $\vec{P}(\vec{R})$ and will be discussed further in Sec. V. Note that this step cannot be carried out in the third term in Eq. (54) containing the long-range function $\vec{F}(\vec{R}_i - \vec{R}_j)$. This term will now be eliminated by using Eq. (26) for $\vec{P}(\vec{R})$. Performing this elimination we obtain the desired constitutive relation between the macroscopic fields $\vec{E}(\vec{R})$ and $\vec{P}(\vec{R})$,

$$\rho\vec{E}(\vec{R}) = (\alpha^{-1} +\tfrac{2}{3}ik^3 -\tfrac{4}{3}\pi\rho -\tfrac{4}{3}\pi\vec{s} \cdot +\vec{s} \cdot)\vec{P}(\vec{R})$$

$$= (\alpha_0^{-1} -\tfrac{4}{3}\pi\rho -\tfrac{4}{3}\pi\rho\vec{s} \cdot +\vec{s} \cdot)\vec{P}(\vec{R}), \quad (58)$$

where we have used the relation (11) between α and α_0.

Before discussing the relation (58), we first derive an alternative expression for the quantity $\vec{s}$, which according to Eqs. (53) and (57) is given by

$$\vec{s} = \sum_j{}' \vec{G}(\vec{R}_i - \vec{R}_j)$$

$$= v^{-1} \sum_j{}' \int_0^v [\vec{T}(\vec{R}_i +\vec{r}_i - \vec{R}_j) - \vec{T}(\vec{R}_i - \vec{R}_j)] d\vec{r}_i. \quad (59)$$

The sum over j of the difference of the two $\vec{T}$ terms in Eq. (59) converges unconditionally and

may be carried out in an infinite crystal, but the sums of the two separate terms do not. To make the values of these separate sums definite, we surround the point $\vec{R}_i$ by a sphere S of volume V_s, restrict the sums over j to the points lying inside j, $j < S$, and take the limit $V_s \to \infty$. In this way we obtain

$$\vec{S} = v^{-1} \lim_{V_s \to \infty} \sum_{j<S}{}' \int_0^v \vec{T}(\vec{R}_i + \vec{r}_i - \vec{R}_j) \, d\vec{r}_i$$

$$- v^{-1} \lim_{V_s \to \infty} \sum_{j<S}{}' \vec{T}(\vec{R}_i - \vec{R}_j). \tag{60}$$

To facilitate the evaluation of the first term in Eq. (60), we introduce a "dummy" dipole moment $\vec{\mu}$ and observe that the quantity $\vec{T}(\vec{R}_i + \vec{r}_i - \vec{R}_j) \cdot \vec{\mu}$ is the field due to a dipole $\vec{\mu}$ at $\vec{R}_j$ at the point $\vec{r}_i$ in cell i. This field is equal to that created by a dipole $\vec{\mu}$ at $\vec{R}_i$ at the point $\vec{r}_{j'} = \vec{r}_i$ in the cell at $\vec{R}_{j'}$, where $\vec{R}_{j'} - \vec{R}_i = -(\vec{R}_j - \vec{R}_i)$, i.e., the pair of cells j', i is obtained from the pair i, j by a lattice translation over the distance $-(\vec{R}_j - \vec{R}_i)$. We therefore have that

$$\sum_{j<S}{}' \int_0^v \vec{T}(\vec{R}_i + \vec{r}_i - \vec{R}_j) \, d\vec{r}_i$$

$$= \sum_{j'<S}{} \int_0^v \vec{T}(\vec{R}_{j'} + \vec{r}_{j'} - \vec{R}_i) \, d\vec{r}_{j'}$$

$$= \sum_{j<S}{}' \int_0^v \vec{T}(\vec{R}_j + \vec{r}_j - \vec{R}_i) \, d\vec{r}_j$$

$$= \int_v^{V_s} \vec{T}(\vec{R} - \vec{R}_i) \, d\vec{R}, \tag{61}$$

where the last integral extends over the sphere S, excluding the cell i at the center. This integral can be evaluated in the same way as was done in Eq. (46), and the result is

$$\int_v^{V_s} \vec{T}(\vec{R} - \vec{R}_i) \, d\vec{R} = \tfrac{4}{3}\pi \vec{s}, \tag{62}$$

where $\vec{s}$ is the same quantity as in Eq. (46). Using the results (61) and (62) in Eq. (60), we get

$$\vec{S} = \tfrac{4}{3}\pi\rho\vec{s} + \vec{K}, \tag{63}$$

where

$$\vec{K} = \lim_{V_s \to \infty} \sum_{j<S}{}' \vec{T}(\vec{R}_i - \vec{R}_j). \tag{64}$$

Using the result (63) in Eq. (58), we obtain the final form of the constitutive relation,

$$\rho\vec{E}(\vec{R}) = [\alpha^{-1} + \tfrac{2}{3}ik^3 - \tfrac{4}{3}\pi\rho - \vec{K} \cdot]\vec{P}(\vec{R})$$

$$= [\alpha_0^{-1} - \tfrac{4}{3}\pi\rho - \vec{K} \cdot]\vec{P}(\vec{R}). \tag{65}$$

To interpret this relation we rewrite it in terms of the average dipole moment of the molecules at the point $\vec{R}$ defined by $\vec{P}(\vec{R}) = \rho\vec{\mu}_{av}(\vec{R})$, giving

$$\vec{\mu}_{av} = \alpha[\vec{E} + \tfrac{4}{3}\pi\vec{P} + \vec{K} \cdot \vec{\mu}_{av} - \tfrac{2}{3}ik^3\vec{\mu}_{av}]. \tag{66}$$

For a static field $(k=0)$, the last term vanishes and the first three terms in the brackets can be interpreted as the average local field at a molecule,

$$\vec{E}_{loc} = \vec{E} + \tfrac{4}{3}\pi\vec{P} + \vec{K} \cdot \vec{\mu}_{av}. \tag{67}$$

The first two terms give the field in a spherical cavity around the central molecule, and according to Eq. (64) the last term gives the field due to dipoles $\vec{\mu}_{av}(\vec{R})$ placed on the lattice sites inside the spherical cavity. This term vanishes for lattices with cubic symmetry but does not vanish for lower symmetry. Because of the rapid convergence of the lattice sum in Eq. (64), the limit to infinite radius of the spherical cavity can be satisfied even for a physically infinitesimal spherical cavity. Thus, Eq. (67) is seen to agree exactly with the standard result for the local field obtained by more heuristic arguments. For $k \neq 0$, we see from Eq. (60) that the expression for the local field is the same as for the static case except for the additional term $-\tfrac{2}{3}ik^3\vec{\mu}_{av}$, the effect of which is clearly to remove from the macroscopic field $\vec{E}$ the average contribution of the field radiated by the central molecule. This contribution must be removed because the polarizability α already contains the effect of the radiative self-damping of the molecule. One can write Eq. (66) in the alternative form

$$\vec{\mu}_{av} = \alpha_0[\vec{E} + \tfrac{4}{3}\pi\vec{P} + \vec{K} \cdot \vec{\mu}_{av}], \tag{68}$$

where $\alpha_0(\omega)$ is the polarizability of the molecule in the absence of the self-damping. Although the quantity $\alpha_0(\omega)$ becomes infinite at a resonance frequency, the dipole moment obtained from Eq. (68) remains finite by virtue of the contribution of the self-field to the macroscopic field $\vec{E}$. The fact that the dipole moments remain finite is more directly evident from Eq. (66), $\alpha(\omega)$ being finite at all frequencies.

