# Local field models for light scattering and the dielectric constant of nonpolar fluids*

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The resummed molecular theory for the dielectric constant and light scattering in nonpolar fluids developed by previous authors is generalized to account for arbitrary local field models in addition to the Lorentz–Lorenz model. In particular, it is shown that the Onsager–Böttcher and Wertheim models for the dielectric constant may be encompassed by this theory. Expressions for Rayleigh's ratio in the Born approximation are obtained, providing a molecular derivation of the "local field factors" for light scattering consistent with these dielectric models. The results are compared with experimental isotropic Rayleigh ratios, indicating that the Wertheim model provides the best agreement. The relation with Einstein's phenomenological theory of light scattering is discussed.

## I. INTRODUCTION

Microscopic theories of light scattering and the dielectric constant in fluids composed of molecules characterized by a constant scalar polarizability $\alpha$ data back to the work of Yvon[1] and Kirkwood.[2] Yvon's theory of light scattering was reformulated by Fixman[3] and by Mazur and Mandel,[4,5] the latter authors also considering variation of the polarizability with intermolecular distances. All these theories are based on expansions in powers of the polarizability and evaluation of the first few terms of the resulting series. Recently, Bedeaux and Mazur[6] and Felderhof[7] have presented theories of light scattering and the dielectric constant which partially overcome this limitation to small values of $\alpha\rho$, where $\rho$ is the number density, by performing a resummation of the Kirkwood–Yvon series. It is the purpose of this paper to show that the "resummed" theory may be generalized in a significant respect.

As discussed by Felderhof,[7] one can regard the resummation as being accomplished in two steps. In the first step, one takes into account from the outset that the local field acting on a particular molecule due to the other molecules in the system is given to a good approximation by the Lorentz local field $\mathbf{E}_L = [(\epsilon+2)/3]\mathbf{E}$, where $\epsilon$ is the dielectric constant and $\mathbf{E}$ the Maxwell field in the medium. Thus the microscopic equations are formally rewritten so that $\mathbf{E}_L$ rather than the vacuum field $\mathbf{E}_0$ appears as the driving field. In the second step, a resummation replaces vacuum electromagnetic propagators by "renormalized" propagators accounting for the fact that the fields propagate through the average medium rather than through vacuum. The resulting equations for the average polarization and microscopic polarization fluctuation are no longer series expansions in powers of $\alpha$, due to the dependence of the renormalized" propagator on $\alpha\rho$, and therefore may be used with some confidence for larger values of the polarizability and/or the density.[6,7]

In this paper we note that the first step described above can be accomplished in an infinite number of ways, so that in addition to the Lorentz field any continuum model of the local field can be used as the driving field in the microscopic equations. This freedom stems from the fact that for molecules with hard cores of diameter $d$, in an *exact* calculation there is no dependence of the final answer on the form of the electromagnetic propagator $\mathbf{F}(\mathbf{r},\mathbf{r}')$ [see Eq. (II.2)] for separations $|\mathbf{r}-\mathbf{r}'| < d$. Thus in the microscopic equations we may replace $\mathbf{F}(\mathbf{r},\mathbf{r}')$ by a propagator which is arbitrary for $|\mathbf{r}-\mathbf{r}'| < R_c$, where $R_c$ can in principle be any distance such that $0 < R_c \le d$. This idea is similar to that employed by Høye and Stell[8] in their recent discussion on the static dielectric constant of rigid polar fluids.

In Sec. II we summarize Felderhof's[7] formal resummed equations for the average polarization and polarization fluctuation, taking account of the available freedom in choosing the propagator for separations less than $R_c$. In Sec. III we discuss three particular choices for the propagator, which correspond to three 'local field' approximations for the dielectric constant of nonpolar fluids; the Lorentz–Lorenz model (considered previously by Bedeaux and Mazur[6] and by Felderhof[7]), the Onsager[9]–Böttcher[10] model, and a model which has recently been proposed by Wertheim.[11]

In Sec. IV we use these results to derive the differential crosssection for Rayleigh light scattering in the Born approximation. This is of interest for several reasons, which are examined in the remainder of the paper. There has been considerable controversy[12–15] in recent years about the correct form of the so-called 'local field' factor to describe isotropic Rayleigh scattering intensities. According to Einstein's[16] phenomenological theory of light scattering, the intensity is proportional to $(\partial\epsilon/\partial\rho)_T^2$. When the Lorentz-Lorenz equation for $\epsilon$ is adopted, one obtains the well-known $(\epsilon+2/3)^4$ local field factor, which was shown by Fixman[3] to be valid to order $\alpha^3$. However, comparison of observed intensities with those calculated using this factor have shown that the latter are generally 10–20% too large,[13,14,17] which has spurred an interest in employing other model theories of the dielectric constant, such as the Onsager–Böttcher model, in conjunction with Einstein's theory. This has culminated in a current debate[15] regarding the density dependence of the 'cavity radius' $R_c$ in the Onsager–Böttcher model.

In this paper we derive the scattering crosssection independently of Einstein's theory, and obtain in Sec. IV a general expression for the 'local field' factor. In Sec. V we examine this factor for the three models introduced in Sec. III, and show that in each case it may be related to the dielectric constant given by these models without specifying either $\alpha$ or $R_c$. Assuming that the latter can be fitted to give agreement between the model expressions and experimental values for the dielectric constant, we may calculate isotropic scattering intensiities from knowledge of the dielectric constant. Comparisons with experimental intensities indicate that the Wertheim model gives the best agreement. These comparisons with experiment should be viewed with some caution since the present theory neglects the variation of the polarizability with interparticle separation.[4,18]

The relation of our results with those obtained using Einstein's theory is also examined in Sec. V. When $R_c$ is regarded as a constant independent of density, we do *not* obtain exact agreement with Einstein's theory for either the Onsager–Böttcher or Wertheim model, although the discrepancy between these two approaches is numerically small. As the present calculation is limited to local field approximations, no firm conclusions can be drawn from these models concerning the validity of the phenomenological theory.[19] We note that some previous authors[20,21] have given microscopic derivations of the Onsager–Böttcher model and obtained density- and temperature-dependent expressions for $R_c$, but a corresponding treatment of the Wertheim model is presently unavailable.

## II. FORMAL THEORY

We consider a system of $N$ molecules in a volume $V$, each characterized by a scalar polarizability $\alpha(\omega)$ and subject to an external electric field $\mathbf{E}_0$ of angular frequency $\omega$. The explicit frequency dependence of $\alpha$ will be omitted in the following. Neglecting the Doppler effect due to the motions of the molecules, we may assume that all quantities oscillate in time with the same factor $\exp[-i\omega t]$, which is henceforth omitted. The induced dipole moment $\mu_i$ of a representative particle $i$ is then given by[5,7]

$$\mu_i = \alpha \mathbf{E}_0(\mathbf{r}_i, k_0) + \alpha \sum_{j(\neq i)}^{N} \mathbf{F}(\mathbf{r}_i, \mathbf{r}_j; k_0) \cdot \mu_j \quad , \tag{II.1}$$

where $\mathbf{F}(\mathbf{r}, \mathbf{r}'; k_0)$ is the vacuum dipole propagator

$$\mathbf{F}(\mathbf{r}, \mathbf{r}'; k_0) = (\nabla_r \nabla_r + k_0^2 \mathbf{I}) \frac{e^{ik_0|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \quad , \tag{II.2}$$

with $k_0 = \omega/C$ the vacuum wavenumber and $\mathbf{I}$ the unit dyadic. In Eq. (II.1) we have neglected the small (at light frequencies) radiation self-reaction fields of the particles.

