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Microscopic Approach to the Lorentz Cavity in Dielectrics

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We develop a microscopic scattering theory for the electromagnetic response of dielectrics. We derive the Lorentz-Lorenz relation for a hard-sphere fluid and for hard-sphere mixtures by summing rigorously the relevant class of multiple scattering events which incorporates particle correlations. The derivation neither makes use of macroscopic concepts such as local and reaction fields nor does it invoke decoupling schemes for high-order correlation functions.

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Understanding the relation between macroscopic electromagnetic response as observed in experiments and microscopic properties such as electronic, atomic, and molecular polarizabilities still presents a challenge. This fundamental problem is relevant at any frequency of the electromagnetic field—from electrostatics up to the x-ray region. Its solution is fierce as it involves a genuine many-body problem. Different forms of matter—metals, semiconductors, insulators, liquids, plasmas, gases, and mesoscopic structures—and different ranges of frequencies are expected to require their own specific solution. However, in 1880 Lorentz [1] developed a generic theory in which 

\[ \varepsilon = 1 + \rho \alpha \alpha \] (1)

in which \( \alpha \) is the polarizability and \( \rho \) the density of the microscopic constituents. (As the polarizability \( \alpha \) depends on the angular frequency \( \omega \) of the electric field, \( \varepsilon \) will also depend on \( \omega \). The obvious dependence on \( \omega \) in all equations will be dropped. We use rationalized Gaussian units and \( c_0 = 1 \).) Lorentz demonstrated that a dramatic improvement over Eq. (1) can be obtained at all frequencies by postulating the existence of a dynamic “local field.” This local field differs from the macroscopic field by a correction factor: the Lorentz local-field factor. In its simplest form this factor is given by \((\varepsilon + 2)/3\). Applying this local-field correction to the dielectric constant results in

\[ \varepsilon = 1 + \rho \alpha \frac{\varepsilon + 2}{3} \] (2)

which is the Lorentz-Lorenz relation (LLR). Historically, the LLR refers to formula (2) when solved explicitly for the polarizability \( \alpha \). Its zero-frequency version is often called the Clausius-Mossotti equation [2]. The success of the LLR in predicting the dielectric constant, in many cases within 1% accuracy, is impressive [3].

From the point of view of many-body physics, the LLR is quite surprising as can best be appreciated by solving Eq. (2) for \( \varepsilon \),

\[ \varepsilon = 1 + \rho \alpha \frac{1}{1 - \frac{1}{3} \rho \alpha} . \] (3)

Apparently, the local-field concept involves terms up to infinite order in the density. The LLR is not expected to be exact, and one would like to know which many-body contributions are included and which are not. To get more insight into the range of validity of the LLR, many alternative or simplified derivations of the original result by Lorentz have been presented over the past century. We mention only a few: Born and Wolf [2], Debye [4], Onsager [5], De Goede and Mazur [6]. Van Kranendonk and Sipe [7] and Schnatterly and Tarrio [8] have reviewed a large number of these derivations. Unfortunately, these approaches rely on the concept of a local field and then apply macroscopic arguments based on Maxwell’s equations. The theoretical base of the LLR is therefore hard to assess, and thus difficult to improve on. We know of no exact microscopic derivation of the LLR, and this Letter is aimed at filling this gap. Microscopic derivations of the second-order term \( \frac{1}{3} \rho \alpha^2 \) of (3) employing point dipoles have already been obtained by Kuz’min et al. [9] and Morice et al. [10].

The electric field seen by one particular point dipole \( i \) can be written schematically as [2]

\[ \mathbf{E}_i = \mathbf{E}_{\text{inc}} + \sum_{j \neq i} \mathbf{E}_{ij} , \] (4)

where \( \mathbf{E}_{\text{inc}} \) is the incoming field and \( \mathbf{E}_{ij} \) is the field received by dipole \( i \) radiated from dipole \( j \). Equation (4) in itself is exact, but the summation over dipoles \( j \) is very difficult to carry out. In the conventional derivations (see, e.g., [2]) it is assumed that the positions of the \( j \) dipoles can be replaced by a continuous dipole density. With this assumption the summation turns into an integration,

\[ \mathbf{E} = \mathbf{E}_{\text{inc}} + J \hat{r}_j \mathbf{E} ( \mathbf{r}, \mathbf{r}_j ) . \] (5)
To include some remnant of the particle correlations this integration is performed by excluding a small sphere—the Lorentz cavity—around the origin (indicated by the prime). The electric fields in Eq. (5) induce polarizations that can be represented by the dielectric dyadic \( \varepsilon \),

\[
\varepsilon - I = \rho \alpha I - \rho \alpha \omega^2 \int dr G_0(r) \cdot [\varepsilon - I],
\]

in which \( I \) is the unit dyadic and \( G_0 \) the free-space Green’s function, to be specified below, signifying the propagation of the scattered light waves. This self-consistent equation for \( \varepsilon \) can be solved and leads to the LLR. This type of intuitive derivation has hitherto been the sole theoretical foundation for the LLR. One of the shortcomings of these derivations of the LLR is readily identified: All light scattering in which more than two correlated particles are involved has been replaced by contributions in which only products of pair correlations occur.