We close this section by making a few remarks about the region of validity of the constitutive relation (65) derived here and discussed further in Sec. V. First of all, Eq. (65) is valid at all interior points at least a distance Δ away from the surface. Since Δ is infinitesimal on a macroscopic scale, Eq. (65) is a valid macroscopic relation throughout the dielectric, even if the fields vary appreciably in a surface layer of thickness of order λ, or if the over-all size of the system is of the order of, or smaller than, λ but, of course, large compared to Δ. Secondly, our

derivation of Eq. (65) is not based on an expansion in powers of $\alpha(\omega)$, and hence is expected to hold for all frequencies and for arbitrary values of $\alpha(\omega)$. However, this is not actually true, and for the model of the resonant dielectric considered here, the constitutive relation (65) is valid at all frequencies only in the presence of a sufficiently strong real damping, as will be shown in more detail in Sec. V.

IV. MACROSCOPIC INTEGRAL EQUATIONS AND THE LORENTZ-LORENZ RELATION

The macroscopic fields $\vec{P}(\vec{R})$ and $\vec{E}(\vec{R})$ defined by Eqs. (24) and (27), respectively, can be easily shown[9] to satisfy the Maxwell equations, which for the dielectric systems considered here take the following form:

$$\vec{\nabla} \cdot \vec{E} = -4\pi \vec{\nabla} \cdot \vec{P}, \quad \vec{\nabla} \cdot \vec{B} = 0,$$
$$c\vec{\nabla} \times \vec{H} = \dot{\vec{E}} + 4\pi \dot{\vec{P}}, \quad c\vec{\nabla} \times \vec{E} = -\dot{\vec{B}}, \tag{69}$$

where $\vec{H} = \vec{B}$. We define as usual

$$\vec{D} = \vec{E} + 4\pi \vec{P} = \vec{\epsilon} \cdot \vec{P}. \tag{70}$$

The tensor $\vec{\epsilon}$ is diagonal, $\epsilon_{ij} = \epsilon_i \delta_{ij}$, in the same frame in which the internal field tensor $\vec{K}$, defined by Eq. (64), is diagonal, $K_{ij} = K_i \delta_{ij}$. Using this frame, and reverting to the time Fourier transforms of the fields, we obtain from Eqs. (65) and (70),

$$\frac{\epsilon_i - 1}{\epsilon_i + 2} = \frac{4\pi}{3} \rho (\alpha_0^{-1} - K_i)^{-1}. \tag{71}$$

For a crystal with cubic symmetry, we have $K_i = 0$, and the relation for $\epsilon_i = \epsilon$ then reduces to

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \rho \alpha_0.$$

From Eq. (69) it can be shown by standard methods that the fields $\vec{E}(\vec{R})$ and $\vec{P}(\vec{R})$ set up in the medium by the external field (21) are related by the equation

$$\vec{E}(\vec{R}) = \vec{E}_0(\vec{R}) - \tfrac{4}{3}\pi \vec{P}(\vec{R}) + \vec{E}_d(\vec{R}), \tag{72}$$

where

$$\vec{E}_d(\vec{R}) = \int_{\epsilon(\vec{R})}^{V} \vec{F}(\vec{R} - \vec{R}') \cdot \vec{P}(\vec{R}') d\vec{R}', \tag{73}$$

the integration being over the entire medium excluding an infinitesimal sphere around the point $\vec{R}$. Neither the Maxwell equations (69) nor the integral equation (72) contains any information about the constitutive relation characterizing the properties of the medium. We can obtain the integral equation for $\vec{P}(\vec{R})$ alone by eliminating $\vec{E}(\vec{R})$ between Eqs. (65) and (72), giving

$$(\alpha^{-1} + \tfrac{2}{3}ik^3 - \vec{K} \cdot)\vec{P}(\vec{R}) = (\alpha_0^{-1} - \vec{K} \cdot)\vec{P}(\vec{R})$$
$$= \rho[\vec{E}_0(\vec{R}) + \vec{E}_d(\vec{R})]. \tag{74}$$

This is the basic integral equation of dispersion theory, from which the extinction theorem and the Lorentz-Lorenz relation may be derived in the usual way.[1] This is a specific example of the more general result that the extinction theorem is contained in the Maxwell equations and the constitutive relations, as has recently been shown by Sein and others.[13] We can therefore identify the index of refraction with $n = \epsilon^{1/2}$, and for cubic symmetry we thus get

$$\frac{n^2 - 1}{n^2 + 1} = \frac{4\pi}{3} \rho \alpha_0. \tag{75}$$

Let us first compare Eq. (74) with the standard result as given by Rosenfeld,[14] which in our notation reads

$$(\alpha_0^{-1} - \tfrac{2}{3}ik^3 - \vec{D} \cdot)\vec{P}(\vec{R}) = \rho[\vec{E}_0(\vec{R}) + \vec{E}_d(\vec{R})], \tag{76}$$

where

$$\vec{D} \cdot \vec{P}(\vec{R}) = \int_{\epsilon(\vec{R})}^{V} g(r) \vec{F}(\vec{R} - \vec{R}') \cdot \vec{P}(\vec{R}') d\vec{R}', \tag{77}$$

where $r = |\vec{R} - \vec{R}'|$, and $g(r)$ is the pair correlation function. For a crystal, the real and imaginary parts of $\vec{D}$ reduce to $\vec{K}$ and $-\tfrac{2}{3}ik^3$, respectively, and Eq. (76) then reduces to Eq. (74). For a perfect gas, on the other hand, one has $g(r) = 0$, and hence $\vec{D} = 0$. The remaining imaginary term on the left-hand side of Eq. (76) gives rise to an imaginary part in the dielectric constant ϵ and hence to the appearance of extinction in the solutions of the macroscopic equations (69) and (76) even in the absence of any real damping ($\Gamma = 0$, α_0 real). This extinction is due to the energy dissipated by the radiative reaction forces, which is found back in the real system in the diffusely scattered light. However, in the macroscopic theory as given by Eqs. (69) and (76), this scattered radiation is absent and only the scattered field due to diffraction is obtained. In general, the macroscopic theory therefore does not satisfy the law of energy conservation. In spite of this defect, the extinction of the radiation due to the diffuse scattering is given correctly by the macroscopic equations. The diffusely scattered field has a random phase due to the thermal motion of the molecules, and its average value at any given point in space and time therefore vanishes and does not make any contribution to the macroscopic field defined as $\vec{E} = \langle \vec{e} \rangle$, where the brackets indicate a time or ensemble averaging appropriate for a fluid system.[10] For the diffuse component $\vec{e}_d$ of the microscopic field, we have $\langle \vec{e}_d \rangle = 0$, but $\langle \vec{e}_d \cdot \vec{e}_d \rangle \neq 0$. We remark that it is not

correct to maintain that diffuse scattering is an exclusively microscopic phenomenon, since the *intensity* of the scattered light is certainly a macroscopic observable, just as, for example, the contribution of the thermal motion of the molecules to the total internal energy in thermodynamics. For a more detailed account of the phenomenological description of diffuse light scattering in the

macroscopic theory we refer to the literature.[15]