The approach of the Kirkwood[2]–Yvon[1] theory of the dielectric constant is to solve Eq. (II.1) iteratively in powers of $\alpha$ and subsequently compute the average polarization $\mathbf{P}$,

$$\mathbf{P}(\mathbf{r}, k_0) = \langle \mathbf{p}(\mathbf{r}, k_0) \rangle \quad , \tag{II.3}$$

where

$$\mathbf{p}(\mathbf{r}, k_0) = \sum_{i=1}^{N} \mu_i \, \delta(\mathbf{r} - \mathbf{r}_i) \quad , \tag{II.4}$$

is the microscopic polarization density. In Eq. (II.3), the brackets $\langle\ \rangle$ denote an equilibrium ensemble average in the absence of the external field $\mathbf{E}_0$. In this case, the molecules are assumed to interact by short-ranged, not necessarily additive, forces including spherical hard core repulsion. In the calculation of $\mathbf{P}$, it follows that there is no contribution from the propagator $\mathbf{F}(\mathbf{r}, \mathbf{r}'; k_0)$ for distances $|\mathbf{r} - \mathbf{r}'| < d$, where $d$ is the hard core diameter, due to the vanishing of the $s$-particle reduced distribution functions,[22]

$$\rho_s(\mathbf{r}_1 \cdots \mathbf{r}_s) = \left\langle \sum_{i_1 \neq i_2 \cdots \neq i_s} \delta(\mathbf{r}_1 - \mathbf{r}_{i_1}) \, \delta(\mathbf{r}_2 - \mathbf{r}_{i_2}) \cdots \delta(\mathbf{r}_s - \mathbf{r}_{i_s}) \right\rangle ,$$

when any two of the particles are separated by a distance less than $d$. This holds also for the calculation of the correlation $\langle \mathbf{p}(\mathbf{r}) \mathbf{p}(\mathbf{r}') \rangle$, which is required in consideration of light scattering intensities.

In an exact calculation, or in a series expansion of the Kirkwood–Yvon type, there is consequently no effect on the calculation of average properties when $\mathbf{F}(\mathbf{r}, \mathbf{r}'; k_0)$ in Eq. (II.1) is replaced by the propagator $\mathbf{L}$, where

$$\begin{aligned} \mathbf{L}(\mathbf{r}, \mathbf{r}'; k_0) &= \mathbf{F}(\mathbf{r}, \mathbf{r}'; k_0) \quad |\mathbf{r} - \mathbf{r}'| \geq R_c \quad , \\ &= \text{arbitrary} \quad |\mathbf{r} - \mathbf{r}'| < R_c \quad . \end{aligned} \tag{II.5}$$

Here $R_c$ can be any distance such that $0 < R_c \leq d$. We shall comment further on the choice of $R_c$ when we consider particular models for the propagator $\mathbf{L}$.

We now consider Eq. (II.1) with $\mathbf{F}$ replaced by the propagator $\mathbf{L}$ of Eq. (II.5). Removing the restriction $j \neq i$ in the summation in Eq. (II.1), this equation can be rewritten as

$$\mu_i = \alpha' \mathbf{E}_0(\mathbf{r}_i, k_0) + \alpha' \sum_{j}^{N} \mathbf{L}(\mathbf{r}_i, \mathbf{r}_j; k_0) \cdot \mu_j \quad , \tag{II.6}$$

where $\alpha'$ is a renormalized polarizability,

$$\alpha' = \alpha(1 + \alpha b)^{-1} \quad , \tag{II.7}$$

and $b$ is defined by

$$b\mathbf{I} = \lim_{|\mathbf{r}-\mathbf{r}'| \to 0} \mathbf{L}(\mathbf{r}, \mathbf{r}'; k_0) \quad . \tag{II.8}$$

Multiplying both sides of Eq. (II.6) by $\delta(\mathbf{r} - \mathbf{r}_i)$ and summing over $i$, we obtain using the definition Eq. (II.4),

$$\begin{aligned} \mathbf{p}(\mathbf{r}, k_0) &= \alpha' n(\mathbf{r}) \mathbf{E}_0(\mathbf{r}, k_0) \\ &\quad + \alpha' n(\mathbf{r}) \int_v d^3\mathbf{r}' \, \mathbf{L}(\mathbf{r}, \mathbf{r}'; k_0) \cdot \mathbf{p}(\mathbf{r}', k_0) \ , \end{aligned} \tag{II.9}$$

where

$$n(\mathbf{r}) = \sum_{i}^{N} \delta(\mathbf{r} - \mathbf{r}_i)$$

is the microscopic number density. This equation will be written in short-hand notation as

$$\mathbf{p} = \alpha' n \mathbf{E}_0 + \alpha' n \, \mathbf{L} * \mathbf{p} \quad , \tag{II.10}$$

where the symbol $*$ denotes the convolution,

$$\mathbf{f} * \mathbf{g} = \int_v d^3\mathbf{r}' \, \mathbf{f}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{g}(\mathbf{r}') \ .$$

Consider the approximation whereby one averages Eq. (II.10) and writes the average of the second term on the rhs as a product of averages. This gives

$$\mathbf{P} \approx \alpha' \rho \mathbf{E}_L \quad , \tag{II.11}$$

where $\rho = \langle n \rangle$ is the average number density and $\mathbf{E}_L$ is defined by

$$\mathbf{E}_L = \mathbf{E}_0 + \mathbf{L} * \mathbf{P} \quad . \tag{II.12}$$

The approximation resulting in Eq. (II.11) amounts to a mean field treatment in which intermolecular correlations are ignored, which will henceforth be designated as the "local field" approximation.

The field defined by Eq. (II.12) will be called the generalized local electric field. It is apparent that the calculation of the average polarization in this approximation is no longer independent of the form of $\mathbf{L}$. An analogous situation occurs in "mean-field" approximations for the dielectric constant of rigid polar fluids.[8]

It will be useful for later purposes to relate the polarization in the same approximation to the external field. One obtains from Eqs. (II.11) and (II.12)

$$(1 - \alpha' \rho \mathbf{L}) * \mathbf{P} \approx \alpha' \rho \mathbf{E}_0 \quad , \tag{II.13}$$

where $1$ denotes the delta function $\mathbf{I}\, \delta(\mathbf{r} - \mathbf{r}')$. Defining the propagator $\mathbf{U}$ by

$$(1 + \alpha' \rho \mathbf{U}) * (1 - \alpha' \rho \mathbf{L}) = 1 \quad , \tag{II.14}$$

and multiplying both sides of Eq. (II.13) by $(1 + \alpha' \rho \mathbf{U})$, we obtain

$$\mathbf{P} \approx \alpha' \rho (1 + \alpha' \rho \mathbf{U}) * \mathbf{E}_0 \quad . \tag{II.15}$$

We note that Eq. (II.14) is equivalent to the integral relation,

$$\begin{aligned} \mathbf{U}(\mathbf{r}, \mathbf{r}'; k_0) &= \mathbf{L}(\mathbf{r}, \mathbf{r}'; k_0) \\ &\quad + \alpha' \rho \int_v d^3\mathbf{r}''\, \mathbf{U}(\mathbf{r}, \mathbf{r}''; k_0) \cdot \mathbf{L}(\mathbf{r}'', \mathbf{r}'; k_0) \quad . \end{aligned} \tag{II.16}$$

The elegant theory presented by Felderhof[7] provides a method for embedding these local field relations in an exact framework. This theory yields expansions in $\alpha'$ (which is equal to the molecular polarizability $\alpha$ in Ref. 7) for the average polarization $\mathbf{P}$ and microscopic polarization fluctuation $\mathbf{p}_1 = \mathbf{p} - \mathbf{P}$. These are not strictly series expansions in powers of $\alpha'$, since they involve the renormalized propagator $\mathbf{U}$ rather than $\mathbf{L}$. For present purposes, we will consider simply the lowest order result for $\mathbf{p}_1$, and the first correction to the local field approximation for $\mathbf{P}$. One finds from Felderhof's[7] results,

$$\mathbf{p}_1 \approx \alpha' (1 + \alpha' \rho \mathbf{U}) * n_1 \mathbf{E}_L \quad , \tag{II.17}$$

$$\begin{aligned} \mathbf{P} &\approx \alpha' \rho \mathbf{E}_L + (\alpha')^2 \langle n_1 \mathbf{U} n_1 \rangle * \mathbf{E}_L \quad , \\ &\equiv \alpha' \rho (1 + \mathbf{C}) * \mathbf{E}_L \quad , \end{aligned} \tag{II.18}$$

where $n_1 = n - \rho$ is the number density fluctuation and Eq. (II.18) defines the matrix $\mathbf{C}$.