The following derivation of the LLR takes into account all particle correlations rigorously and, indeed, up to infinite order. We shall also be able to generalize the microscopic theory for the dielectric response to mixtures of hard spheres, and we will derive the LLR for mixtures [3], which is closely related to the Maxwell-Garnett formula [11].

The basis of our approach is multiple-scattering theory. The generic microscopic building block that we consider is the finite-size hard sphere with radius \( R \) (being much smaller than the wavelength of light) and polarizability \( \alpha \) [12]. Our analysis includes the case of the point dipole [13].

The dielectric function originates from the collective response of dipoles excited by the incoming field and the rescattered fields of all other dipoles. The scattering of the three electric field components from position \( r_1 \) to position \( r_2 \) by a particle located at \( R \), is completely described by the \( t \) matrix, denoted by the second-rank tensor \( t_i(r_1, r_2) \).

For a spherical Rayleigh scatterer this \( t \) matrix is given by

\[
t_i(r_1, r_2) = -\frac{\alpha \omega^2}{v}\delta(r_1 - r_2)\theta(R - |r_1 - R|)|I|,
\]

in which \( \theta \) denotes the Heaviside step function and \( v = 4\pi R^3/3 \) is the volume of the scatterer. The step function ensures that the scattering takes place only when the light has propagated into the scatterer, and the delta function signifies that in the Rayleigh limit, as in the Born approximation, the wave only interacts once with the scattering potential. From now on, \( \theta_i(r) = \theta(R - |r - R|) \).

The free-field propagator \( G_0(r_1, r_2) = G_0(r_1 - r_2) \) describes how the electric field propagates from \( r_1 \) to \( r_2 \) [14].

\[
G_0(r) = -\frac{\exp(i\omega r)}{4\pi r}[P(\omega r)(I - \hat{r}\hat{r}) + Q(\omega r)\hat{r}\hat{r}] + \frac{I}{3\omega^2}\delta(r),
\]

in which \((\hat{r}\hat{r})_{ij} = r_ir_j/r^2\), and \( P, Q \) are known functions [14].

Inside a medium, the propagator \( G(r_1, r_2) \) will be different from the free propagator. For liquids and gases we have to average this quantity over the disorder, usually performed by averaging over the positions of the scatterers [15]: \( \langle G(r_1, r_2) \rangle = G(r_1 - r_2) \).

To calculate its Fourier transform \( G(k) \), it is expedient to introduce the self-energy \( \Sigma(k) \) defined by

\[
G(k) = \frac{1}{\omega^2 I - k^2 I + kk - \Sigma(k)}.
\]

\( \Sigma(k) \) characterizes the response of the medium and vanishes in empty space. The Green’s function \( G \) can be expanded into a series of scattering events that can be classified either as singly or multiply connected [15]. A singly connected event can, in contrast to a multiply connected event, be written as the product of lower-order events. The expedience of the self-energy \( \Sigma \) arises from the fact that it represents solely multiply connected scattering events. The dielectric function \( \varepsilon(k) \) is related to the self-energy by

\[
\varepsilon(k) = I - \frac{\Sigma(k)}{\omega^2}.
\]

The widely used independent scattering approximation (ISA) amounts to keeping in \( \Sigma \) only the term which is lowest order in the density. This means that light can scatter from as many particles as many times as possible, but never more than once from the same particle. In addition, particle correlations are not considered within the ISA. The ISA self-energy reads

\[
\Sigma^{(1)}(r_1 - r_2) = \rho \int dRt_i(r_1, r_2),
\]

\[
= -\rho \alpha \omega^2 \delta(r_1 - r_2)I,
\]

so that \( \Sigma^{(1)}(k) = -\rho \alpha \omega^2 I \). The superscript in \( \Sigma^{(1)} \) indicates that only the first-order terms in the density \( \rho \) are accounted for. Equation (11) implies that ISA gives for the dielectric function

\[
\varepsilon^{(1)} = I + \rho \alpha I,
\]

which is equivalent to Eq. (1) following from response theory. To improve on this result we go beyond ISA and include particle correlations.