We now compare our result (74) with the corresponding equation derived by Vlieger,[7] which in our notation reads

$$(\alpha^{-1} + \vec{\vec{G}} \cdot)\vec{P}(\vec{R}) = \rho[\vec{E}_0(\vec{R}) + \vec{E}_d(\vec{R})] . \tag{78}$$

The quantity $\vec{\vec{G}}$ is given by

$$\vec{\vec{G}} = \sum_{\lambda}{}' \vec{\vec{T}}_3(\vec{r}_\lambda) \operatorname{erfc}\left(\frac{\pi^{1/2} r_\lambda}{a}\right) + \frac{2}{a} \sum_{\lambda}{}' \vec{\vec{T}}_2(r_\lambda) e^{-\pi r_\lambda^2/a^2} - \frac{4\pi}{a^3} \sum_{\lambda}{}' \frac{\vec{r}_\lambda \vec{r}_\lambda}{r_\lambda^2} e^{-\pi r_\lambda^2/a^2} - \sum_{\lambda}{}' \frac{\vec{h}_\lambda \vec{h}_\lambda}{h_\lambda^2} e^{-\pi a^2 h_\lambda^2} , \tag{79}$$

where $\vec{h}_\lambda = 2\pi \vec{k}_\lambda$ is a reciprocal lattice vector, and

$$\vec{\vec{T}}_3(\vec{r}) = r^{-1} \vec{\vec{T}}_2(\vec{r}) = -\vec{\vec{T}}(\vec{r}) = r^{-3}(\vec{\vec{U}} - 3\vec{r}\vec{r}/r^2) , \tag{80}$$

$\vec{\vec{T}}(\vec{r})$ giving the unretarded dipole field according to Eq. (42). From the presence of $\vec{\vec{T}}_2$ and the reciprocal lattice sum in Eq. (79), it might appear that retardation effects are included in $\vec{\vec{G}}$ and that, therefore, Eq. (78) is more rigorous than the standard result (74). This is not so, however, and the quantity $\vec{\vec{G}}$ is in fact exactly equal to our quantity $-\vec{\vec{K}}$, the unretarded dipole sum,

$$\vec{\vec{G}} = \lim_{v_s \to \infty} \sum_{\lambda < s}{}' \vec{\vec{T}}_3(\vec{r}_\lambda) = -\vec{\vec{K}} , \tag{81}$$

as is shown in the Appendix. The only difference between Eqs. (74) and (78) is thus the radiation damping term $-\frac{2}{3} i k^3$ in the first member in Eq. (74), which has been neglected by Vlieger, but which can be obtained in his formalism by retaining the appropriate higher-order terms.[16]

V. LIMITS OF VALIDITY OF THE MACROSCOPIC EQUATIONS

Assuming for simplicity a molecular polarizability of the resonance form of Eq. (8), with a dissipative damping term Γ added,

$$\alpha(\omega) = \frac{\frac{3}{2} c^3 \gamma}{\omega_0^2 - \omega^2 - i\omega^3 \gamma - i\omega\Gamma} , \tag{82}$$

we obtain from Eqs. (11) and (76) the following expression for the Lorentz-Lorenz relation for a crystal with cubic symmetry,

$$\frac{n^2 - 1}{n^2 + 2} = \frac{2\pi\rho c^3 \gamma}{\omega_0^2 - \omega^2 - i\omega\Gamma} . \tag{83}$$

The corresponding susceptibility χ is given by

$$\chi = \frac{n^2 - 1}{4\pi} = \frac{\frac{3}{2} \rho c^3 \gamma}{\omega_s^2 - \omega^2 - i\omega\Gamma} , \tag{84}$$

where

$$\omega_s^2 = \omega_0^2 - 2\pi\rho c^3 \gamma \tag{85}$$

is the "susceptibility" resonance frequency result-

ing from the internal field effect. The generalization to noncubic symmetry is straightforward and will not be discussed explicitly.

From Eq. (84) for the susceptibility it is seen that n is very large for ω at and near ω_s. Since in the macroscopic theory the variation of the average dipole moments with position is characterized by a wavelength equal to λ/n, where $\lambda/2\pi = c/\omega$, the macroscopic equations predict that for frequencies sufficiently close to ω_s the average dipole moments vary rapidly over distances of the order of a few lattice spacings. For $\Gamma = 0$, Eq. (84) even predicts that n becomes infinite at $\omega = \omega_s$, which is clearly unphysical. This breakdown of the macroscopic equations at and near ω_s is not due to any inconsistency in the microscopic model but occurs because the derivation of the constitutive relation (65) is based on the assumption that the dipole moments vary little over distances of the order of the lattice spacing. In our opinion it is highly likely that, for $\Gamma = 0$, there are always frequencies for which the dipole moments in the actual system assume a staggered, or antiferromagneticlike, arrangement with a period of the order of the lattice spacing. A macroscopic description of such "antiresonant" behavior does not seem possible, and at such frequencies one is forced to consider the medium as a many-body system and to describe it on a microscopic level. A rigorous proof of these assertions cannot be given at present because no exact solutions of the microscopic equations for a finite three-dimensional resonant dielectric are available. However, the exact results for a pair of interacting molecules to be presented in Sec. VI, as well as the breakdown of the macroscopic theory signalled by the prediction of infinitely large values of n, strongly suggest the actual occurrence of antiresonant behavior in three-dimensional systems for $\Gamma = 0$.

That the derivation of the constitutive relation (65) is based on the assumption that the dipole moments vary little over distances of the order of a lattice spacing becomes apparent when one retains the higher-order terms in the reduction of Eq. (55)

to Eq. (56). Using the expansion

$$\Delta(\vec{R}_i - \vec{R}) = \Delta(\vec{R}_j - \vec{R}) - (\vec{R}_i - \vec{R}_j) \cdot \vec{\nabla}_{\vec{R}} \Delta(\vec{R}_j - \vec{R}) + \cdots , \tag{86}$$

in Eq. (55), we obtain instead of Eq. (56),

$$\sum_i \Delta(\vec{R}_i - \vec{R}) \sum_j{}' \vec{G}(\vec{R}_i - \vec{R}_j) \cdot \vec{\mu}_j$$

$$= \vec{S} \cdot \vec{P}(\vec{R}) - \vec{S}' \cdot \vec{\nabla}_{\vec{R}} \vec{P}(\vec{R}) + \cdots , \tag{87}$$

where

$$\vec{S}' = \sum_i{}' (\vec{R}_i - \vec{R}_j) \vec{G}(\vec{R}_i - \vec{R}_j) . \tag{88}$$

If the change in $\vec{P}(\vec{R})$ over a distance of the order of magnitude of the range of $\vec{G}$ is comparable to $\vec{P}(\vec{R})$, the higher-order terms in Eq. (87), which represent corrections to the Lorentz local field, must be taken into account. These terms correspond, of course, to spatial dispersion,[17] and their inclusion leads to a nonlocal constitutive relation. We shall not pursue this problem further in this paper except to note that the formal treatment of the higher-order terms in Eq. (87) is difficult since tensors of the form $\vec{R}^p \vec{G}$, $p \geq 1$, where $\vec{G}$ is defined by Eq. (53), have an infinite range, and the correction terms in the constitutive relation therefore depend on the external shape of the medium. In addition to these spatial-dispersion terms, which are of the usual type,[17] and which represent contributions from the part of the dipole fields in phase with the radiating dipoles, one must also consider the contributions from the out-of-phase part coming from the higher-order terms in the expansion (41) of the retarded dipole field. That retention of these higher-order terms is essential in spite of the fact that $kR \ll 1$ for all relevant values of R, is shown by the example of two interacting molecules to be discussed in Sec. IV, and is due to a cancellation of the lowest-order terms.