The susceptibility $\chi$, which is generally a nonlocal operator in space, is defined by

$$\mathbf{P}(\mathbf{r}, k_0) = \int_v d^3\mathbf{r}'\, \chi(\mathbf{r}, \mathbf{r}'; k_0) \cdot \mathbf{E}(\mathbf{r}', k_0) \equiv \chi * \mathbf{E} \quad . \tag{II.19}$$

Here $\mathbf{E}$ is the macroscopic (Maxwell) field in the medium, which is related to the external field, from Maxwell's equations, by

$$\mathbf{E}(\mathbf{r}, k_0) = \mathbf{E}_0(\mathbf{r}, k_0) + \int_v d^3\mathbf{r}'\, \mathbf{F}(\mathbf{r}, \mathbf{r}'; k_0) \cdot \mathbf{P}(\mathbf{r}', k_0) \quad . \tag{II.20}$$

As discussed by several authors[7,23] some care is needed in evaluating the integral in Eq. (II.20) due to the singularity in the propagator $\mathbf{F}(\mathbf{r}, \mathbf{r}'; k_0)$ as $|\mathbf{r} - \mathbf{r}'| \to 0$. For an arbitrary continuous function $\mathbf{f}(\mathbf{r})$ of $\mathbf{r}$, we may write

$$\int_v d^3\mathbf{r}'\, \mathbf{F}(\mathbf{r}, \mathbf{r}'; k_0) \cdot \mathbf{f}(\mathbf{r}') = \int_{v-\sigma} d^3\mathbf{r}'\, \mathbf{F}(\mathbf{r}, \mathbf{r}'; k_0) \cdot \mathbf{f}(\mathbf{r}') - \frac{4\pi}{3} \mathbf{f}(\mathbf{r}),$$

where an infinitesmal sphere $\sigma$ around $\mathbf{r}$ is excluded from the integral on the rhs. With this interpretation, Eq. (II.20) in concise notation is

$$\mathbf{E} = \mathbf{E}_0 + \mathbf{F} * \mathbf{P} \quad . \tag{II.21}$$

Combined with Eq. (II.12), this provides an alternative expression for $\mathbf{E}_L$,

$$\mathbf{E}_L = \mathbf{E} + \mathbf{G} * \mathbf{P} \quad , \tag{II.22}$$

where $\mathbf{G}$ is, explicitly

$$\mathbf{G}(\mathbf{r}, \mathbf{r}'; k_0) = \mathbf{L}(\mathbf{r}, \mathbf{r}'; k_0) - \mathbf{F}(\mathbf{r}, \mathbf{r}'; k_0) \quad . \tag{II.23}$$

We note, from the definition of $\mathbf{L}$ in Eq. (II.5), that $\mathbf{G}(\mathbf{r}, \mathbf{r}'; k_0)$ is zero for $|\mathbf{r} - \mathbf{r}'| > R_c$.

As discussed by Felderhof,[7] the kernel $\langle n_1 \mathbf{U} n_1 \rangle$ in Eq. (II.18), and at least two higher order terms in the expansion for $\mathbf{P}$ which are not explicitly shown in Eq. (II.18), have the property of being short ranged. Hence, to the order of approximation with which we are dealing, the susceptibility $\chi$ may be evaluated for an infinite medium. In this case it is convenient to employ a Fourier transform representation, defining for example

$$\begin{aligned} \hat{\chi}(\mathbf{k}, k_0) &= \int d^3\mathbf{r}'\, \chi(\mathbf{r}, \mathbf{r}'; k_0)\, e^{i\mathbf{k} \cdot (\mathbf{r}' - \mathbf{r})} \\ &\equiv \hat{\chi}^{\text{tr}}(k, k_0)\, (\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}) + \hat{\chi}^{l}(k, k_0)\, \hat{\mathbf{k}}\hat{\mathbf{k}} \quad , \end{aligned}$$

where $\hat{\mathbf{k}}$ is the unit vector $(\mathbf{k}/\mathrm{k})$ and we have introduced the transverse (tr) and longitudinal ($l$) components of the susceptibility tensor. By Fourier transforming Eqs. (II.18), (II.19), and (II.22), we obtain

$$\hat{\chi}(\mathbf{k}, k_0) \cdot [\mathbf{I} + \hat{\mathbf{G}}(\mathbf{k}, k_0) \cdot \hat{\chi}(\mathbf{k}, k_0)]^{-1} = \alpha' \rho [\mathbf{I} + \hat{\mathbf{C}}(\mathbf{k}, k_0)] \quad . \tag{II.24}$$

The corresponding expression when we use the local field approximation for P, Eq. (II.11), is obtained by neglecting $\hat{\mathbf{C}}$ in Eq. (II.24). The resulting approximation for the susceptibility, denoted by $\hat{\chi}_L$, is

$$\hat{\chi}_L(\mathbf{k}, k_0) \cdot [\mathbf{I} + \hat{\mathbf{G}}(\mathbf{k}, k_0) \cdot \hat{\chi}_L(\mathbf{k}, k_0)]^{-1} = \alpha' \rho \mathbf{I} \quad . \tag{II.25}$$

The refractive index $n(k_0)$ is given by

$$n^2(k_0) = \hat{\epsilon}^{\text{tr}}(k(k_0), k_0) \quad , \tag{II.26}$$

where we have defined the dielectric tensor $\hat{\boldsymbol{\epsilon}}$ by

$$\hat{\boldsymbol{\epsilon}}(\mathbf{k}, k_0) = 4\pi\, \hat{\chi}(\mathbf{k}, k_0) + \mathbf{I} \equiv \hat{\epsilon}^{\text{tr}}(k, k_0)\, (\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}) + \hat{\epsilon}^{l}(k, k_0)\, \hat{\mathbf{k}}\hat{\mathbf{k}} \quad ,$$

and $k(k_0)$ is the solution of the dispersion relation

$$k^2(k_0) = k_0^2\, \hat{\epsilon}^{\text{tr}}(k(k_0), k_0) \quad . \tag{II.27}$$

These results may be obtained by taking the solution $\mathbf{E}$ of Maxwell's equations to be the transverse plane wave

$$\mathbf{E}(\mathbf{r}, k_0) = E\, \hat{\mathbf{a}}\, e^{i\mathbf{k}(k_0) \cdot \mathbf{r}} \quad , \tag{II.28}$$

where $\mathbf{k}(k_0)$ is a vector in the direction of propagation with magnitude $k(k_0)$, $\hat{\mathbf{a}}$ is a real unit vector perpendicular to $\mathbf{k}(k_0)$, and $E$ is a complex amplitude factor. Writing the local field $\mathbf{E}_L(\mathbf{r}, k_0)$ in the same form as Eq. (II.28), we obtain from Eqs. (II.19) and (II.22) relation

$$\mathbf{E}_L(\mathbf{r}, k_0) = [1 + \hat{G}^{\mathrm{tr}}(k(k_0), k_0)\,\hat{\chi}^{\mathrm{tr}}(k(k_0), k_0)]\,\mathbf{E}(\mathbf{r}, k_0) \qquad (\mathrm{II.29})$$

