Retardation correction to the Lorentz-Lorenz formula for the refractive index of a disordered system of polarizable point dipoles

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An approximate expression for the effective dielectric tensor of a fluid or suspension of spherical particles with a polarizable point dipole at the center is derived by a selection of terms in the cluster expansion. Full account is taken of the effect of retardation. The effective dielectric tensor depends on wave vector and frequency. In the limit of zero frequency the derived expression reduces to the wave-vector-dependent tensor found from electrostatics by the same procedure. In the limit of zero frequency and zero wave vector it reduces to the Clausius-Mossotti formula. The transverse part of the tensor may be regarded as a generalization of the well-known Lorentz-Lorenz formula for the refractive index. It is shown that the generalization leads to unphysical results if the damping of the individual spherical particles is too small. This implies that correlation corrections must be taken into account. [S1063-651X(97)11912-2]

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I. INTRODUCTION

A well-defined coherent monochromatic electromagnetic plane wave can propagate in a disordered system of polarizable particles, provided the wavelength is much larger than the average distance between particles. The extinction theorem [1–5] shows that multiple scattering has the effect of replacing the vacuum wavelength by a modified one. The ratio of the two wavelengths is the refractive index. The coherent wave satisfies Maxwell's equations on the macroscopic level and the refractive index may be calculated from the effective dielectric tensor of the medium. If the wavelength is sufficiently short the wave-vector- and frequency-dependent dielectric tensor must be used [6]. The latter can in principle be calculated from a cluster expansion [7,8], but in practice only a limited number of terms of the expansion can be evaluated and one is forced to make approximations.

In the following we study the same selection of terms of the cluster expansion that in the electrostatic case led to the Clausius-Mossotti formula and its nonlocal generalization [9]. We take full account of retardation and are therefore led to a nonlocal generalization of the Lorentz-Lorenz formula [3]. For simplicity we consider a system of spherical particles with a polarizable point dipole at the center. For this case the same expression for the effective dielectric tensor was derived by Pellegrini *et al.* [10] from Lax's quasicrystalline approximation [11] with neglect of correlations, but with account of the nonoverlap condition.

We study in particular the Drude-Lorentz model for the single-particle polarizability. We find that the nonlocal generalization of the Lorentz-Lorenz formula leads to unphysical results if the damping of the single-particle oscillator is too small. This indicates that in such a case it is essential to take the effect of correlation corrections into account.

The Drude-Lorentz model is particularly useful for a study of behavior at resonance. In the absence of damping and with neglect of retardation one deals with a set of identical harmonic oscillators coupled by electrostatic dipole interactions. The dielectric constant of a large number of such oscillators, either in a regular crystalline arrangement [12–14], or in a disordered array [14], reflects the frequency spectrum of the coupled system. Furthermore, the dielectric constant at zero wave number has a spectral representation, i.e., it may be expressed as an integral over a positive spectral density [15]. The imaginary part of the dielectric constant as a function of frequency is directly related to the spectral density. The shape of the latter is determined by local-field effects. In the mean-field approximation and for cubic crystals the dielectric constant at zero wave number is given by the Clausius-Mossotti formula. According to this formula, the line shape remains sharp and the dipolar interactions merely cause a redshift of the single-particle resonance. This is the well-known Lorentz shift. For a disordered system the spectral density shows inhomogeneous line broadening, as determined by the local microstructure. The deviations from the Clausius-Mossotti formula are large near resonance.

For a system of harmonic oscillators coupled by retarded dipole interactions the frequency-dependent refractive index describes the mean propagation of coherent transverse waves. In light of the above, the behavior of the complex refractive index near the shifted resonance is of particular interest. We cannot expect that the generalized Lorentz-Lorenz formula derived in the following provides a full and accurate description of the line shape, which will again be strongly influenced by the local microstructure. Nonetheless, a study of the generalized Lorentz-Lorenz formula is an indispensable prerequisite. The formula should not be regarded as a somewhat arbitrary effective-medium approximation [16], but rather as an important ingredient of a full statistical theory. A supplementary study of microstructural correlation corrections must follow.

The system of polarizable point dipoles can be studied conveniently by computer simulation [15]. We stress that for atomic liquids retardation effects are negligible because the

atomic diameter is much smaller than the optical wavelength. Retardation corrections are important in suspensions of uniform spherical particles of sufficiently large size. Due to the appearance of higher-order multipole effects both the statistical theory and simulations [17] of realistic suspensions become more involved. It seems wise to restrict preliminary study to the dipolar system.

II. MICROSCOPIC AND MACROSCOPIC EQUATIONS

We consider electromagnetic fields in a polarizable system of identical nonoverlapping spherical inclusions of radius a embedded in a uniform background. At frequency ω the dielectric constant $\varepsilon_1(\omega)$ and magnetic permeability $\mu_1(\omega)$ of the background medium may be complex. The system is assumed to be linear, so that the electric and magnetic fields and the induced charge and current density oscillate with the same time factor $\exp(-i\omega t)$. The common time factor may be canceled from the equations, so that at each frequency ω we deal with a purely geometrical problem. The response of a single inclusion to an incident electromagnetic field will be treated in the electric-dipole approximation. This implies that the inclusion is replaced by a sphere of radius a with dielectric constant $\varepsilon_1(\omega)$ and magnetic permeability $\mu_1(\omega)$, with a pointlike dipole polarizability $\alpha(\omega)$ at its center. If such a polarizable point inclusion is placed with its center at $\boldsymbol{R}$ in an external field $\boldsymbol{E}_0(\boldsymbol{r})$, then the induced electric field, within and without the inclusion, is that of a point dipole of moment $\boldsymbol{p}=\alpha(\omega)\boldsymbol{E}_0(\boldsymbol{R})$ at the center of the inclusion. The dipole generates an electric field

$$\boldsymbol{E}(\boldsymbol{r})=\boldsymbol{G}_1(\boldsymbol{r}-\boldsymbol{R})\cdot\boldsymbol{p}, \tag{1}$$

where $\boldsymbol{G}_1(\boldsymbol{r})$ is the tensor Green's function

$$\boldsymbol{G}_1(\boldsymbol{r})=\frac{1}{\varepsilon_1}(\nabla\nabla+k_1^2\mathbf{1})G_1(r) \tag{2}$$