Let \( g_m(1, \ldots, m) \) be the probability distribution for observing \( m \) particles at positions \( R_1, \ldots, R_m \). These distributions can be decomposed by employing the so-called irreducible correlation functions \( h_m(1, \ldots, m) \) according to

\[
g_1(1) = h_1(1) = 1,
\]

\[
g_2(12) = h_1(1)h_1(2) + h_2(12),
\]

\[
g_3(123) = 1 + h_1(1)h_2(23) + h_1(2)h_2(13)
\]

\[
+ h_1(3)h_2(12) + h_3(123),
\]

and so on. The irreducible correlation function \( h_m \) contains that part of \( g_m \) that cannot be written as a linear combination of products of correlation functions \( h \) of lower
order. As a result, the terms in the sum represent all possible partitions of the \( m \) arguments of \( g_m \). Within the ISA, all \( h_m \) are taken to vanish for \( m > 1 \). Except for \( h_1 \), the physical content and mathematical structure of the irreducible correlation functions \( h_m \)'s are highly nontrivial. Fortunately, for classical hard spheres [16] the \( h_m \)'s are required only for those coordinates in configuration space for which all \( m \) spheres overlap, to be referred to as the forbidden region. Correlation functions in this region will be denoted by a union sign: \( g_{m}^U \) and \( h_{m}^U \). Obviously, \( g_m = 0 \) for \( m > 1 \), from which one finds \( h_2^U = -1 \), \( h_3^U = +2 \), and \( h_4^U = -6 \). The computation of high-order \( h_m^U \) becomes quickly cumbersome. The correlation functions (14) enter when the Green's function \( G \), expanded as a series of scattering events, is averaged over the particle positions. One can then unambiguously distinguish singly and multiply connected events. For the self-energy only the latter should be considered: All relevant particle correlations in \( G \) are then automatically taken into account.

Within ISA, the scattering from particle \( i \) to particle \( j \) has been counted as \( t_i G_0 t_j \) in the Green's function \( G \) for all possible positions of particles \( i \) and \( j \). To account for the forbidden region up to second order in \( \rho \), we include in \( \Sigma \) the following contribution:

\[
\Sigma^{(2)}(r_1 - r_2) = \rho^2 \int dr_3 \int dr_4 \int dR_i \int dR_j \\
\times h_2(ij) t_i(r_1, r_3) \cdot G_0 (r_3 - r_4) \cdot t_j(r_4, r_2) .
\]

For Rayleigh scatterers the range of \( h_2(ij) \) is always smaller than the wavelength, and the dominant contribution to the integral comes from the delta function in the Green's function (8). The other contributions are of order \( (\omega R)^2 \) and will be neglected. Using Eq. (7) shows that \( \Sigma^{(2)}(r_1 - r_2) = \Sigma^{(2)} \delta(r_1 - r_2) I \) with

\[
\Sigma^{(2)} = \frac{\rho^2 \alpha^2 \omega^2}{3 v^2} \int r_i \int dR_i h_2(ij) \hat{t}_i(r_1) \hat{t}_j(r_1) ,
\]

\[
= \frac{\rho^2 \alpha^2 \omega^2}{3 v^2} h_2^U \int \hat{t}_i(r_1) dR_i \int \hat{t}_j(r_1) dR_j ,
\]

\[
= - \frac{\rho^2 \alpha^2 \omega^2}{3} ,
\]

where \( h_2(ij) \) is only required in the forbidden region. This result agrees with the LLR if the latter is expanded to second order in the density.

Subsequent contributions due to correlations turn out to obey \( \Sigma^{(m)}(r_1 - r_2) = \Sigma^{(m)} \delta(r_1 - r_2) I \). The third-order contribution follows from the three-particle events \( t_i G_0 t_j G_0 t_k \) in which particles \( i, j, \) and \( k \) overlap. By considering \( \Sigma^{(2)} \) we have already taken into account the following singly connected three-particle events in \( G \): \( h_2(ij) t_i G_0 t_j G_0 t_k \) and \( h_2(jk) t_j G_0 t_k G_0 t_i \), but not yet \( h_2(ijk) t_i G_0 t_j G_0 t_k \) and \( h_3(ijk) t_i G_0 t_j G_0 t_k \) which are multiply connected events. Note that the order of the particles in the functions \( h_m \) is important. The remaining three-particle correlations to be included are thus

\[
\Sigma^{(3)} = \frac{\rho^3 \alpha^3 \omega^2}{9 v^3} \int dR_i \int dR_j \int dR_k \\
\times [h_3(ij) h_2(ik) + h_3(ji) k] \hat{t}_i(r_1) \hat{t}_j(r_1) \hat{t}_k(r_1) ,
\]

\[
\Sigma^{(3)} = \frac{H_3 \rho^3 \alpha^3 \omega^2}{9} = \frac{\rho^3 \alpha^3 \omega^2}{9} \sum_m H_{m+1}(\frac{-\rho \alpha}{3})^m .
\]

The first three orders have been determined, where \( \Sigma^{(1)} = 1, \Sigma^{(2)} = -1, \) and \( \Sigma^{(3)} = 1 \).