We note that this equation involves the exact susceptibility. When the latter is replaced by $\hat{\chi}_L^{\mathrm{tr}}$, we obtain the approximate relation

$$\mathbf{E}_L(\mathbf{r}, k_0) \approx [1 + \hat{G}^{\mathrm{tr}}(k(k_0), k_0)\hat{\chi}_L^{\mathrm{tr}}(k(k_0), k_0)]\,\mathbf{E}(\mathbf{r}, k_0)\ , \qquad (\mathrm{II.30})$$

which, using Eq. (II.25), can be expressed as

$$\mathbf{E}_L(\mathbf{r}, k_0) \approx \frac{1}{\alpha'\rho}\hat{\chi}_L^{\mathrm{tr}}(k(k_0), k_0)\,\mathbf{E}(\mathbf{r}, k_0)\ . \qquad (\mathrm{II.31})$$

Before proceeding to consider particular examples of the local field approximation, it is worthwhile to make the following observations. We note that $\hat{\mathbf{G}}(\mathbf{k}, k_0)$ is the Fourier transform of a function $\mathbf{G}(\mathbf{r}, \mathbf{r}'; k_0)$, Eq. (II.23), which is nonzero only for separations $|\mathbf{r} - \mathbf{r}'| < R_c$, where $R_c$ is less than or equal to a molecular diameter. Since at optical frequencies the condition $k_0 R_c \ll 1$ is satisfied, the $k_0$ dependence of the propagators $\mathbf{F}(\mathbf{r}, \mathbf{r}'; k_0)$ and $\mathbf{L}(\mathbf{r}, \mathbf{r}', k_0)$ may, to an excellent approximation, be neglected for the models considered below in computing $\hat{\mathbf{G}}(\mathbf{k}, k_0)$. Using the notation,

$$\begin{aligned} \hat{\mathbf{G}}(k) &= \lim_{k_0 \to 0} \hat{\mathbf{G}}(\mathbf{k}, k_0)\ , \\ \hat{\chi}_L(k) &= \lim_{k_0 \to 0} \hat{\chi}_L(\mathbf{k}, k_0)\ , \end{aligned} \qquad (\mathrm{II.32})$$

to an excellent approximation we may set $\hat{\mathbf{G}}(\mathbf{k}, k_0) \approx \hat{\mathbf{G}}(\mathbf{k})$ and $\hat{\chi}_L(\mathbf{k}, k_0) \approx \hat{\chi}_L(\mathbf{k})$. The latter result follows from the relation between $\hat{\chi}_L$ and $\hat{\mathbf{G}}$, Eq. (II.25). In making these approximations, we must remember that the polarizability $\alpha$ is actually a function of $k_0$, and that the above limiting procedure should not be applied to $\alpha$.

For typical fluids, the refractive index at optical frequencies (away from resonances) is of the order of unity so that the dispersion wavenumber $k(k_0)$, Eq. (II.27), is of the order of $k_0$. Since $\hat{\mathbf{G}}(\mathbf{k})$ is an integral over the volume of a molecular sphere, at optical wavelengths the further approximation $\hat{\mathbf{G}}[\mathbf{k}(k_0)] \approx \hat{\mathbf{G}}(0)$ holds to an excellent degree. Hence defining

$$\begin{aligned} \chi_L &= \lim_{k \to 0} \hat{\chi}_L^{\mathrm{tr}}(k) = \lim_{k \to 0} \hat{\chi}_L^{l}(k) \\ \mathbf{G}^{(0)} &= \lim_{k \to 0} \hat{\mathbf{G}}(\mathbf{k}) \end{aligned} \qquad (\mathrm{II.33})$$

we may further approximate $\hat{\chi}_L^{\mathrm{tr}}[k(k_0)] \approx \chi_L \equiv (\epsilon_L - 1)/4\Pi$.

## III. LOCAL FIELDS MODELS

### A. Lorentz model

The choice of the propagator $\mathbf{L}$ for this model has been discussed by Bedeaux and Mazur[6] and by Felderhof[7]

$$\begin{aligned} \mathbf{L}(\mathbf{r}, \mathbf{r}'; k_0) &= 0 & |\mathbf{r} - \mathbf{r}'| < R_c\ , \\ &= \mathbf{F}(\mathbf{r}, \mathbf{r}'; k_0) & |\mathbf{r} - \mathbf{r}'| \geq R_c\ . \end{aligned} \qquad (\mathrm{III.1})$$

We note that in this case the renormalized polarizability $\alpha'$, Eqs. (II.7) and (II.8), is equal to $\alpha$. It has already been mentioned that $R_c$ could have any value $0 < R_c \leq d$, where $d$ is the hard core diameter. Bedeaux and Mazur[6] take $R_c = d$, while Felderhof chooses $R_c$ infinitesimal. For calculating the local field dielectric constant in the limit $k_0 R_c \ll 1$ and $kR_c \ll 1$, both choices give the same answer. Using the static approximation, $\mathbf{F}(\mathbf{r}, \mathbf{r}'; k_0) \underset{k_0 \to 0}{\approx} \mathbf{T}(\mathbf{r}, \mathbf{r}')$, where

$$\mathbf{T}(\mathbf{r}, \mathbf{r}') = \nabla_{\mathbf{r}} \nabla_{\mathbf{r}} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \qquad (\mathrm{III.2})$$

is the static dipole–dipole tensor, we obtain from Eqs. (II.23) and (III.1), in the notation introduced previously,

$$\mathbf{G}^{(0)} = -\int_{|\mathbf{r}-\mathbf{r}'|<R_c} d^3\mathbf{r}'\,\mathbf{T}(\mathbf{r}, \mathbf{r}') = \tfrac{4}{3}\pi\mathbf{I}\ . \qquad (\mathrm{III.3})$$

Substituting this into Eq. (II.25) gives for $k_0 R_c \ll 1$, $kR_c \ll 1$,

$$\frac{\epsilon_L - 1}{\epsilon_L + 2} = \frac{4\pi\alpha\rho}{3}\ , \qquad (\mathrm{III.4})$$

which is the Lorentz–Lorenz relation. Also using Eq. (III.3) in Eq. (II.29), we obtain the familar Lorentz local field,

$$\mathbf{E}_L(\mathbf{r}, k_0) = \tfrac{1}{3}[\hat{\epsilon}^{\mathrm{tr}}(k(k_0), k_0) + 2]\,\mathbf{E}(\mathbf{r}, k_0)\ ,$$

which contains the exact transverse dielectric constant.

### B. The Onsager-Böttcher model

In phenomenological derivations[9,10] of the Onsager-Böttcher model for nonpolar dielectrics, a molecule is represented by a spherical cavity of radius $R_c$ immersed in a continuous medium characterized by a dielectric constant $\epsilon_L$. The total local field acting on a point dipole at the center of the sphere is composed of the cavity field $\mathbf{E}_c$, which is the field inside the cavity due to the macroscopic field in the surrounding medium, and the reaction field $R$, which is the field at the center of the cavity due to polarization of the surroundings by the dipole moment of the molecule. Standard treatments[9,10] show that the reaction field $R$ results in an enhanced polarizability of the molecule to a value

$$\alpha' = \alpha(1 - \alpha R)^{-1}\ , \qquad (\mathrm{III.5})$$

which is reminiscent of the general expression for the renormalized polarizability, Eq. (II.7). Comparison with Eq. (II.11), which defines generally the local field approximation, suggests that we identify the local field $\mathbf{E}_L$ with the cavity field $\mathbf{E}_c$.