On the basis of the nature of the terms neglected in the derivation of the constitutive relation (65), we conclude that the Lorentz-Lorenz relation (83) gives an adequate description at all frequencies, provided Γ is large enough so that $k|n|a \ll 1$. A somewhat lengthy but straightforward analysis of Eq. (83) yields the relations

$$(ka)^2 (n')^2_{\max} \cong (ka)^2 (n'')^2_{\max} \cong (3\pi/ka)(\omega^3 \gamma / \omega \Gamma) . \tag{89}$$

Since $ka \ll 1$, we see that $k|n|a \ll 1$ implies that the dissipative damping $\omega\Gamma$ must be considerably larger than the radiative damping per molecule $\omega^3 \gamma$, to allow the unrestricted use of Eq. (83) and the

usual macroscopic equations for all frequencies. If the last member of Eq. (89) is not small compared to one, the macroscopic equations may be used only in frequency regions where $k|n|a \ll 1$. Because of the smallness of ka, quite large values of $|n|$ are possible in the allowed frequency regions, and it is therefore gratifying that our derivation of the macroscopic equations is not based on an expansion in powers of the polarizability.

Finally, we briefly comment on the usual method of treating spatial-dispersion problems from the standpoint of a purely macroscopic, bulk theory.[17, 18] By means of a spatial Fourier decomposition, one first derives a relation of the form

$$\vec{P}(\vec{R}) = \int \chi(\vec{R} - \vec{R}') \vec{E}(\vec{R}') d\vec{R}' \tag{90}$$

for an *infinite* medium. The assumption is then made[18] that for a *finite* medium one may write

$$\vec{P}(\vec{R}) = \int_V \chi(\vec{R} - \vec{R}') \vec{E}(\vec{R}') d\vec{R}' , \tag{91}$$

where the integral extends over the volume of the medium and the kernel $\chi(\vec{R} - \vec{R}')$ is the same as in Eq. (90). First we note that in the standard treatments[18] of spatial dispersion a kernel is obtained which, for $\Gamma = 0$, has an *infinite* range at a frequency which would correspond to the frequency ω_s defined by Eq. (85) if there were no spatial dispersion. The transition from Eq. (90) to Eq. (91), therefore, does not seem to be justified except in the presence of sufficiently strong dissipative damping. Second, we remark that the usual expressions for the kernel $\chi(\vec{R} - \vec{R}')$ for $\Gamma = 0$ also lead to infinite values of n, the only difference with Eq. (84) being that in the presence of strong spatial dispersion the singular frequency may be appreciably different from ω_s. It may be noted, however, that the microscopic analysis[19] of the effect of the spatial dispersion due to dipole-dipole interaction for a medium in the form of a slab shows that in this case this effect is very weak, so that the breakdown of the macroscopic theory occurs practically at and near ω_s.

In conclusion, we remark that the usual spatial-dispersion analysis provides an improved description of the electromagnetic response of an infinite crystal in which, in contrast to pure dipole-dipole coupling, the spatial dispersion is large. However, for $\Gamma = 0$, regardless of the strength of the spatial dispersion, the treatment of the properties of a finite crystal by such an analysis is not well founded. Furthermore, the breakdown of the theory signalled by the divergence of n still occurs in the presence of spatial dispersion. Several treatments of spatial-dispersion problems have been published which go beyond the above-mentioned theory and

discuss, for half-space and slab geometries, the variation of the dipole moments near the surface using a microscopic analysis.[19] The work of Mahan and Obermair is most relevant in the present context, as it is based on the equivalent of our molecular equations (22) extended to include other than pure dipole coupling. Using their analysis, it can be shown that for many types of coupling the dipole moments vary greatly over distances on the order of the lattice spacing, provided Γ is sufficiently small. Since this "antiresonance" phenomenon appears in the microscopic theory, it is clearly not just an artifact of the approximate macroscopic theory. We will return to these questions in detail in a subsequent publication on the analysis of specific microscopic models. However, after the example presented in Sec. VI we briefly discuss the role played by radiation damping in these antiresonant oscillations.

VI. RESONANT AND ANTIRESONANT SCATTERING FROM A PAIR OF INTERACTING MOLECULES

We consider the scattering of a plane electromagnetic wave of wavelength λ from a pair of molecules with identical polarizabilities $\alpha(\omega)$, given by Eq. (8), and separated by a distance $l \ll \lambda$ in the direction of propagation of the wave. The incident field has the amplitude $\vec{E}_0 e^{ikz}$ and the molecules are located at the positions $\vec{R}_j = (0, 0, \frac{1}{2} jl)$, where $j = \pm 1$ refers to the two molecules. The dipole moments $\vec{\mu}_j$ induced by the two molecules in the stationary state corresponding to the frequency ω are given by

$$\vec{\mu}_j = \alpha(\omega)\vec{E}_j = \alpha_0(\omega)(\vec{E}_j + \tfrac{2}{3} ik^3 \vec{\mu}_j), \qquad (92)$$

where $\alpha_0(\omega)$ is given by Eq. (11) and $\vec{E}_j$ is the total electric field at $\vec{R}_j$, excluding the radiative part of the field from $\vec{\mu}_j$, which is displayed explicitly in the last member of Eq. (92). The field produced by $\vec{\mu}_j$ outside its charge distribution is given by

$$\vec{e}_j(\vec{R}) = \vec{\nabla} \times \vec{\nabla} \times \frac{e^{ik|\vec{R} - \vec{R}_j|}}{|\vec{R} - \vec{R}_j|} \vec{\mu}_j = \vec{F}(\vec{R} - \vec{R}_j) \cdot \vec{\mu}_j, \qquad (93)$$

and the local fields $\vec{E}_j$ are equal to

$$\vec{E}_j = \vec{E}_0 e^{1/2 ij\phi} + \vec{e}_{-j}(\vec{R}_j), \qquad (94)$$

where $\phi = kl$ is the phase difference in the incident field at the two molecules. Since by assumption we have $\phi \ll 1$, it is appropriate to use expansions in powers of ϕ. We look for solutions of the coupled Eqs. (92) and (94) with $\vec{\mu}_j$ parallel to $\vec{E}_0$, which may be chosen as the x directior. Expanding the exponential in Eq. (93), we get

$$\vec{e}_j(\vec{R}_{-j}) = (C_1 + iC_2)\vec{\mu}_j, \qquad (95)$$

where

$$C_1 = l^{-3}[-1 + O(\phi)],$$

$$C_2 = l^{-3}[\tfrac{2}{3} \phi^3 - \tfrac{2}{15} \phi^5 + O(\phi^7)]. \qquad (96)$$