derived from the scalar function

$$G_1(r)=\frac{e^{ik_1r}}{r}. \tag{3}$$

We abbreviate $\varepsilon_1=\varepsilon_1(\omega)$ and $\mu_1=\mu_1(\omega)$. The wave number $k_1=\sqrt{\varepsilon_1\mu_1}k$ is chosen to have a positive imaginary part. Here $k=\omega/c$, with c the velocity of light, is the vacuum wave number. The tensor Green's function in Eq. (2) may be expressed alternatively as

$$\boldsymbol{G}_1(\boldsymbol{r})=\frac{1}{3\varepsilon_1}ik_1^3\{[2h_0^{(1)}(k_1r)-h_2^{(1)}(k_1r)]\mathbf{1}+3h_2^{(1)}(k_1r)\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}\}, \tag{4}$$

with spherical Hankel functions $h_n^{(1)}(k_1r)$ of the first kind [18].

The magnetic field may be eliminated. On the microscopic level Maxwell's equations for the system described above may be reduced to

$$\nabla\times(\nabla\times\boldsymbol{E})-k_1^2\boldsymbol{E}=4\pi i\frac{\mu_1 k}{c}\boldsymbol{j}, \tag{5}$$

where $\boldsymbol{j}(\boldsymbol{r})$ is the current density. Taking the divergence of this equation and using the continuity equation we find

$$\nabla\cdot\boldsymbol{E}=\frac{4\pi}{\varepsilon_1}\rho, \tag{6}$$

where ρ is the charge density. If the electric field is separated into longitudinal and transverse parts $\boldsymbol{E}=\boldsymbol{E}_{/\!/}+\boldsymbol{E}_t$, then the longitudinal part $\boldsymbol{E}_{/\!/}$ is determined from Eq. (6), whereas the transverse part $\boldsymbol{E}_t$ satisfies the inhomogeneous wave equation

$$\nabla^2\boldsymbol{E}_t+k_1^2\boldsymbol{E}_t=-4\pi i\frac{\mu_1 k}{c}\boldsymbol{j}_t. \tag{7}$$

For a given configuration of N inclusions with centers at $\boldsymbol{R}_1,\ldots,\boldsymbol{R}_N$ the charge density $\rho(\boldsymbol{r})$ is given by

$$\rho=-\nabla\cdot\boldsymbol{P}+\rho_{\mathrm{ex}}, \tag{8}$$

where $\boldsymbol{P}(\boldsymbol{r})$ is the microscopic polarization

$$\boldsymbol{P}(\boldsymbol{r})=\sum_{j=1}^{N}\boldsymbol{p}_j\delta(\boldsymbol{r}-\boldsymbol{R}_j) \tag{9}$$

and $\rho_{\mathrm{ex}}(\boldsymbol{r})$ is the external charge density. The current density $\boldsymbol{j}(\boldsymbol{r})$ is given by

$$\boldsymbol{j}=-i\omega\boldsymbol{P}+\boldsymbol{j}_{\mathrm{ex}}, \tag{10}$$

where $\boldsymbol{j}_{\mathrm{ex}}$ is the external current density.

We assume that the statistical distribution of inclusion configurations is known, as described by a given probability distribution of centers $W(\boldsymbol{R}_1,\ldots,\boldsymbol{R}_N)$. The external charge and current densities ρ_{ex} and $\boldsymbol{j}_{\mathrm{ex}}$ are independent of this distribution. Averaging over the probability distribution, we find from Eq. (5)

$$\nabla\times(\nabla\times\langle\boldsymbol{E}\rangle)-k_1^2\langle\boldsymbol{E}\rangle=4\pi i\frac{\mu_1 k}{c}\langle\,\boldsymbol{j}\rangle, \tag{11}$$

with mean current density

$$\langle\,\boldsymbol{j}\rangle=-i\omega\langle\boldsymbol{P}\rangle+\boldsymbol{j}_{\mathrm{ex}}. \tag{12}$$

Averaging Eq. (6) we find

$$\nabla\cdot\langle\boldsymbol{E}\rangle=\frac{4\pi}{\varepsilon_1}\langle\rho\rangle, \tag{13}$$

with mean charge density

$$\langle\rho\rangle=-\nabla\cdot\langle\boldsymbol{P}\rangle+\rho_{\mathrm{ex}}. \tag{14}$$

These equations are equivalent to Maxwell's equations on the macroscopic level. The solution is given by

$$\langle\boldsymbol{E}(\boldsymbol{r})\rangle=\boldsymbol{E}_0(\boldsymbol{r})+\int\boldsymbol{G}_0(\boldsymbol{r}-\boldsymbol{r}')\cdot\langle\boldsymbol{P}(\boldsymbol{r}')\rangle d\boldsymbol{r}', \tag{15}$$

where $\boldsymbol{E}_0(\boldsymbol{r})$ is the applied field generated by the external charge and current density, and with the tensor Green's function $\boldsymbol{G}_0(\boldsymbol{r}-\boldsymbol{r}')$,

$$\boldsymbol{G}_0(\boldsymbol{r}-\boldsymbol{r}')=\boldsymbol{G}_1(\boldsymbol{r}-\boldsymbol{r}')-\frac{4\pi}{3\varepsilon_1}\mathbf{1}\delta(\boldsymbol{r}-\boldsymbol{r}') \tag{16}$$

with the prescription that in Eq. (15) the integral over the Green's function $\boldsymbol{G}_1(\boldsymbol{r}-\boldsymbol{r}')$ is carried out with exclusion of a little sphere of infinitesimal radius about the field point $\boldsymbol{r}$. The prescription arises from the interchange of differentiation and integration, which has been performed to arrive at the form (15).