The cavity field at the center of a sphere of radius $R_c$ can be related, at optical wavelengths $k_0 R_c \ll 1$, to the average field in the medium by[24,25]

$$\mathbf{E}_L(\mathbf{r}, k_0) = \mathbf{E}(\mathbf{r}, k_0) - \int_{|\mathbf{r}-\mathbf{r}'|<R_c} d^3\mathbf{r}'\,[\mathbf{T}(\mathbf{r}, \mathbf{r}') + \mathbf{R}(\mathbf{r}, \mathbf{r}'; \epsilon_L)] \cdot \mathbf{P}(\mathbf{r}', k_0), \qquad (\mathrm{III.6})$$

where $\mathbf{R}(\mathbf{r}, \mathbf{r}'; \epsilon_L) \cdot \mu$ is the reaction field at the center of the sphere due to a point dipole $\mu$ at the position $\mathbf{r}'$ inside the sphere. Comparing Eq. (III.6) with Eqs. (II.22) and (II.23) (replacing $\mathbf{F}(\mathbf{r}, \mathbf{r}'; k_0)$ by $\mathbf{T}(\mathbf{r}, \mathbf{r}')$ in the latter), immediately suggests the identification

$$\mathbf{L}(\mathbf{r},\mathbf{r}') = -\mathbf{R}(\mathbf{r},\mathbf{r}';\epsilon_L)\ , \quad |\mathbf{r}-\mathbf{r}'| < R_c\ . \tag{III.7}$$

Since the reaction field factor $R$ in Eq. (III.5) is related to the tensor $\mathbf{R}(\mathbf{r},\mathbf{r}';\epsilon_L)$ by

$$R\mathbf{I} = \lim_{|\mathbf{r}-\mathbf{r}'|\to 0} \mathbf{R}(\mathbf{r},\mathbf{r}';\epsilon_L)\ , \tag{III.8}$$

the last two equations show that Eq. (III.5) indeed agrees with the general relation for the renormalized polarizability $\alpha'$, Eq. (II.7).

An expression for $\mathbf{R}(\mathbf{r},\mathbf{r}';\epsilon_L)$ valid at arbitrary wavelengths has been given by Titulaer and Deutch.[25] At optical wavelengths this reduces to the familiar result,

$$\mathbf{R}(\mathbf{r},\mathbf{r}';\epsilon_L) \underset{k_0R_c\ll 1}{\approx} \frac{2(\epsilon_L-1)}{(2\epsilon_L+1)}\frac{1}{R_c^3}\mathbf{I}\ . \tag{III.9}$$

We then find that

$$\mathbf{G}^{(0)} = -\int_{|\mathbf{r}-\mathbf{r}'|<R_c} d^3\mathbf{r}'[\mathbf{T}(\mathbf{r},\mathbf{r}') + \mathbf{R}(\mathbf{r},\mathbf{r}';\epsilon_L)]\ ,$$

$$= \frac{4\pi}{(2\epsilon_L+1)}\mathbf{I}\ . \tag{III.10}$$

In the limit $k_0R_c \ll 1$ and $kR_c \ll 1$, we obtain using Eqs. (III.10) and (II.25)

$$\frac{(2\epsilon_L+1)(\epsilon_L-1)}{12\pi\epsilon_L} = \alpha'\rho\ , \tag{III.11}$$

and from Eqs. (III.5) and (III.9)

$$\alpha' = \alpha\left[1 - \frac{2(\epsilon_L-1}{(2\epsilon_L+1)}\frac{\alpha}{R_c^3}\right]^{-1}\ . \tag{III.12}$$

The last two equations are the usual expressions[10] for the dielectric constant of a nonpolar fluid according to the Onsager–Böttcher model. From Eqs. (III.10) and (II.30), or taking

$$\mathrm{P}(\mathbf{r}',k_0) \approx \chi_L \mathrm{E}(\mathbf{r},k_0)\ , \tag{III.13}$$

when $|\mathbf{r}-\mathbf{r}'|$ is of the order of $R_c$ and using Eqs. (III.10) and (III.13) in Eq. (III.6), we obtain the familiar result for the cavity field for this model

$$\mathrm{E}_L(\mathbf{r},k_0) \approx \frac{3\epsilon_L}{2\epsilon_L+1}\mathrm{E}(\mathbf{r},k_0)\ .$$

This is only an approximation, consistent with Eq. (III.13), since the local field given exactly by Eq. (II.29) will depend also on the exact transverse dielectric constant.

Our purpose here is to show that the Onsager–Böttcher model can be obtained by making an appropriate choice for the propagator $\mathbf{L}$, namely Eq. (III.7). Apart from this "justification" for choosing $\mathbf{L}$, we shall not dwell upon the physical motivation for this model. Høye and Stell[8] have discussed at length the rationale for the Onsager model in the case of rigid polar fluids, and their discussion can be applied to nonpolar polarizable fluids in the limit $k_0R_c \ll 1$ and $kR_c \ll 1$ with appropriate translation of the physical quantities that enter.

Böttcher[10] has shown that Eqs. (III.11) and (III.12) may be fitted to experimental values of the dielectric constant with $R_c$ having values intermediate between the molecular radius and molecular diameter. The present formalism gives no prescription for determining $R_c$, which is an artifice that would not appear in an exact calculation of the dielectric constant. Several authors[20,21] have considered alternative, but somewhat related, methods of embedding the Onsager–Böttcher model in a microscopic theory of the dielectric constant with the aim of deducing *a priori* the value of $R_c$.

## C. The Wertheim model

The final local field model we shall examine is motivated by consideration of the relation [Eq. (II.15)] between the external field $\mathbf{E}_0$ and the average polarization in the mean field approximation. In explicit notation this is

$$\mathrm{P}(\mathbf{r},k_0) \approx \alpha'\rho\mathbf{E}_0(\mathbf{r},k_0) + (\alpha'\rho)^2\int_v d^3\mathbf{r}'\,\mathbf{U}(\mathbf{r},\mathbf{r}';k_0)\circ\mathbf{E}_0(\mathbf{r},k_0)\ . \tag{III.14}$$

Wertheim[11] has examined diagramatically the Kirkwood–Yvon series expansion (at wavelengths large compared with $V$, so that the radiation propagator $\mathbf{F}$ may be replaced by $\mathbf{T}$, Eq. (III.2)), and obtains an exact relation between $\mathbf{P}$ and $\mathbf{E}_0$ of the same form as Eq. (III.14). In his notation,

$$\mathrm{P}(\mathbf{r},k_0) = B\mathbf{E}_0(\mathbf{r},k_0) + B^2\int_v d^3\mathbf{r}'\,\mathbf{H}(\mathbf{r},\mathbf{r}';k_0)\circ\mathbf{E}_0(\mathbf{r}',k_0)\ . \tag{III.15}$$

For molecules with hard-core diameter $R_c$, $\mathbf{H}(\mathbf{r},\mathbf{r}';k_0)$ satisfies the core condition,

$$\mathbf{H}(\mathbf{r},\mathbf{r}';k_0) = 0 \quad |\mathbf{r}-\mathbf{r}'| < R_c\ . \tag{III.16}$$

Tentatively assuming, on comparison of Eq. (III.14) and (III.15), that the renormalized functions $\alpha'\rho$ and $\mathbf{U}$ are approximations to $B$ and $\mathbf{H}$ respectively, the last equation suggests imposing the condition on $\mathbf{U}$

$$\mathbf{U}(\mathbf{r},\mathbf{r}';k_0) = 0 \quad |\mathbf{r}-\mathbf{r}'| < R_c\ . \tag{III.17}$$

In principle, we can determine $\mathbf{U}(\mathbf{r},\mathbf{r}';k_0)$ for $|\mathbf{r}-\mathbf{r}'| \geqslant R_c$ and $\mathbf{L}(\mathbf{r},\mathbf{r}';k_0)$ for $|\mathbf{r}-\mathbf{r}'| < R_c$ from Eqs. (III.17), (II.5), and the integral relation Eq. (II.16). Solving these equations yields both $\mathbf{U}$ and $\mathbf{L}$ for all separations $|\mathbf{r}-\mathbf{r}'|$; these functions depend parametrically on $\alpha'\rho$. A closed set of relations for the latter are obtained by invoking Eqs. (II.7) and (II.8).