Introducing the normal modes

$$\vec{\mu}_{\pm} = \vec{\mu}_1 \pm \vec{\mu}_{-1}, \qquad (97)$$

we obtain from Eqs. (92), (94), and (95),

$$\vec{\mu}_+ = \alpha_+[2\vec{E}_0 + i(\tfrac{2}{3} k^3 + C_2)\vec{\mu}_+],$$

$$\vec{\mu}_- = \alpha_-[i\phi\vec{E}_0 + i(\tfrac{2}{3} k^3 - C_2)\vec{\mu}_-], \qquad (98)$$

where

$$\alpha_{\pm} = \tfrac{3}{2} c^3 \gamma / (\omega_{\pm}^2 - \omega^2), \qquad (99)$$

and

$$\omega_{\pm}^2 = \omega_0^2 \mp \tfrac{3}{2} c^3 \gamma C_1, \qquad (100)$$

and where we have kept only the first-order terms in the sum and difference of the incident field at the two molecules. In Eq. (98) the expression for the resonant and antiresonant modes ($\vec{\mu}_+$ and $\vec{\mu}_-$ respectively) have been written in a form similar to that of an isolated molecule. Away from the resonance frequencies $\omega_{\pm}$, we have $\mu_- \ll \mu_+$, as expected. From Eqs. (96) and (98) we see that the damping of the resonant mode is very nearly twice that of an isolated molecule, and is clearly due to the fact that the molecules are oscillating in phase and acting as one "giant" dipole. For $\vec{\mu}_-$, on the other hand, the radiative self-field is almost completely cancelled by the radiative field from the other molecule and a finite damping is obtained only if the higher-order terms in Eq. (96) for C_2 are retained. Thus in this case the standard approximation (41) for $\vec{F}(\vec{r}) \cdot \vec{\mu}$ is not adequate in spite of the fact that $kr \ll 1$. Because of this small resulting damping the molecules can be expected to respond with a large amplitude of the $\vec{\mu}_-$ mode when subjected to a field of frequency ω_-. From Eqs. (98) and (99) we obtain

$$\vec{\mu}_+(\omega) = \tfrac{3}{2} c^3 \gamma \frac{2\vec{E}_0}{\omega_+^2 - \omega^2 - 2i\gamma\omega^3}, \qquad (101)$$

$$\vec{\mu}_-(\omega) = \tfrac{3}{2} c^3 \gamma \frac{i\phi\vec{E}_0}{\omega_-^2 - \omega^2 - \tfrac{1}{5} i\phi^2 \gamma\omega^3}, \qquad (102)$$

where $\phi = kl$, so that in fact we have

$$|\vec{\mu}_-(\omega_-)| \cong \phi^{-1}|\vec{\mu}_+(\omega_+)| \gg |\vec{\mu}_+(\omega_+)|, \qquad (103)$$

since $\phi \ll 1$.

We may calculate the field scattered by the system from the current distribution

$$\vec{J}(\vec{R}) = -i\omega[\vec{\mu}_1\delta(\vec{R} - \vec{R}_1) + \vec{\mu}_{-1}\delta(\vec{R} - \vec{R}_{-1})]. \qquad (104)$$

Using the Lorentz gauge, we obtain for the fields outside the charge distribution,

$$\vec{B} = \vec{\nabla} \times \vec{A}, \quad \vec{E} = (i/k)\vec{\nabla} \times \vec{\nabla} \times \vec{A}, \tag{105}$$

where

$$\vec{A}(\vec{R}) = \frac{1}{c} \int \vec{J}(\vec{R}') \frac{e^{ik|\vec{R}-\vec{R}'|}}{|\vec{R}-\vec{R}'|} d\vec{R}'. \tag{106}$$

Expanding the kernel in Eq. (106) and using Eq. (104), we get

$$\vec{A}(\vec{R}) = -ik (e^{ikR}/R)[\vec{\mu}_+ + \tfrac{1}{2} ikl \, \vec{\mu}_- (\hat{R} \cdot \hat{z})], \tag{107}$$

where

$$\hat{R} = \vec{R}/R \tag{108}$$

and $\hat{z}$ is a unit vector in the z direction. Thus the resonant mode of the two molecules radiates via the electric dipole moment of the total charge-current distribution, and the antiresonant mode via a combination of the magnetic dipole and electric quadrupole moments. In spite of the inequality (103) which shows that the amplitude of excitation

of the antiresonant mode is much larger than that of the resonant mode, one can therefore expect that the scattered intensity at the two frequencies $\omega_\pm$ is of comparable magnitude. To calculate these intensities, we note that in first order in the coupling the resonance frequencies are given by

$$\omega_\pm^2 = \omega_0^2(1 \pm \eta),$$

$$\eta = 3c^3\gamma/2l^3\omega_0 = \alpha_0(0)/l^3. \tag{109}$$

The static polarizability $\alpha_0(0)$ is of the order of magnitude of the molecular volume and in all cases of interest we therefore have $\eta \ll 1$. The separation between the two resonance frequencies is hence equal to $\omega_+ - \omega_- = \eta\omega_0$, which for $kl \ll 1$ is much greater than the widths of the lines, so that in calculating the scattered intensity from Eq. (107) we may neglect the cross terms between the two modes. For the scattered intensity as a function of the frequency ω of the incident field we obtain the expression

$$I(\omega) = \tfrac{1}{3} ck^4(|\vec{\mu}_+|^2 + \tfrac{1}{10} \phi^2 |\vec{\mu}_-|^2)$$

$$= \tfrac{3}{4} c^7 k^4 \gamma^2 E_0^2 \left[\frac{4}{(\omega_+^2 - \omega^2)^2 + (2\gamma\omega^3)^2} + \frac{5}{2} \frac{(\phi^2/5)^2}{(\omega_-^2 - \omega^2)^2 + (\phi^2\gamma\omega^3/5)^2} \right]. \tag{110}$$

In addition to the scattering due to the "giant" dipole, represented by the first term in the square brackets, there is a very much narrower line in the cross section due to scattering from the antiresonant mode. The integrated intensity of this line is very small, but the peak intensity is of the same order of magnitude as that of the resonant line. This phenomenon is not apparent in a discussion of the emission, rather than the scattering, by these two modes. In emission the predominant feature of the antiresonant mode is the small radiative damping leading to a long lifetime and a negligible oscillator strength. It is because of the small damping, however, that the antiresonant mode can attain a large amplitude in a scattering process at the frequency ω, even though the mode is driven only by the small difference in the incident field at the positions of the two molecules [cf. Eq. (102)]. A small amount of dissipative damping will, of course, "wash out" the antiresonant peak at ω_- in the cross section, while leaving the main resonant line at ω_+ virtually unchanged. In conclusion, we stress once more that for $\Gamma = 0$ there are two lines of roughly equal height in the scattering cross section for a pair of molecules. This result remains valid in the presence of an additional, possibly strong coupling between the molecules, which in a many-body system would give rise to spatial dispersion, the only effect

being a shift of the resonance frequencies $\omega_\pm$ from the values (100).