The macroscopic constitutive equation of the system is derived from the solution of the set of coupled equations for the induced dipoles and a subsequent average over the probability distribution $W(\boldsymbol{R}_1,\ldots,\boldsymbol{R}_N)$. This procedure leads to a linear relation between average polarization $\langle\boldsymbol{P}(\boldsymbol{r})\rangle$ and average electric field $\langle\boldsymbol{E}(\boldsymbol{r}')\rangle$, which is of short range in the distance $|\boldsymbol{r}-\boldsymbol{r}'|$. For a macroscopic spatially uniform sample of volume Ω the constitutive relation takes the form

$$\langle\boldsymbol{P}(\boldsymbol{r})\rangle=\int \boldsymbol{X}(\boldsymbol{r}-\boldsymbol{r}')\cdot\langle\boldsymbol{E}(\boldsymbol{r}')\rangle d\boldsymbol{r}' \tag{17}$$

in the thermodynamic limit $N\to\infty$, $\Omega\to\infty$ at constant number density $n=N/\Omega$, with a translationally invariant susceptibility kernel $\boldsymbol{X}(\boldsymbol{r}-\boldsymbol{r}')$. The nature of the kernel is determined by the local microstructure. Formally, it may be expressed in terms of a cluster expansion involving cluster integrals over partial distribution functions [7,8]. After a spatial Fourier transform the constitutive relation (17) may be expressed as

$$\langle\boldsymbol{P}_{\boldsymbol{q}\omega}\rangle=\boldsymbol{\chi}(\boldsymbol{q},\omega)\cdot\langle\boldsymbol{E}_{\boldsymbol{q}\omega}\rangle, \tag{18}$$

where we have made the dependence on frequency explicit. The susceptibility tensor $\boldsymbol{\chi}(\boldsymbol{q},\omega)$ is related to the susceptibility kernel $\boldsymbol{X}(\boldsymbol{r},\omega)$ by

$$\boldsymbol{\chi}(\boldsymbol{q},\omega)=\frac{1}{8\pi^3}\int \boldsymbol{X}(\boldsymbol{r},\omega)e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}d\boldsymbol{r}. \tag{19}$$

The effective dielectric tensor $\boldsymbol{\varepsilon}(\boldsymbol{q},\omega)$ is given by

$$\boldsymbol{\varepsilon}(\boldsymbol{q},\omega)=\varepsilon_1(\omega)\mathbf{1}+4\pi\boldsymbol{\chi}(\boldsymbol{q},\omega). \tag{20}$$

We assume that the system on average is isotropic. Then the susceptibility tensor takes the form

$$\boldsymbol{\chi}(\boldsymbol{q},\omega)=\chi_{/\!/}(q,\omega)\hat{\boldsymbol{q}}\hat{\boldsymbol{q}}+\chi_t(q,\omega)(\mathbf{1}-\hat{\boldsymbol{q}}\hat{\boldsymbol{q}}) \tag{21}$$

with scalar functions $\chi_{/\!/}(q,\omega)$ and $\chi_t(q,\omega)$. The dielectric tensor takes the same form with scalar functions

$$\varepsilon_{/\!/,t}(q,\omega)=\varepsilon_1(\omega)+4\pi\chi_{/\!/,t}(q,\omega). \tag{22}$$

In the long-wavelength limit $q\to0$ the longitudinal and transverse susceptibility functions tend to the same value $\chi(\omega)\equiv\chi_{/\!/}(0,\omega)=\chi_t(0,\omega)$. The corresponding dielectric constant is

$$\varepsilon(\omega)=\varepsilon_1(\omega)+4\pi\chi(\omega). \tag{23}$$

The propagation of transverse electromagnetic waves is described by the solution of the dispersion equation

$$q^2c^2=\omega^2\varepsilon_t(q,\omega)\mu_1(\omega). \tag{24}$$

A particular solution $q(\omega)$ of this equation defines the refractive index $\mathsf{N}(\omega)$ as the ratio of wave numbers

$$\mathsf{N}(\omega)\equiv\frac{q(\omega)}{k_1}, \tag{25}$$

with $k_1=\sqrt{\varepsilon_1(\omega)\mu_1(\omega)}\,\omega/c$. In the following we are concerned with an approximate calculation of the refractive index $\mathsf{N}(\omega)$.

III. OVERLAP APPROXIMATION

Clausius [19] and Mossotti [20] have derived a well-known approximation to the dielectric constant ε in electrostatics. The approximation is of mean-field nature and neglects correlations in particle positions. The Clausius-Mossotti formula reads

$$\frac{\varepsilon-\varepsilon_1}{\varepsilon+2\varepsilon_1}=\frac{4\pi}{3\varepsilon_1}n\alpha. \tag{26}$$

One derives it easily by approximating the average local field acting on a selected dipole by the Lorentz local field

$$\boldsymbol{F}_L=\langle\boldsymbol{E}\rangle+\frac{4\pi}{3\varepsilon_1}\langle\boldsymbol{P}\rangle. \tag{27}$$

In the derivation the electrostatic dipolar Green's function is used. It was shown by Lorentz [21] and Lorenz [22] that if retardation is taken into account the average local field is still very well approximated by Eq. (27). On this basis they found the Lorentz-Lorenz formula for the refractive index [23]

$$\frac{\mathsf{N}^2(\omega)-\varepsilon_1(\omega)\mu_1(\omega)}{\mathsf{N}^2(\omega)+2\varepsilon_1(\omega)\mu_1(\omega)}=\frac{4\pi}{3\varepsilon_1(\omega)}n\alpha(\omega). \tag{28}$$

This expression provides a good approximation to the refractive index of polarizable fluids, even at optical frequencies. Of course, in that case $\varepsilon_1(\omega)=\mu_1(\omega)=1$.