One may verify that this model is equivalent, in the static limit $k_0 \to 0$, to the approximate model considered by Wertheim.[11] (In this case, $\mathbf{L}$ corresponds to the function denoted as $\mathbf{C}$ by Wertheim.) At optical wavelengths $k_0R_c \ll 1$, Wertheim's results[11] should provide a very good approximation to the propagator $\mathbf{L}(\mathbf{r},\mathbf{r}';k_0)$ for separations $|\mathbf{r}-\mathbf{r}'| < R_c$. It follows that his expressions for the static dielectric constant may be employed for the optical dielectric constant $\epsilon_L$ according to this model. Wertheim's results for the dielectric constant are summarized in the equations:

$$\epsilon_L = \frac{q(2\xi)}{q(-\xi)}\ , \quad q(\xi) = \frac{(1+2\xi)^2}{(1-\xi)^4}\ , \tag{III.18}$$

where the parameter $\xi$ is determined from the relation

$$q(2\xi) - q(-\xi) = \frac{4\pi\alpha\rho}{(1-16\alpha\xi/R_c^3)} = 4\pi\alpha'\rho\ . \tag{III.19}$$

The fact that the present model follows from the condition on **U**, Eq. (III.17), which is imposed by analogy with the exact core condition Eq. (III.16), leads one to expect that this model for $\epsilon_L$ is the most realistic local field approximation.

It should be pointed out that Wertheim takes $R_c = d$, the exact hard sphere diameter, since it is for this choice that Eq. (III.16) is exact. In the context of this paper, however, $R_c$ may be regarded as a parameter which could have a value less than $d$. To our knowledge, no work has been performed on fitting Eqs. (III.18) and (III.19) to experimental dielectric constants similar to investigations based on the Onsager–Böttcher model, although Stell and Rushbrooke[26] have presented some numerical calculations of Wertheim's equations.

## IV. LIGHT SCATTERING IN THE BORN APPROXIMATION

We now employ the results obtained in previous sections to discuss Rayleigh light scattering. Departing somewhat from previous approaches,[3,7] we compute the light scattered from a macroscopic region within a sample to a point *outside* the sample. Examination of this actual situation in light scattering experiments will enable us to obtain refractive-index-dependent correction factors to the usual scattering formulae.[27,28]

A narrow beam of light which is assumed to be a plane wave

$$\mathbf{E}_0(\mathbf{r}, k_0) = E_0 \hat{\mathbf{a}}\, e^{i\mathbf{k}_0\cdot\mathbf{r}} \ , \tag{IV.1}$$

is incident on the sample fluid which fills a cell of volume $V$. Here $\mathbf{k}_0$ is a vector of magnitude $k_0$ in the direction of propagation of the incident light in vacuum, $\hat{\mathbf{a}}$ is a unit vector ("polarization" vector) perpendicular to $\mathbf{k}_0$, and $E_0$ is an amplitude factor. The scattered light is detected at an angle $\theta$ relative to $\mathbf{k}_0$ and at a large distance from the sample. An aperture placed between the cell and the detector allows only the light scattered from a subvolume $\psi$ of the sample to be detected.[1] As an idealization, we assume that only a small region within $\psi$, denoted by $V_I$, is illuminated by the incident beam. The scattered electric field $\mathbf{e}_1(\mathbf{r}, k_0)$ at the detector due to the molecules in $\psi$ is given by[7]

$$\begin{aligned}\mathbf{e}_1(\mathbf{r}, k_0) &= \int_\psi d^3\mathbf{r}'\, \mathbf{F}(\mathbf{r}, \mathbf{r}'; k_0) \cdot \mathbf{p}_1(\mathbf{r}', k_0) \ , \\ &\approx \frac{k_0^2 e^{ik_0R}}{R} (1 - \hat{\mathbf{q}}\hat{\mathbf{q}}) \cdot \int_\psi d^3\mathbf{r}'\, e^{-ik_0\hat{\mathbf{q}}\cdot\mathbf{r}'}\, \mathbf{p}_1(\mathbf{r}', k_0) \ ,\end{aligned} \tag{IV.2}$$

where the fact that the detector is far from the sample permits $\mathbf{F}(\mathbf{r}, \mathbf{r}'; k_0)$ to be approximated by its asymptotic form. In Eq. (IV.2), $\hat{q} = (\mathbf{R}/R)$, where $\mathbf{R}$ is a vector to the detector from a conveniently chosen origin within the illuminated volume $V_I$. As is customary, it is assumed that $R$ is much larger than the dimensions of $\psi$.

In the Born approximation, the microscopic polarization fluctuation $\mathbf{p}_1$ is given by Eq. (II.17). In explicit notation, this is

$$\mathbf{p}_1(\mathbf{r}, k_0) = \alpha' n_1(\mathbf{r}) \mathbf{E}_L(\mathbf{r}, k_0) + (\alpha')^2 \rho \int_{V_I} d^3\mathbf{r}'\, \mathbf{U}(\mathbf{r}, \mathbf{r}'; k_0) \cdot n_1(\mathbf{r}')\, \mathbf{E}_L(\mathbf{r}', k_0) \ , \tag{IV.3}$$

where we have used the fact that the macroscopic fields in the sample are nonzero only within the illuminated volume.

The detector measures the component of the scattered light polarized in a direction $\hat{\mathbf{b}}$ perpendicular to $\hat{\mathbf{q}}$. Substituting Eqs. (IV.3) into (IV.2) and interchanging the order of integration over $\psi$ and $V_I$, we obtain

$$\begin{aligned}\hat{\mathbf{b}} \cdot \mathbf{e}_1(\mathbf{r}, k_0) = \frac{\alpha' k_0^2}{R} e^{ik_0R} \int_{V_I} d^3\mathbf{r}'\, n_1(\mathbf{r}') \Big[ \hat{\mathbf{b}}\, e^{-ik_0\hat{\mathbf{q}}\cdot\mathbf{r}'} \\ + \alpha'\rho \int_\psi d^3\mathbf{r}''\, \hat{\mathbf{b}} \cdot \mathbf{U}(\mathbf{r}'', \mathbf{r}'; k_0)\, e^{-ik_0\hat{\mathbf{q}}\cdot\mathbf{r}''} \Big] \\ \cdot \mathbf{E}_L(\mathbf{r}', k_0) \ .\end{aligned} \tag{IV.4}$$

From Eqs. (III.14) and (II.11), one sees that the term enclosed in brackets in Eq. (IV.4) can be written, to terms consistent with the Born approximation,

$$\begin{aligned}\hat{\mathbf{b}}\, e^{-ik_0\hat{\mathbf{q}}\cdot\mathbf{r}'} + \alpha'\rho \int_\psi d^3\mathbf{r}''\, \hat{\mathbf{b}} \cdot \mathbf{U}(\mathbf{r}'', \mathbf{r}'; k_0)\, e^{-ik_0\hat{\mathbf{q}}\cdot\mathbf{r}''} \\ = \frac{1}{{}'E_0'}\, {}'\mathbf{E}_L'(\mathbf{r}', k_0) \ .\end{aligned} \tag{IV.5}$$

Here ${}'E_L'(\mathbf{r}, k_0)$ is the local field in the medium due to a fictitious external transverse field ${}'\mathbf{E}_0'(\mathbf{r}, k_0)$ incident on the sample from the direction of observation, which within the region occupied by the sample is described by

$${}'\mathbf{E}_0'(\mathbf{r}, k_0) = {}'E_0'\, \hat{\mathbf{b}}\, e^{-ik_0\hat{\mathbf{q}}\cdot\mathbf{r}'}\, h(\mathbf{r}) \ , \tag{IV.6}$$

where

$$h(\mathbf{r}) = \begin{cases} 1 & \mathbf{r} \text{ in } \psi \\ 0 & \text{otherwise} \end{cases} \ .$$