For a scattering system consisting of more than two molecules, we expect the same type of phenomenon, viz., a broad line in the scattering cross section due to the resonant, or superradiant scattering by the molecules, plus a number of narrow peaks corresponding to a response of the system in the form of staggered arrangements of the dipole moments with effective wavelengths extending down to the intermolecular separation. Because of a near cancellation of the radiative damping terms, these antiresonant modes can be expected to attain large amplitudes and thus to give significant contributions to the scattering pattern.

We suggest, then, that n approaching infinity according to Eq. (83) for $\Gamma = 0$ is due to the onset of these antiresonant oscillations. Although of course not accurate in describing the scattering in this region, the Lorentz-Lorenz relation indicates the breakdown of the macroscopic nature of the scattering as microscopic oscillations become important. We believe that strong spatial dispersion may displace the antiresonances in frequency, but that they will nevertheless occur. Whether the antiresonances are separated in frequency from the main resonance line also depends on the external shape of the system, as illustrated by the examples discussed in Sec. VII. The amplitude of the os-

cillations depends, of course, on Γ and for suffi-
ciently large Γ the antiresonant scattering is in-
significant, and thus a macroscopic description is
adequate at all frequencies.

VII. SCATTERING BY MACROSCOPIC RESONANT DIELECTRICS

Using the macroscopic equations and in particu-
lar the Lorentz-Lorenz relation (83), we investi-
gate in this section the scattering by a resonant
dielectric medium for the simple geometries of a
sphere and an infinite slab. The results are then
restricted to frequencies for which $k|n|a \ll 1$.
From Eq. (84) we see that, for $\Gamma = 0$, the suscep-
tibility is real and hence that $\vec{P}$ is in phase with
$\vec{E}$. Nevertheless, a medium of finite extent will,
of course, scatter incident radiation not diffusely
but coherently, because $\vec{P}$ is not in phase with the
external field $\vec{E}_0$.

We consider first a small sphere of volume V
and radius R such that $kR \ll 1$. For frequencies
where $|n| \cong 1$, the polarization can be expected to
vary little over the volume of the sphere. For
such frequencies we neglect the variation of $\vec{E}_0(\vec{R})$
and $\vec{P}(\vec{R})$ over the sphere and then obtain from Eq.
(73)

$$\vec{E} = \vec{E}_0 + \int_\epsilon^V \vec{\nabla} \times \vec{\nabla} \times \frac{\vec{P}}{|\vec{R} - \vec{R}'|} \, d\vec{R}' + \tfrac{2}{3} i k^3 V \vec{P} - \tfrac{4}{3} \pi \vec{P}$$

$$= \vec{E}_0 + \tfrac{2}{3} i k^3 V \vec{P} - \tfrac{4}{3} \pi \vec{P} \, , \tag{111}$$

where we have used Eq. (41) and the fact that
$k|\vec{R} - \vec{R}'| \ll 1$. Thus we find that $\vec{E}$ is uniform, in
agreement with our assumption that $\vec{P}$ is uniform.
From Eq. (111) and $\vec{P} = \chi \vec{E}$, we get

$$\vec{P} = \frac{\tfrac{3}{2} c^3 \rho \gamma \vec{E}_0}{\omega_0^2 - \omega^2 - i N \gamma \omega^3 - i \omega \Gamma} \, , \tag{112}$$

where $N = \rho V$ is the total number of molecules in
the sphere. The total dipole moment of the sphere
is equal to

$$\vec{\mu} = \int \vec{P} \, d\vec{R} = \frac{\tfrac{3}{2} c^3 N \gamma \vec{E}_0}{\omega_0^2 - \omega^2 - i N \gamma \omega^3 - i \omega \Gamma} \, , \tag{113}$$

from which it is apparent that the N molecules
are scattering collectively and acting as a giant
dipole. For $\Gamma = 0$, the linewidth is N times that
for a single molecule. The strong damping occurs
because each molecule sees not only its own radi-
ative field but also the equally strong fields from
all the other molecules, which are contained in
the field $\vec{E}$, as is evident from Eq. (111). We note
that the result (113) indicates that the sphere res-
onates at $\omega = \omega_0$, the resonance frequency of an
isolated molecule, rather than at $\omega = \omega_s$, the fre-

quency at which the susceptibility χ becomes in-
finite. This comes about because the Coulomb
field from the sphere counteracts the local field
shift (85) of the resonance frequency. Since at
$\omega = \omega_0$, $|n| \cong 1$ and χ are finite even for $\Gamma = 0$, we
expect that our neglect of the small variation of
$\vec{E}_0$ and $\vec{P}$ over the medium is justified at all fre-
quencies for which $\vec{P}$, as given by Eq. (112), is
appreciably different from zero. The result (112)
can in fact be derived more rigorously from the
Mie theory, although more care must be taken in
keeping leading terms than is exercised in the
usual analysis.[5,7,16]

For frequencies in the neighborhood of the fre-
quency ω_s at which $n = \infty$ according to Eq. (83), the
reasoning leading to Eq. (112) is of course invalid,
at least for $\Gamma = 0$. Instead of being roughly con-
stant, the polarization varies greatly as the medi-
um responds to the small varying component of
the incident field. The macroscopic theory does
not describe the scattering correctly at these fre-
quencies, but indicates the onset of the antireso-
nant response by predicting that n becomes indef-
initely large. From Eqs. (85) and (112) it can be
shown, however, that the main resonance line at
ω_0 for increasingly larger spheres does not cover
the $\omega \cong \omega_s$ region until $R \cong \lambda$. Thus for small
spheres ($kR \ll 1$) the resonant and antiresonant
scattering occur in separate frequency regions,
as in the example of two molecules, and the main
resonance is described correctly by the macro-
scopic theory.

For a large sphere $kR \gg 1$, we refer to the work
of Zaidi.[5] He has treated the resonant scattering
from a gas of spherical external shape on the
basis of the macroscopic equations assuming a
Lorentz-Lorenz relation which differs from Eq.
(83) by the inclusion of a term $-i\gamma\omega^3$ in the de-
nominator corresponding to the diffuse scattering
by such a system. His result that for a large
sphere the over-all radiative linewidth increases
only proportionally to the radius of the sphere,
rather than to the volume as is true for a small
sphere, will also hold for the scattering from a
crystalline sphere with the Lorentz-Lorenz rela-
tion (83). For $\Gamma = 0$ the scattering profile calcu-
lated by Zaidi's method but using Eq. (83) is valid
at all frequencies except in a small region in the
neighborhood of the frequency ω_s, where $k|n|a$
is not small compared to one. Since for a large
sphere the width of the main resonance line is
large compared with the frequency difference
$\omega_0 - \omega_s$, the antiresonance occurs within the ex-
tent of the main line and the exact shape of this
line therefore cannot be obtained entirely on the
basis of the macroscopic theory. Nonetheless,
the over-all width Δ_r of the line should be given

correctly by the macroscopic theory and in our notation it is therefore equal to[5]

$$\Delta_r \cong (3/2\pi)(\rho\lambda^2 R)\gamma\omega_0^3 \ . \tag{114}$$

Finally, we remark that purely macroscopic scattering phenomena such as the "anomalous diffraction" discussed by Van de Hulst[20] also modify the line shape so that in contrast to a small sphere one cannot expect an exact Lorentzian line shape for a large sphere.