In the following we study retardation corrections to the Lorentz-Lorenz formula (28) in detail. We follow the procedure of Felderhof *et al.* [9], who showed how to derive the Clausius-Mossotti formula (26) for a dielectric suspension of spherical inclusions by a selection of terms in the cluster expansion for the effective dielectric constant. The same selection of terms was then used to obtain an approximate expression for the wave-vector-dependent effective dielectric tensor. For a system of spheres with a polarizable point dipole at the center the expression was evaluated in closed form. The derivation was performed in electrostatics, but can be generalized to include retardation. The selection of terms in the cluster expansion leads to the approximate expression for the susceptibility tensor

$$\boldsymbol{\chi}_{\rm ov}(\boldsymbol{q},\omega)\equiv\sum_{s=1}^{\infty}(-1)^{s-1}n^{s}\times\int_{V_0(1|2|\cdots|s)}\cdots\int d\boldsymbol{R}_2\cdots d\boldsymbol{R}_s\times(\boldsymbol{q}|\mathsf{M}(1)\cdot\mathsf{L}(2)\cdot\ldots\cdot\mathsf{L}(s)|\boldsymbol{q}),\tag{29}$$

where the subscript ov indicates that only virtual overlap terms are taken into account. The overlap region $V_0(1|2|\cdots|s)$ corresponds to the restriction

$$|\boldsymbol{R}_j-\boldsymbol{R}_{j-1}|<2a,\quad j=2,3,\ldots,s.\tag{30}$$

The linear operator $\mathsf{M}(1)$ represents the polarizability kernel of the selected sphere labeled 1. The linear operator $\mathsf{L}(j)$ represents the induced field generated by sphere j. The notation

$$(\boldsymbol{q}|\mathcal{O}|\boldsymbol{q}')=\int d\boldsymbol{r}\int d\boldsymbol{r}'\,e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}\mathcal{O}(\boldsymbol{r},\boldsymbol{r}')e^{i\boldsymbol{q}'\cdot\boldsymbol{r}'}\tag{31}$$

is used for a plane-wave matrix element of an operator $\mathcal{O}$ with kernel $\mathcal{O}(\boldsymbol{r},\boldsymbol{r}')$.

Thus one considers a plane-wave applied field of the form

$$\boldsymbol{E}_0(\boldsymbol{r})=\boldsymbol{E}_{\boldsymbol{q}}e^{i\boldsymbol{q}\cdot\boldsymbol{r}},\tag{32}$$

and first evaluates the induced field due to an inclusion placed at $\boldsymbol{R}_s$. This is

$$\boldsymbol{E}_{\rm ind}(\boldsymbol{r};\boldsymbol{R}_s)=\alpha(\omega)\boldsymbol{G}_0(\boldsymbol{r}-\boldsymbol{R}_s)\cdot\boldsymbol{E}_{\boldsymbol{q}}e^{i\boldsymbol{q}\cdot\boldsymbol{R}_s}.\tag{33}$$

Since in Eq. (29) we must integrate this field over positions $\boldsymbol{R}_s$ within a sphere of radius $2a$ centered at $\boldsymbol{R}_{s-1}$, we need the Green's function $\boldsymbol{G}_0(\boldsymbol{r}-\boldsymbol{r}')$, as given by Eq. (16), with the nature of the singularity specified. Because the polarizability of the inclusion centered at $\boldsymbol{R}_{s-1}$ is pointlike, the integrated field is needed only at $\boldsymbol{R}_{s-1}$. We therefore calculate

$$\int_{|\boldsymbol{R}_s-\boldsymbol{R}_{s-1}|<2a}d\boldsymbol{R}_s\boldsymbol{E}_{\rm ind}(\boldsymbol{R}_{s-1};\boldsymbol{R}_s)=-4\pi\frac{\alpha(\omega)}{\varepsilon_1(\omega)}e^{i\boldsymbol{q}\cdot\boldsymbol{R}_{s-1}}\boldsymbol{K}(\boldsymbol{q},\omega)\cdot\boldsymbol{E}_{\boldsymbol{q}},\tag{34}$$

with the tensor $\boldsymbol{K}(\boldsymbol{q},\omega)$ defined by

$$\boldsymbol{K}(\boldsymbol{q},\omega)=-\frac{\varepsilon_1(\omega)}{4\pi}\int_{R<2a}e^{i\boldsymbol{q}\cdot\boldsymbol{R}}\boldsymbol{G}_0(\boldsymbol{R},\omega)d\boldsymbol{R}.\tag{35}$$

The tensor is found to be given by

$$\boldsymbol{K}(\boldsymbol{q},\omega)=\frac{k_1^2\mathbf{1}-\boldsymbol{q}\boldsymbol{q}}{k_1^2-q^2}-\frac{i}{3}\frac{k_1^3d}{k_1^2-q^2}\{[2j_0(qd)-j_2(qd)]k_1d\times h_1^{(1)}(k_1d)-qdj_1(qd)[2h_0^{(1)}(k_1d)-h_2^{(1)}\times(k_1d)]\}\mathbf{1}+i\frac{k_1^3d}{k_1^2-q^2}[qdj_1(qd)h_2^{(1)}(k_1d)-j_2(qd)k_1dh_1^{(1)}(k_1d)]\hat{\boldsymbol{q}}\hat{\boldsymbol{q}},\tag{36}$$

where $j_n(z)$ is a spherical Bessel function and $d=2a$. The tensor may be separated into longitudinal and transverse parts as

$$\boldsymbol{K}(\boldsymbol{q},\omega)=K_{/\!/}(q,\omega)\hat{\boldsymbol{q}}\hat{\boldsymbol{q}}+K_t(q,\omega)(\mathbf{1}-\hat{\boldsymbol{q}}\hat{\boldsymbol{q}}).\tag{37}$$

Repeating the calculation $s-1$ times we obtain

$$\int_{V_0(1|2|\cdots|s)}\cdots\int d\boldsymbol{R}_2\cdots d\boldsymbol{R}_s\{\mathsf{L}(2)\cdot\cdots\cdot\mathsf{L}(s)\cdot\boldsymbol{E}_0\}_{\boldsymbol{r}=\boldsymbol{R}_1}=e^{i\boldsymbol{q}\cdot\boldsymbol{R}_1}\left(-\frac{4\pi\alpha}{\varepsilon_1}\right)^{s-1}\{[K_{/\!/}(q,\omega)]^{s-1}\hat{\boldsymbol{q}}\hat{\boldsymbol{q}}+[K_t(q,\omega)]^{s-1}(\mathbf{1}-\hat{\boldsymbol{q}}\hat{\boldsymbol{q}})\}\cdot\boldsymbol{E}_{\boldsymbol{q}}.\tag{38}$$