We shall assume that the macroscopic fields within the illuminated volume may be represented by plane waves. Consistent with the Born approximation, the local fields $\mathbf{E}_L$ and ${}'\mathbf{E}_L'$ are related to corresponding Maxwell fields $\mathbf{E}$ and ${}'\mathbf{E}'$ by Eq. (II.31), where the wavenumber $k(k_0)$ in the medium may be approximated by $k_L$ defined as

$$k_L^2 = \epsilon_L k_0^2 \ . \tag{IV.7}$$

In general the directions of propagation and polarization of the macroscopic fields within the medium are not identical to those of the external fields, and must be determined by solving Maxwell's equations with the appropriate boundary conditions. We shall, however, assume that these differences may be neglected, in which case we obtain using Eq. (II.31),

$$\begin{aligned}\mathbf{E}_L(\mathbf{r}, k_0) &= \frac{\chi_L}{\alpha'\rho} E\, \hat{\mathbf{a}}\, e^{i\mathbf{k}_L\cdot\mathbf{r}} \ , \\ {}'\mathbf{E}_L'(\mathbf{r}, k_0) &= \frac{\chi_L}{\alpha'\rho}\, {}'E'\, \hat{\mathbf{b}}\, e^{-ik_L\hat{\mathbf{q}}\cdot\mathbf{r}} \ ,\end{aligned} \tag{IV.8}$$

where $\mathbf{k}_L$ is a vector of magnitude $k_L$ in the same direction as $\mathbf{k}_0$ [cf. Eq. (IV.1)], and $E$, ${}'E'$ are amplitude factors for the Maxwell fields in the medium.

Using Eqs. (IV.5) and (IV.8), Eq. (IV.4) becomes

$$\hat{\mathbf{b}} \cdot \mathbf{e}_1(\mathbf{r}, k_0) = \frac{\chi_L^2 k_0^2}{\alpha' \rho^2} \frac{e^{ik_0R}}{R} \frac{E\,'E'}{'E_0'} \cos\phi \int_{V_I} d^3\mathbf{r}'\, n_1(\mathbf{r}')\, e^{i\Delta\mathbf{k}_L \cdot \mathbf{r}'} , \tag{IV.9}$$

where $\cos\phi = \hat{\mathbf{a}} \cdot \hat{\mathbf{b}}$ and $\Delta\mathbf{k}_L$ is the scattering wave vector,

$$\Delta\mathbf{k}_L = \mathbf{k}_L - k_L \hat{\mathbf{q}} \ . \tag{IV.10}$$

The ratio of the intensity of light scattered into the solid angle $d\Omega_{\hat{q}}$ to the intensity of the incident light is given by

$$\frac{I}{I_0} = \frac{\langle |\hat{\mathbf{b}} \cdot \mathbf{e}_1(\mathbf{r}, k_0)|^2 \rangle}{|E_0|^2} \ . \tag{IV.11}$$

Using Eq. (IV.9), we thus obtain

$$\frac{R^2 I}{V_I I_0} = \left(\frac{\chi_L^2 k_0^2}{\alpha'\rho}\right)^2 \left|\frac{E\,'E'}{E_0\,'E_0'}\right|^2 \cos^2\phi \, \frac{S(\Delta\mathbf{k}_L)}{\rho^2} , \tag{IV.12}$$

where

$$S(\Delta\mathbf{k}_L) = \int_{V_I} d^3\mathbf{r}' \langle n_1(\mathbf{r}) n_1(\mathbf{r}') \rangle e^{i\Delta\mathbf{k}_L \cdot (\mathbf{r}' - \mathbf{r})} \ . \tag{IV.13}$$

The term $|E\,'E'/E_0\,'E_0'|^2 \cong 1/C_n$ in Eq. (IV.12) is a refractive-index-dependent correction factor. Under the assumption that reflection losses are negligible, and with the previous approximation that the directions of propagation of the fields in the medium are identical to those of the external fields, conservation of energy[1,29] leads to

$$\left|\frac{E}{E_0}\right| = \left|\frac{'E'}{'E_0'}\right| = \frac{1}{n_L^{1/2}} , \tag{IV.14}$$

where $n_L$ is the (local field) refractive index of the sample fluid. Under these conditions, $C_n = n_L^2$, in agreement with the correction factor obtained previously by several authors.[27,28] A more rigorous derivation of $C_n$, avoiding the approximations made here, can in principle be achieved by solving Maxwell's equations taking account of the geometry of the scattering cell.

The isotropic Rayleigh ratio, $R_{is}(\Omega_{\hat{q}})$, is obtained by averaging Eq. (IV.12) over all directions of the detector polarizer.[30] We use

$$\cos\phi = \sin\psi_{\hat{q}} \cos\phi_{\hat{b}} ,$$

where $\psi_{\hat{q}}$ is the angle between the polarization direction $\hat{\mathbf{a}}$ of the incident light and the scattering direction $\hat{\mathbf{q}}$, and $\phi_{\hat{b}}$ is the angle between the detector polarizer $\hat{\mathbf{b}}$ and the plane determined by $\hat{\mathbf{a}}$ and $\hat{\mathbf{q}}$. Averaging Eq. (IV.12) over $\phi_{\hat{b}}$, the result may be written

$$R_{is}(\Omega_{\hat{q}}) = \left(\frac{k_0^2}{4\pi}\right)^2 f^2 \sin^2\psi_{\hat{q}} \frac{S(\Delta\mathbf{k}_L)}{\rho^2} , \tag{IV.15}$$

where

$$f = \frac{(\epsilon_L - 1)^2}{4\pi\alpha'\rho} , \tag{IV.16}$$

is a 'local field factor' which will be examined in the next section. In Eq. (IV.15), the factor $C_n$ has been subsumed in the definition of $R_{is}$.

The turbidity $\tau$ is obtained by integrating Eq. (IV.15) over all solid angles $d\Omega_{\hat{q}}$.[30] Alternatively, the turbidity is given by[6,7]

$$\tau = 2k_0 \operatorname{Im} n(k_0) = 2k_0 \operatorname{Im}[\hat{\epsilon}^{tr}(k(k_0), k_0)]^{1/2} \ . \tag{IV.17}$$

In the Born approximation, the dielectric constant may be obtained from Eq. (II.24), employing the matrix $\hat{\mathbf{C}}$ defined in Eq. (II.18). Techniques for evaluating the turbidity from these formulae are described in Refs. 6 and 7, and are omitted here. The result agrees with that obtained from Eq. (IV.15), apart from the implicit presence in the latter equation of the factor $C_n$. Since this factor is due to refraction effects at the boundaries of the scattering cell, it is not expected to arise in a calculation of the shape-independent dielectric constant.

## V. LOCAL FIELD EFFECT ON LIGHT SCATTERING

According to Einstein's[16] phenomenological theory of light scattering, the Rayleigh ratio is given by an expression similar to Eq. (IV.15), where $f$ is replaced by the density derivative $[\rho(\partial\epsilon(k_0)/\partial\rho)_T]$, with $\epsilon(k_0)$ the real part of the optical dielectric constant at wavenumber $k_0$. While values of $R_{is}$ computed from this theory using measured values of $[\partial\epsilon(k_0)/\partial\rho]_T$ agree well with experimental Rayleigh ratios,[15,17] the agreement has not been as good when $(\partial\epsilon(k_0)/\partial\rho)_T$ is computed from theoretical equations of state for $\epsilon(k_0)$.

Most investigations[12-15] have considered the Lorentz and Onsager–Böttcher models for the dielectric constant in order to evaluate $[\partial\epsilon(k_0)/\partial\rho]_T$. Equations (IV.15) and (IV.16) provide expressions for $R_{is}$ in the Born approximation consistent with these models, as well as with the Wertheim model, and it is natural to inquire into the relation of the local field factor $f$ and the density derivative $(\rho\,\partial\epsilon_L/\partial\rho)_T$ of the local field dielectric constant $\epsilon_L$.