Now we focus solely on the properties of \( H_m \), and we shall prove that

\[
H_m = (-1)^{m+1} .
\]

The proof entails the generating function

\[
F(\lambda) = \frac{1}{1 - \sum_{i=1}^{\infty} \lambda^i H_i} .
\]

Let us expand the generating function in powers of \( \lambda, F(\lambda) = 1 + \sum_{m=1}^{\infty} \lambda^m p_m \). The coefficient \( p_m \) is the linear combination of all possible ordered products of \( H_i \) with indices adding up to \( m \). These terms can be associated one-to-one with the diagrams of all possible scattering events involving \( m \) particles, therefore \( p_m = g_m^U \). Finally, one obtains that

\[
F(\lambda) = 1 + \sum_{m=1}^{\infty} \lambda^m g_m^U = 1 + \lambda .
\]

Using Eqs. (23) and (24) yields Eq. (22). Let us remind the reader that the proof requires infinite-order particle correlation functions.

The remarkable property that \( H_{m+1} = H_{m+1} \times H_n \) involves that uncontrolled approximations, such as the one involved in the transition from Eq. (4) to Eq. (5), may turn out to give correct answers. The decoupling property of \( H_m \) looks deceivingly simple. To appreciate its meaning, it is worthwhile to rewrite the \( H \) correlation functions in terms of the irreducible particle correlations \( h \). For instance, for three-particle correlations the exact decoupling property implies \( h_3^U = -3 h_2^U - h_1^U \). This result can be contrasted with the well-known (Kirkwood) superposition
spheres, we first look at the contributions to the dielectric
function in the forbidden regime $h^U_1 = (h^U_2)^3 + 3(h^U_2)^2$.

We have used hard-core interaction potentials. It is ex-
pected that this is not a severe limitation. Any realistic
intermolecular potential will have an inner region that con-
ists of a hard repulsive part. As most of the polarizability
of the molecule will be localized within this region, our
treatment can be employed for this case as well.

We can apply our microscopic theory to mixtures. To
describe a mixture of type $A$ and type $B$ hard Rayleigh
spheres, we first look at the contributions to the dielectric
tensor that are linear in $\rho_A$ and contain all orders of $\rho_B$.
To obtain the events linear in $\rho_A$ we just look at all $B$
events in which we are allowed to replace one $t$ matrix of
$B$ by a $t$ matrix of $A$. This changes only the multiplicity
of the contributions, as, for instance, the two-particle
contribution $t_3G_0t_B$ has now become distinguishable, but
equal in size, from the $t_BG_0t_A$ contribution. The resulting,
more complicated, series can again be summed exactly
and gives $\rho_A\alpha_A/(1 - \frac{1}{2}\rho_B\alpha_B)^2$, and can, for instance, be
used to calculate the medium-enhanced absorption of small
concentrations of $A$ in $B$. In fact, it is straightforward
to include all orders of $\rho_A$ and $\rho_B$, and the LLR for $AB$
mixtures becomes

$$\epsilon_{AB} = I + \frac{\rho_A\alpha_A + \rho_B\alpha_B}{(1 - \frac{1}{2}\rho_A\alpha_A - \frac{1}{2}\rho_B\alpha_B)} I,$$

which, if the densities are transformed into volume fractions,
represents essentially the well-known Maxwell-Garnett
formula.

Having established a microscopic framework that by
summing a class of events generates the LLR, one can now
ponder over systematic extensions. Events not
included in our theory are the events in which the same
scatterer is visited more than once, often called dependent
scattering, as well as correlations with a range comparable
to or larger than the wavelength. Dependent scattering
becomes important when $\frac{1}{2}\rho\alpha = 1$.

Dependent scattering for two point particles has been
considered in the static limit [9] and near an internal
resonance. In the latter regime these contributions appear
to become important [18]. Near internal resonances, one
can consider the modification of the Einstein coefficient
for spontaneous emission, where local-field concepts play
an important role [19]. Recently, the Lorentz local-field
corrections to nonlinear optical susceptibilities have been
calculated [20]. At present, we are not able to extend our
theory to include these nonlinear effects.

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Note added.—Our derivation is valid for finite fre-
quency. The limit to zero frequency can be taken in our
theory. It was pointed out to us that a derivation for pre-
cisely zero frequency actually exists [21]. In that paper,
the values for the correlations functions $H_m$ have been
obtained in an alternative way. We thank B. U. Felderhof
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0) = -1$ does not apply: For free bosons, $h_2(r_{12} = 0) = 1$
above the critical temperature. As shown in
[10], however, the second-order $\Sigma(2)$ does not depend on
$h_2(r_{12} = 0)$.