Finally, forming the matrix element with the bra $(\boldsymbol{q}|\boldsymbol{M}(1)$ in Eq. (29) we find

$$\boldsymbol{\chi}_{\rm ov}(\boldsymbol{q},\omega)=n\alpha\sum_{s=1}^{\infty}\left(\frac{4\pi n\alpha}{\varepsilon_1}\right)^{s-1}\{[K_{/\!/}(q,\omega)]^{s-1}\hat{\boldsymbol{q}}\hat{\boldsymbol{q}}+[K_t(q,\omega)]^{s-1}(\mathbf{1}-\hat{\boldsymbol{q}}\hat{\boldsymbol{q}})\}.\tag{39}$$

This can be written as

$$\boldsymbol{\chi}_{\rm ov}(\boldsymbol{q},\omega)=\chi_{/\!/}(q,\omega)\hat{\boldsymbol{q}}\hat{\boldsymbol{q}}+\chi_t(q,\omega)(\mathbf{1}-\hat{\boldsymbol{q}}\hat{\boldsymbol{q}})\tag{40}$$

with longitudinal and transverse susceptibility

$$\chi_{/\!/,t}(q,\omega)=\frac{n\alpha}{1-(4\pi n\alpha/\varepsilon_1)K_{/\!/,t}(q,\omega)}.\tag{41}$$

From Eq. (36) we find for the longitudinal part

$$K_{/\!/}(q,\omega)=1-2i\frac{j_1(qd)}{qd}\,k_1^2d^2h_1^{(1)}(k_1d)\tag{42}$$

and for the transverse part

$$K_t(q,\omega)=\frac{k_1^2}{k_1^2-q^2}\left[1-\frac{i}{3}k_1d\{[2j_0(qd)-j_2(qd)]k_1d\times h_1^{(1)}(k_1d)-qdj_1(qd)[2h_0^{(1)}(k_1d)-h_2^{(1)}\times(k_1d)]\}\right].\tag{43}$$

In the limit of zero frequency these expressions reduce to those calculated in electrostatics [9], provided $\varepsilon_1(\omega)$ is finite at zero frequency.

The overlap approximation is equivalent to the replacement of the so-called recurrence operator $\boldsymbol{R}(\boldsymbol{q};\mathbf{s},\mathbf{s}')$ occurring in the generalized Foldy-Lax formula [24] by its overlap part

$$\boldsymbol{R}_{\mathrm{ov}}(\boldsymbol{q};\mathbf{s},\mathbf{s}')=-\int_{R<2a}\boldsymbol{G}_0(\mathbf{s}-\mathbf{s}'-\boldsymbol{R})\exp(i\boldsymbol{q}\cdot\boldsymbol{R})d\boldsymbol{R}. \tag{44}$$

Earlier we have studied [25] this integral for arbitrary $\mathbf{s},\mathbf{s}'$. For the point dipole model it suffices to consider $\mathbf{s}=\mathbf{s}'=\mathbf{0}$. It is easily shown that our previous result, given by Eq. (8.9) in Ref. [25], reduces to Eqs. (42) and (43) for $\mathbf{s}=\mathbf{s}'=\mathbf{0}$.

The so-called quasicrystalline approximation of Lax [11] amounts to the approximation for the recurrence operator [24]

$$\boldsymbol{R}(\boldsymbol{q};\mathbf{s},\mathbf{s}')\approx\int h(\boldsymbol{R})\boldsymbol{G}_0(\mathbf{s}-\mathbf{s}'-\boldsymbol{R})\exp(i\boldsymbol{q}\cdot\boldsymbol{R})d\boldsymbol{R}, \tag{45}$$

where $h(\boldsymbol{R})$ is the pair-correlation function. If the latter is approximated by $-\theta(2a-R)$, where $\theta(x)$ is the Heaviside step function, then the integral in Eq. (45) reduces to $\boldsymbol{R}_{\mathrm{ov}}(\boldsymbol{q};\mathbf{s},\mathbf{s}')$ in Eq. (44). This is the approximation used by Pellegrini *et al.* [10]. Their expression for the dielectric tensor, when generalized to arbitrary point dipole polarizability, is easily shown to be equivalent to Eqs. (40)–(43).

IV. NONLOCAL GENERALIZATION OF THE LORENTZ-LORENZ FORMULA

An approximation to the frequency-dependent refractive index $\mathrm{N}(\omega)$ is found by use of Eq. (41) in Eqs. (22), (24), and (25). The limiting value of the function $K_t(q,\omega)$ at zero wave number and zero frequency is $K_t(0,0)=\frac{1}{3}$. If this value is used in Eq. (41), one recovers the Lorentz-Lorenz formula (28). Corrections to the Lorentz-Lorenz formula are due to the wave-number and frequency dependence of the function $K_t(q,\omega)$. In this section we show how to cast the dispersion equation (24) into a form from which the corrections to the Lorentz-Lorenz formula can be easily calculated.

We use the abbreviations

$$x=k_1a,\quad y=qa \tag{46}$$

and write Eq. (43) in the form

$$K_t(q,\omega)=\frac{x^2}{x^2-y^2}[1-S_t(x,y)], \tag{47}$$

with the function $S_t(x,y)$ defined by

$$S_t(x,y)=\frac{4}{3}ix\{2j_0(2y)-j_2(2y)]xh_1^{(1)}(2x)-yj_1(2y)\times[2h_0^{(1)}(2x)-h_2^{(1)}(2x)]\}. \tag{48}$$

Moreover, we define the dimensionless function $A(x)$ by

$$A(x)=4\pi n\frac{\alpha(\omega)}{\varepsilon_1(\omega)}. \tag{49}$$

Substituting into Eq. (41), using Eq. (22), and solving for q^2 from the dispersion equation (24) we find

$$\frac{y^2}{x^2}=1+A(x)S_t(x,y). \tag{50}$$

The function $S_t(x,y)$ has the property

$$S_t(x,x)=1, \tag{51}$$

so that Eq. (50) has a root $y(x)$ that tends to x at large x, since the polarizability $\alpha(\omega)$ tends to zero and the dielectric constant $\varepsilon_1(\omega)$ to a constant at high frequency. For $y=0$,

$$S_t(x,0)=\frac{8}{3}ix^2h_1^{(1)}(2x). \tag{52}$$

This tends to $S_t(0,0)=\frac{2}{3}$ as $x\to0$. However, the function $S_t(x,y)$ is singular at $x=0$ for $y\neq0$. If we expand in y^2, then

$$S_t(x,y)=S_t(x,0)+S_t^{(2)}(x)y^2+O(y^4) \tag{53}$$

with, in the second term,

$$S_t^{(2)}(x)=-\frac{8}{9}ix\left[2h_0^{(1)}(2x)+\frac{12}{5}xh_1^{(1)}(2x)-h_2^{(1)}(2x)\right]. \tag{54}$$