As a final example we consider an infinite slab extending over the region defined by $-\infty < x, y < +\infty$, $-\frac{1}{2}L < z < \frac{1}{2}L$. For normal incidence, $\vec{P}$ and $\vec{E}$ are then functions only of z. Integrating over x' and y', we now obtain from Eq. (73),

$$\vec{E}(z) = \vec{E}_0 e^{ikz} + 2\pi i k \int_{-L/2}^{+L/2} \vec{P}(z') e^{ik|z-z'|} dz' \ . \tag{115}$$

For a thin slab $kL \ll 1$, we first try the argument used for a small sphere and assume that $\vec{P}$, $\vec{E}$ and the incident field are uniform over the slab, giving

$$\vec{E} = \vec{E}_0 + 2\pi i k L \vec{P} \ . \tag{116}$$

Putting $\vec{P} = \chi\vec{E}$, where χ is given by Eq. (84), we get

$$\vec{P} = \frac{\frac{3}{2}c^3\rho\gamma\vec{E}_0}{\omega_s^2 - \omega^2 - iN_c\gamma\omega^3 - i\omega\Gamma} , \tag{117}$$

where

$$N_c = (3/4\pi)L\lambda^2\rho \tag{118}$$

is the effective number of molecules radiating collectively. This result can be understood by remembering that the radiative field from a dipole is equal to $\frac{2}{3}ik^3\vec{\mu}$ only for distances small compared to λ. At large distances, the field oscillates and the net contribution to the radiative field at a central molecule due to the molecules further than a wavelength away from the central molecule tends to vanish.

From Eq. (117) we see that the peak in the response comes at $\omega = \omega_s$, whereas for a sphere the main resonance comes at $\omega = \omega_0$ and for a sufficiently small sphere is well separated from the antiresonant frequency region. For a slab there is no long-range Coulomb field to counteract the frequency shift due to the local field, and the resonance and antiresonance therefore occur in the same frequency region. The argument based on the assumption of a uniform $\vec{P}$ and $\vec{E}$ leading to Eq. (117) is hence suspect. In the macroscopic theory it is, of course, possible to solve the slab problem rigorously, the result being[21]

$$\vec{P}(z) = (1/4\pi)(n^2 - 1)\vec{E}_0 e^{-(1/2)ikL}$$

$$\times \frac{(n+1)e^{ikn(z-\frac{1}{2}L)} + (n-1)e^{-ikn(z-\frac{1}{2}L)}}{2n\cos knL - i(n^2+1)\sin knL} , \tag{119}$$

where n is to be determined from Eq. (83). The solution (119) is equivalent to satisfying simultaneously Eq. (115) and the relation $\vec{P} = \chi\vec{E}$. The result (119) is a good deal more complicated than (117), but in fact reduces to it in the limit $knL \ll 1$. If the dissipative damping Γ is sufficiently large so that $knL \ll 1$ [a considerably stronger condition than that for the validity of Eq. (83)], then all the antiresonance modes are effectively damped out and the reflection and transmission by the slab are given correctly by the simple expression (117). Otherwise, the full expression (119) must be used to describe correctly the oscillations occurring in $\vec{P}(z)$ as ω approaches ω_s. However, Eq. (119) is of course valid only as long as $kna \ll 1$, and for $\Gamma = 0$ or small cannot be used for ω near ω_s.

For a slab large compared with the wavelength $kL \gg 1$, the overlap of the resonance and antiresonance persists, and we must use Eq. (119) as long as Eq. (83) is applicable. The reflected field following from Eq. (119) is given by $\vec{E}_0' e^{-ikz}$, where

$$E_0' = \frac{ie^{ikL}(n^2-1)\sin knL}{2n\cos knL - i(n^2+1)\sin knL}E_0 \ . \tag{120}$$

Although not valid in the neighborhood of ω_s, we may conclude from Eq. (120) that the back scattering will be large when n is large and real, and when n^2 is negative and thus n imaginary. Eq. (84) then implies that for $\Gamma = 0$ we can expect large back scattering for frequencies between approximately $\omega^2 = \omega_s^2$ and $\omega^2 = \omega_s^2 + 6\pi\rho c^3\gamma$, although the scattering pattern is complicated and shows many oscillations. Nevertheless, this result indicates a linewidth of the back-scattered light roughly equal to $3\pi\rho c^3\gamma/\omega_s$ and hence to an effective number of collectively radiating molecules equal to

$$N_c = (3/8\pi^2)\lambda^3\rho \ . \tag{121}$$

This number and hence the width are independent of the thickness L of the slab, in contrast to the linewidth for a large sphere which increases proportionally to the radius R of the sphere. The difference is due to the true, three-dimensional scattering by the sphere, including effects such as diffraction, which are not present for a slab.

VIII. CONCLUDING REMARKS

We have shown in this paper how the macroscopic Maxwell equations may be used to describe the resonant scattering, over large frequency ranges,

of dielectrics composed of molecules interacting via the retarded dipole fields. The crucual point in this analysis is the proper handling of the radiative fields, as occurring in both the molecular polarizability and the Maxwell field $\vec{\bar{E}}(\vec{R})$, in the derivation of the constitutive relation. Since the constitutive relation was derived for a finite dielectric, resonant scattering from dielectrics of various shapes and sizes, both small and large compared to λ, may be investigated macroscopically. We have considered the simple geometries of the sphere and the infinite slab; the results indicate that both the resonance frequency and the effective natural linewidth depend strongly on the shape of the dielectric, as expected in view of the long-range nature of the retarded dipole-dipole interaction.

In the absence of dissipative damping ($\Gamma = 0$), there appear to be frequencies for which a macroscopic theory is not possible, in that the dipole moments take on an "antiresonant" behavior, varying greatly over the order of a lattice spacing. The scattering cross section in such regions is expected to be quite complicated, and the resonant scattering may or may not be separated from this frequency region depending on the external shape of the dielectric. In the presence of strong coupling between the molecules due to interactions other than retarded dipole-dipole coupling, which is present in many systems of physical interest but was not discussed here explicitly, the resultant spatial dispersion may be expected to shift the frequency of the antiresonant behavior. Thus,

in physical systems of interest, accurate descriptions of the spatial *and* the dissipative damping appear essential in determining in what frequency ranges a macroscopic theory of resonant scattering is possible.