This function behaves as

$$S_t^{(2)}(x)=\frac{1}{3x^2}-\frac{6}{5}+O(x) \tag{55}$$

for small x. Substituting into Eq. (47), we see that $K_t(0,0)=\frac{1}{3}$, as mentioned before. It is convenient to define the function

$$S_d(x,y)=\frac{S_t(x,y)-S_t(x,0)}{y^2}. \tag{56}$$

With this definition Eq. (50) may be written in the form

$$\frac{y^2}{x^2}=\frac{1+A(x)S_t(x,0)}{1-x^2A(x)S_d(x,y)}. \tag{57}$$

If here $S_t(x,0)$ is replaced by its value $\frac{2}{3}$ for small x and $x^2S_d(x,y)$ is replaced by its value $\frac{1}{3}$ for small x and y, then this becomes

$$\frac{y^2}{x^2}\approx\frac{3+2A(x)}{3-A(x)}, \tag{58}$$

which is equivalent to the Lorentz-Lorenz formula (28). One may obtain corrections to the Lorentz-Lorenz formula by solving Eq. (57) by iteration. The iteration converges rapidly, in contrast to Eq. (50), which is numerically unstable under iteration. Therefore, we regard Eq. (57) as the proper nonlocal generalization of the Lorentz-Lorenz formula.

V. ANALYSIS OF THE GENERALIZED LORENTZ-LORENZ FORMULA

In this section we analyze the generalized Lorentz-Lorenz formula (57) in more detail. It is useful to regard the square of the refractive index $\mathsf{N}^2(\omega)=y^2/x^2$ corresponding to the appropriate solution $y(x)$ of Eq. (57) as a function of dimensionless polarizability A and size parameter x. Since we want to consider large polarizability it is convenient to use the variable

$$\zeta=-\frac{1}{A}. \tag{59}$$

Thus we consider the function $\mathsf{N}^2(\zeta,x)$ for complex ζ and positive x. From Eq. (58) we see that the usual Lorentz-Lorenz formula corresponds to

$$\mathsf{N}^2(\zeta,0)=1-\frac{1}{\zeta+\frac{1}{3}}, \tag{60}$$

with a simple pole at $\zeta=-\frac{1}{3}$. For size parameter $x>0$ the analytic structure of the function $\mathsf{N}^2(\zeta,x)$ becomes more complicated.

It is of interest to consider the Drude-Lorentz model with polarizability

$$\alpha(\omega)=\varepsilon_1\frac{C}{\omega_0^2-\omega^2}a^3, \tag{61}$$

where C is the coupling constant and ω_0 the resonance frequency. Moreover, we consider constant ε_1, for example, $\varepsilon_1=1$ for vacuum. From Eq. (49) we see that for this model the variable ζ takes real values for real frequencies, with $\zeta=0$ at the resonance frequency ω_0. The pole at $\zeta=-\frac{1}{3}$ in Eq. (60) corresponds to the Lorentz-shifted resonance [26] at

$$\omega_L=\sqrt{\omega_0^2-\frac{4\pi}{3}na^3C}. \tag{62}$$

One would expect that for size parameter $x>0$ the pole gets shifted to a position in the lower half of the complex ζ plane, corresponding to a shifted and broadened Lorentzian line. However, the analytic behavior turns out to be more complicated and a branch cut singularity in the upper half of the complex ζ plane develops.

To analyze $\mathsf{N}^2(\zeta,x)$ as a function of the complex variable ζ for fixed x we cast it in the form of the continued fraction

$$\mathsf{N}^2(\zeta,x)=1-\cfrac{1}{b_1+\zeta-\cfrac{a_1}{b_2+\zeta-\cfrac{a_2}{\ddots}}} \tag{63}$$

with coefficients a_j,b_j that depend on x. These can be determined from the coefficients in the series expansion in inverse powers of ζ,

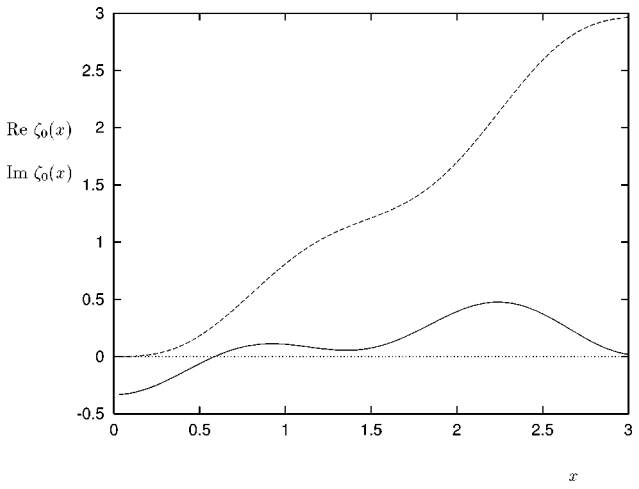

FIG. 1. Plot of the real and imaginary parts of the center of singularities $\zeta_0(x)$, defined by Eq. (67), as a function of size parameter x (solid curve and dashed curve, respectively).

$$\mathsf{N}^2(\zeta,x)=1+\sum_{j=0}^{\infty}\frac{c_j(x)}{\zeta^{j+1}}, \tag{64}$$

by an algorithm due to Stieltjes [27]. The latter expansion is in effect an expansion in powers of the polarizability. The coefficients c_j can be determined from Eq. (50), cast in the form

$$\mathsf{N}^2(\zeta,x)=1-\frac{1}{\zeta}S_t(x,y). \tag{65}$$

From Eq. (51) we find

$$c_0=-1. \tag{66}$$

The higher-order coefficients can be found by expansion of $S_t(x,y)$ about $y=x$ in powers of the difference $y-x$. In particular we find $b_1=c_1=-\zeta_0(x)$ with

$$\zeta_0(x)=\frac{1}{16x^3}[(i+4x-4ix^2-4x^3)e^{4ix}-i-4ix^2+4x^3+16ix^4]. \tag{67}$$

For large ζ we find from Eq. (63)

$$\mathsf{N}^2(\zeta,x)\approx 1-\frac{1}{\zeta-\zeta_0(x)}. \tag{68}$$

Hence $\zeta_0(x)$ is the weighted center of singularities. For small x

$$\zeta_0(x)=-\frac{1}{3}+\frac{22}{15}x^2+\frac{16}{9}ix^3+O(x^4). \tag{69}$$

In Fig. 1 we plot the real and imaginary parts $\mathrm{Re}\zeta_0(x)$ and $\mathrm{Im}\zeta_0(x)$ as functions of x. The positivity of $\mathrm{Im}\zeta_0(x)$ implies that the preponderant weight of the singularities resides in the upper half of the complex ζ plane. Numerically we find a

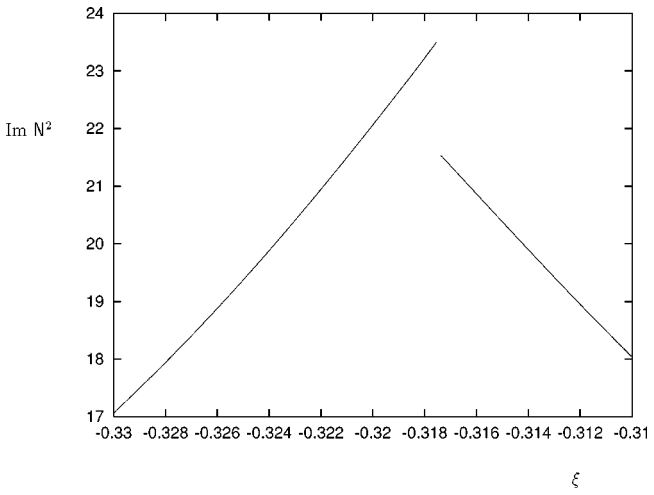

FIG. 2. Plot of $\mathrm{Im}\mathsf{N}^2(\zeta,\mathsf{x})$ for $x=0.1$ as a function of ξ for $\zeta=\xi+0.06i$.

branch cut near $\zeta=-\frac{1}{3}$ for small x. In Fig. 2 we plot the imaginary part $\mathrm{Im}\mathsf{N}^2(\zeta,x)$ for $x=0.1$ as a function of ξ for $\zeta=\xi+0.06i$.

VI. DRUDE-LORENTZ MODEL

The fact that the singularity center $\zeta_0(x)$ lies in the upper half of the complex ζ plane implies that the generalized Lorentz-Lorenz formula (57) does not provide a satisfactory approximation for the refractive index $\mathsf{N}^2(\omega)$ as a function of frequency. For the Drude-Lorentz model without damping, defined by Eq. (61), the exact refractive index $\mathsf{N}^2(\omega)$ should obey the Kramers-Kronig relations, but the generalized Lorentz-Lorenz formula predicts a violation of causality for this model. This shows that correlation corrections cannot be neglected. Proper account of these corrections should restore causality for a disordered system of undamped Drude-Lorentz oscillators.

To get an impression of the nature of the generalized Lorentz-Lorenz formula we consider the Drude-Lorentz model with damping, as given by the polarizability,

$$\alpha(\omega)=\varepsilon_1\frac{C}{\omega_0^2-\omega^2-i\omega\gamma_0}a^3, \tag{70}$$

where γ_0 is the damping constant. Expression (70) is used for atomic spectral lines [23], as well as for the description of polaritons in solid suspensions [28]. The damping constant γ_0 will be chosen sufficiently large that causality is not violated by the generalized Lorentz-Lorenz formula. Upon substitution of Eq. (70) into Eq. (49) we find for the function $A(x)$

$$A(x)=\frac{3p}{x_0^2-x^2-ixg_0}, \tag{71}$$

with

$$p=\phi\varepsilon_1\mu_1\frac{a^2}{c^2}C, \quad g_0=\sqrt{\varepsilon_1\mu_1}\,\frac{a}{c}\gamma_0, \tag{72}$$

where $\phi=(4\pi/3)na^3$ is the volume fraction. The background properties ε_1 and μ_1 are taken to be real constants. The Lorentz-Lorenz formula in the form (58) becomes

$$N_L^2(\omega)=1+\frac{3p}{x_0^2-x^2-ixg_0-p}, \tag{73}$$

showing a Lorentzian resonance at

$$x_L=\sqrt{x_0^2-p} \tag{74}$$

of half-width g_0. The difference x_0-x_L is the well-known Lorentz shift. The parameter

$$x_0=\sqrt{\varepsilon_1\mu_1}\,\frac{a}{c}\omega_0 \tag{75}$$

measures the importance of retardation.

In comparing different systems it is natural to keep the ratio $g_0/x_0=\gamma_0/\omega_0$ fixed. We shall analyze the square of the refractive index $\mathsf{N}^2(\omega)$ as a function of dimensionless frequency x for various values of x_0 and p, keeping g_0/x_0 fixed. In the limit of zero frequency the refractive index is given by Eq. (58), so that

$$\mathsf{N}^2(0)=\frac{3+2A(0)}{3-A(0)}, \tag{76}$$

corresponding to the Lorentz-Lorenz formula (28), taken at zero frequency. From Eq. (71) we find for the present case

$$\mathsf{N}^2(0)=\frac{x_0^2+2p}{x_0^2-p}. \tag{77}$$

This clearly depends on the resonance frequency ω_0. We shall vary the parameter p in proportion to x_0^2, so that both $\mathsf{N}^2(0)$ and the ratio x_L/x_0 remain fixed as x_0 varies. As a