APPENDIX

We show in this Appendix that the expression (78) for the tensor $\vec{\bar{G}}$ obtained by Vlieger is exactly equal to the simple static dipole sum (64). The sum over the reciprocal lattice vectors $\vec{h}_\lambda$ in Eq. (73) can be transformed into a sum over the lattice vectors $\vec{r}_\lambda$ in ordinary space by means of the formula

$$\sum_\lambda F(\vec{h}_\lambda) = v \sum_\lambda f(\vec{r}_\lambda),\tag{A1}$$

where v is the volume of the unit cell in ordinary space, $f(\vec{r})$ is an arbitrary continuous function satisfying the necessary integrability conditions, and

$$F(\vec{h}) = \int f(\vec{r})e^{2\pi i \vec{h}\cdot\vec{r}}\,d\vec{r}\tag{A2}$$

is the Fourier transform of $f(\vec{r})$. Using (A1) we obtain

$$\sum_\lambda{}' e^{-\pi a^2 h_\lambda^2} = \sum_\lambda e^{-\pi a^2 h_\lambda^2} - 1 = \sum_\lambda e^{-\pi r_\lambda^2/a^2} - 1$$

$$= \sum_\lambda{}' e^{-\pi r_\lambda^2/a^2},\tag{A3}$$

and we may therefore write Eq. (78) in the form

$$\vec{\bar{G}} = \sum_\lambda{}' \vec{\bar{T}}_3(\vec{r}_\lambda)\,\mathrm{erfc}(x_\lambda) + \frac{2}{a}\sum_\lambda{}' \vec{\bar{T}}_2(\vec{r}_\lambda)e^{-x_\lambda^2} - \frac{4\pi}{a^3}\left[\sum_\lambda{}'\left(\hat{r}_\lambda\hat{r}_\lambda - \frac{1}{3}\vec{\bar{U}}\right)e^{-x_\lambda^2} - \sum_\lambda{}'\left(\hat{h}_\lambda\hat{h}_\lambda - \frac{1}{3}\vec{\bar{U}}\right)e^{-\pi a^2 h_\lambda^2}\right],\tag{A4}$$

where $x_\lambda = (\pi^{1/2}r_\lambda/a)$. Consider the reciprocal-lattice sum

$$\vec{\bar{S}} = \sum_\lambda{}'\left(\hat{h}_\lambda\hat{h}_\lambda - \frac{1}{3}\vec{\bar{U}}\right)e^{-\pi a^2 h_\lambda^2} = \sum_\lambda{}' \vec{\bar{F}}(\vec{h}_\lambda),\tag{A5}$$

where

$$\vec{\bar{F}}(\vec{h}) = (\hat{h}\hat{h} - \frac{1}{3}\vec{\bar{U}})e^{-\pi a^2 h^2}.\tag{A6}$$

This function is singular at $\vec{h} = 0$, since its value at $\vec{h} = 0$ depends on the direction of approach to $\vec{h} = 0$. To obtain a function which satisfies the Fourier integral theorem at all points, we replace $\vec{\bar{F}}(\vec{h})$ at each point $\vec{h}$ by the average value of $\vec{\bar{F}}(\vec{h})$ over an infinitesimal sphere surrounding the point $\vec{h}$. This amounts to leaving the value of $\vec{\bar{F}}(\vec{h})$ unchanged at all points $\vec{h} \neq 0$ and to put $\vec{\bar{F}}(0) = 0$. The averaging procedure shows that the modified function satisfies the Fourier integral theorem at all points.

Denoting the modified function again by $\vec{\bar{F}}(\vec{h})$, we have from (A1) and (A5)

$$\vec{\bar{S}} = \sum_\lambda{}' \vec{\bar{F}}(\vec{h}_\lambda) = \sum_\lambda \vec{\bar{F}}(\vec{h}_\lambda) = v\sum_\lambda \vec{\bar{f}}(\vec{r}_\lambda),\tag{A7}$$

where

$$\vec{\bar{f}}(\vec{r}) = \int \vec{\bar{F}}(\vec{h})e^{-2\pi i \vec{h}\cdot\vec{r}}\,d\vec{h}$$

$$= -\frac{1}{4\pi}\vec{\nabla}\vec{\nabla}\frac{1}{r}\,\mathrm{erf}(x) - \frac{1}{3a^3}\vec{\bar{U}}e^{-x^2}.\tag{A8}$$

Using the definitions (79), we obtain from (A8)

$$4\pi\vec{\bar{f}}(\vec{r}) = \vec{\bar{T}}_3(\vec{r})\,\mathrm{erf}(x) - \frac{2}{a}\vec{\bar{T}}_2(\vec{r})e^{-x^2}$$

$$+ \frac{4\pi}{a^3}(\hat{r}\hat{r} - \frac{1}{3}\vec{\bar{U}})e^{-x^2}.\tag{A9}$$

Expanding the right-hand side of (A9) in powers of

x, one easily verifies that $\bar{\mathsf{f}}(0)=0$, and hence that

$$\bar{\mathsf{S}} = v \sum_\lambda{}' \dot{\bar{\mathsf{f}}}(\vec{r}_\lambda) . \tag{A10}$$

Using (A10) and (A9) in (A4), we get

$$\bar{\mathsf{G}} = \sum_\lambda{}' \bar{\mathsf{T}}_3(\vec{r}_\lambda) . \tag{A11}$$

That the sum in (A11) must be interpreted as a "spherical" sum, as indicated in Eq. (64), is clear from the fact that all the convergence factors in (A4) have spherical symmetry.

---

*Supported by the National Research Council of Canada.

[1] L. Rosenfeld, Theory of Electrons (North-Holland, Amsterdam, 1951).

[2] S. R. de Groot, The Maxwell Equations (North-Holland, Amsterdam, 1959).

[3] R. H. Dicke, Phys. Rev. 93, 99 (1954).

[4] H. Freedhoff and J. Van Kranendonk, Can. J. Phys. 45, 1833 (1967).

[5] H. R. Zaidi, Can. J. Phys. 50, 1427 (1972).

[6] H. Hoek, Ph.D. thesis (Leiden, 1939) (unpublished).

[7] J. Vlieger, Can. J. Phys. 49, 1384 (1972).

[8] B. R. A. Nyboer and F. W. de Wette, Physica (Utrecht) 23, 309 (1957); Physica (Utrecht) 24, 422 (1958).

[9] G. Russakoff, Amer. J. Phys. 38, 1188 (1970).

[10] P. Mazur and B. R. A. Nyboer, Physica (Utrecht) 19, 971 (1953).

[11] Reference 1, p. 73.

[12] J. R. Ackerhalt, P. L. Knight, and J. H. Eberly, Phys. Rev. Lett. 30, 456 (1973).

[13] J. J. Sein, Opt. Comm. 2, 170 (1970); J. de Goede and P. Mazur, Physica (Utrecht) 58, 568 (1972); D. N. Pattanayak, Ph.D. thesis (University of Rochester, 1973) (unpublished).

[14] Reference 1, Chap. VI, Eq. (12).

[15] Reference 1, Chap. V; L. D. Landau and E. M. Lifshitz, Electrodynamics of Continuous Media (Pergamon, London, 1960), Chap. XIV; S. Hess, Z. Naturforschung 24, 1675 (1969).

[16] J. Vlieger (private communication).

[17] J. J. Hopfield and D. G. Thomas, Phys. Rev. 132, 563 (1963).

[18] G. S. Agarwal, D. N. Pattanayak, and E. Wolf, Phys. Rev. Lett. 27, 1022 (1971).

[19] C. W. Deutsche and C. A. Mead, Phys. Rev. 158, A63 (1965); G. D. Mahon and G. Obermair, Phys. Rev. 183, 834 (1969); T. Skettrup and I. Balslev, Phys. Rev. B 3, 1457 (1971); R. Zeyher, J. L. Birman, and W. Brenig, Phys. Rev. B 6, 4613 (1972).

[20] H. C. Van de Hulst, Light Scattering by Small Particles (Wiley, New York, 1957).

[21] M. Born and E. Wolf, Principles of Optics (Pergamon, London, 1965).