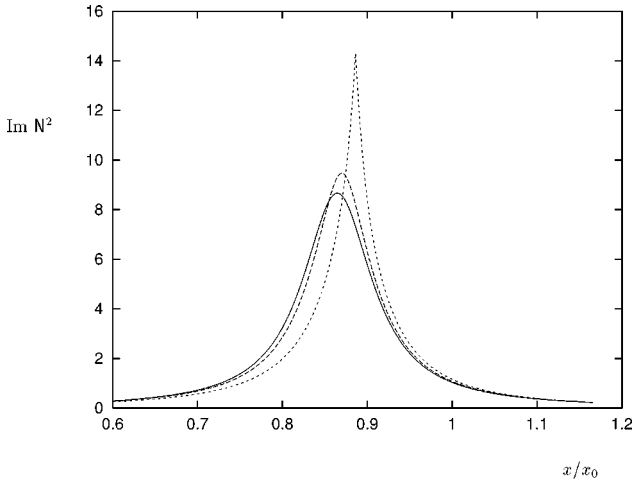

FIG. 3. Plot of $\mathrm{Im}\,\mathsf{N}^2(\zeta,x)$ as a function of x/x_0 for $x_0=0.1$ (dashed curve) and $x_0=0.2$ (dotted curve) for the Drude-Lorentz model with damping coefficient $g_0=0.1x_0$ and coupling parameter $p=0.25x_0^2$. We compare with the Lorentzian $\mathrm{Im}\,\mathsf{N}_L^2(\omega)$, as given by Eq. (73) (solid curve).

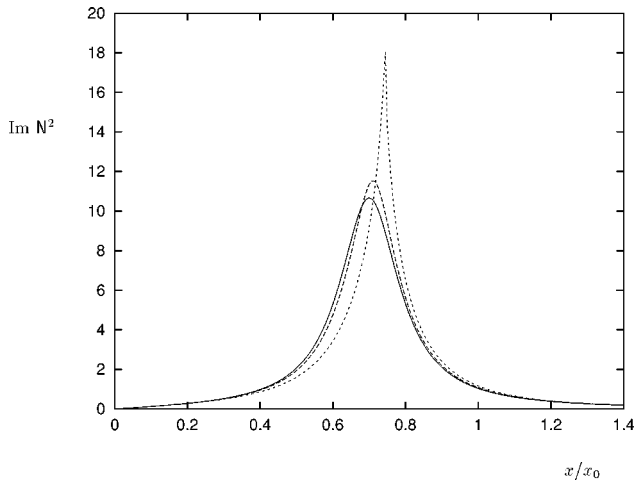

FIG. 4. Same as in Fig. 3 for damping coefficient $g_0=0.2x_0$ and coupling parameter $p=0.5x_0^2$.

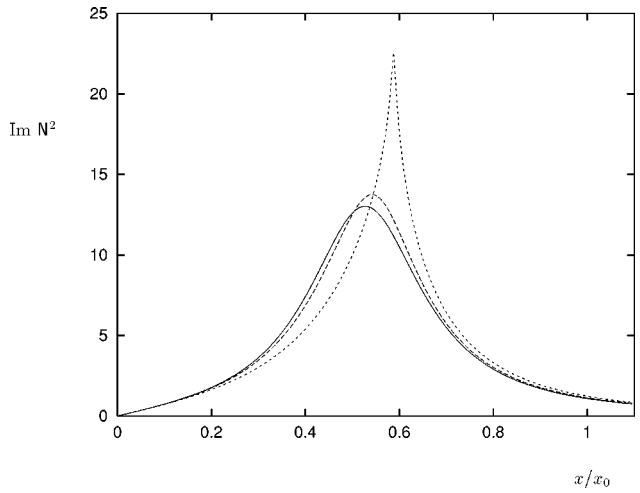

FIG. 5. Same as in Fig. 3 for damping coefficient $g_0=0.3x_0$ and coupling parameter $p=0.7x_0^2$.

consequence, the Lorentz-Lorenz function $N_L^2(\omega)$ given by Eq. (73) takes the same form for different values of x_0 when plotted as a function of x/x_0.

In Fig. 3 we plot $\mathrm{Im}N^2(\omega)$ as a function of dimensionless frequency $x/x_0=\omega/\omega_0$ for two values $x_0=0.1$ and $x_0=0.2$ with damping coefficient $g_0=0.1x_0$ and coupling parameter $p=0.25x_0^2$, so that $N^2(0)=2$. We compare with the Lorentzian $\mathrm{Im}N_L^2(\omega)$, which follows from Eq. (73). As the retardation parameter x_0 increases the absorption line shifts to the right, becomes narrower, and takes a non-Lorentzian form. In Fig. 4 we present similar plots for the values $x_0=0.1$ and $x_0=0.2$ with damping coefficient $g_0=0.2x_0$ and coupling parameter $p=0.5x_0^2$, corresponding to $N^2(0)=4$. In Fig. 5 we present plots for $x_0=0.1$ and $x_0=0.2$ with damping coefficient $g_0=0.3x_0$ and coupling parameter $p=0.7x_0^2$, corresponding to $N^2(0)=8$. In all cases we have chosen the damping coefficient sufficiently large that the generalized Lorentz-Lorenz formula does not violate causality.

VII. DISCUSSION

We have studied the nonlocal generalization of the Lorentz-Lorenz formula for the refractive index that follows from a selection of terms in the cluster expansion for the effective dielectric tensor. In turns out that the corresponding refractive index as a function of the complex single-particle polarizability has surprising features with a singularity structure in the physical part of the complex plane that causes violation of causality if the damping of the single-particle polarizability is too weak. This implies that the generalized Lorentz-Lorenz formula must be used with caution. For weak damping it is essential to include correlation corrections in the calculation of the effective dielectric tensor in order to restore causality. Calculations in electrostatics of the inhomogeneous line broadening corresponding to correlation corrections show that this provides sufficiently large effective damping [29]. These calculations should be extended to include retardation.

We have considered a simple model of spherical particles with a polarizable point dipole at the center. In previous work [25] we have derived a mathematical identity that allows one to study more general models. In particular, the case of uniform dielectric spheres can be investigated. Due to the occurrence of higher-order multipole polarizabilities the calculation becomes rather more involved [30]. It is desirable to have a better understanding of correlation corrections for the point dipole model before embarking on elaborate calculations for more complicated systems.

ACKNOWLEDGMENT

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