In computing $(\partial\epsilon_L/\partial\rho)_T$ from the expressions in Sec. III, the molecular polarizability $\alpha$ is treated as a constant independent of density, consistent with the model we have adopted for a polarizable fluid; the parameter $R_c$ will also be regarded as density independent.

The comparison of $f$ with $(\rho\,\partial\epsilon_L/\partial\rho)_T$ for the three local field models is given in Table I. The results may be presented in a number of ways; for convenience we have adopted the following approach. In Eq. (IV.16) for $f$ we substitute results from Sec. III which express $\alpha'\rho$ in terms of the dielectric constant for the respective local field models. Thus $f$ is related to the dielectric constant $\epsilon_L$ for each model and it is not required that $\alpha$ or $R_c$ be independently specified. This cannot be achieved in the calculation of $(\rho\,\partial\epsilon_L/\partial\rho)_T$ for either the Onsager–Böttcher or Wertheim model. Instead, we have set

$$\rho\left(\frac{\partial\epsilon_L}{\partial\rho}\right)_T = zf , \tag{V.1}$$

and determined expressions for $z$ in terms of the variables $\epsilon_L$ and $\alpha\rho$. Table I presents results for the quantities $f$ and $z$.

In the case of the Wertheim model, Eq. (III.18) can be inverted numerically to determine the parameter $\xi$ and hence $q(-\xi)$ as functions of $\epsilon_L$. Equation (III.19) can be written

$$4\pi\alpha'\rho = (\epsilon_L - 1)\, q(-\xi) , \tag{V.2}$$

TABLE I. Local field factors for light scattering according to various models.

| Model | $f$ | $z$ |
|---|---|---|
| Lorentz | $\frac{(\epsilon_L-1)(\epsilon_L+2)}{3}$ | 1 |
| Onsager–Böttcher | $\frac{3\epsilon_L(\epsilon_L-1)}{(2\epsilon_L+1)}$ | $\left[1+\frac{1}{(2\epsilon_L+1)}\left((\epsilon_L+2)-\frac{3(\epsilon_L-1)}{4\pi\alpha\rho}\right)\right]^{-1}$ |
| Wertheim | $\frac{(\epsilon_L-1)}{q(-\xi)}$<br>$(\epsilon_L=q(2\xi)/q(-\xi))$ | $\frac{\epsilon_L q(-\xi)[A(\xi)+B(\xi)]}{[\epsilon_L A(\xi)+B(\xi)+[(\epsilon_L-1)/\xi](1-(\epsilon_L-1)q(-\xi)/4\pi\alpha\rho)]}$<br>$A(\xi)=\frac{16(1+\xi)}{(1-2\xi)(1+4\xi)}$<br>$B(\xi)=\frac{4(2-\xi)}{(1+\xi)(1-2\xi)}$ |

which upon substitution into Eq. (IV.16) gives the result for $f$ shown in Table I.

The factor $z$ is unity in the case of the Lorentz model, so that $R_{is}$ computed from Eq. (IV.15) agrees in this instance with Einstein's theory for scattering from a medium with dielectric constant $\epsilon_L$ satisfying the Lorentz–Lorenz relation, Eq. (III.4). The result has already been noted by Bedeaux and Mazur[6] and by Felderhof.[7]

Neither the Onsager–Böttcher nor the Wertheim model lead to a value of $z$ equal to one. Since the Lorentz–Lorenz relation is usually a good approximation to the actual dielectric constant, however, we see from Table I that $z$ corresponding to the Onsager–Böttcher model will not differ from unity by more than a few percent. While it is not immediately apparent from Table I that a similar result will emerge from the Wertheim model, the numerical examples presented below indicate that $z$ differs only slightly from unity for this model also.

The Rayleigh ratio $R_{is}(\Omega_{\hat{q}})$ is usually measured at a scattering angle of 90° in the plane perpendicular to the polarization vector $\hat{\mathbf{a}}$ of the incident light, so that $\psi_{\hat{q}} = 90°$. It is usually assumed that the correlation length of fluctuations is much smaller than the wavelength of light, in which case $S(\Delta\mathbf{k}_L)$ may be approximated by its value for $\Delta\mathbf{k}_L = 0$

$$S(0)=\int d^3\mathbf{r}'\,\langle n_1(\mathbf{r})\,n_1(\mathbf{r}')\rangle=\rho^2 k_B T\beta_T \;,$$

where $k_B$ is Boltzmann's constant, $T$ the absolute temperature, and $\beta_T$ the isothermal compressibility.

With $S(\Delta\mathbf{k}_L)$ approximated by $S(0)$, Eq. (IV.15) may be written as

$$f^2=\frac{\lambda_0^4 R_{is}(90°)}{\pi^2 k_B T\beta_T} \;, \tag{V.3}$$

where $\lambda_0 = 2\pi/k_0$ is the wavelength of the incident light. The rhs of this equation, denoted by $f^2(\mathrm{exp})$, contains experimentally accessible quantities, while the lhs can be related to the dielectric constant $\epsilon_L$ using the local field expressions given in Table I.

In Table II we list some values for $f^2(\mathrm{exp})$[31] obtained using data in Refs. 15 and 17. Values of $f^2$ for the various local field models are calculated in the manner indicated above, using values of the dielectric constant given in the preceeding references. Included in this table are the factors $z$ for the Onsager–Böttcher and

TABLE II. Comparison of experimental and theoretical local field factors.

| | $f^2$(exptl) | | $f^2$ | | | $z$ | |
|---|---|---|---|---|---|---|---|
| Molecule | Ref. 15 | Ref. 17 | Lorentz | Onsager–Böttcher | Wertheim | Onsager–Böttcher | Wertheim |
| Benzene | 2.70 | 2.74 | 3.20 | 2.39 | 2.75 | 1.012 | 1.019 |
| Carbon tetrachloride | 2.09 | 2.12 | 2.43 | 1.89 | 2.14 | 1.003 | 1.007 |
| Chloroform | 1.89 | ··· | 2.21 | 1.74 | 1.96 | 1.029 | 1.039 |
| Carbon disulfide | 5.55 | 5.62 | 6.76 | 4.45 | 5.43 | 0.988 | 0.992 |
| Chlorobenzene | 3.29 | ··· | 3.57 | 2.62 | 3.04 | 1.006 | 1.012 |
| Toluene | 2.47 | 2.50 | 3.12 | 2.34 | 2.69 | 1.011 | 1.019 |
| Nitrobenzene | 3.83 | ··· | 4.54 | 3.21 | 3.79 | 1.017 | 1.029 |
| Cyclohexane | ··· | 1.66 | 1.93 | 1.55 | 1.73 | 1.011 | 1.019 |
| Isooctane | ··· | 1.32 | 1.50 | 1.24 | 1.36 | 1.014 | 1.019 |
| $n$-hexane | ··· | 1.16 | 1.32 | 1.11 | 1.21 | 1.007 | 1.010 |
| $n$-octane | ··· | 1.39 | 1.58 | 1.30 | 1.43 | 1.009 | 1.013 |
| $n$-decane | ··· | 1.59 | 1.76 | 1.43 | 1.58 | 1.010 | 1.014 |
| Methyl ethyl ketone | ··· | 1.28 | 1.38 | 1.15 | 1.25 | 1.011 | 1.016 |

Wertheim models, which were calculated from the expressions in Table I employing values of the dielectric constant and polarizability $\alpha\rho$ listed in the above references.

It is seen that in most cases the Wertheim model gives values of $f^2$ in closest agreement with the experimental values. This observation is consistent with the expectation that Wertheim's is the most realistic local field model.

## VI. CONCLUDING REMARKS

As mentioned in the introduction, the comparisons presented in Table II must be viewed with some caution, since it is known[18] that the polarizabilities of molecules in a fluid are distorted by interactions between the molecules. However, treatments of this quantum mechanical effect in the case of *dense* fluids are unavailable. A classical model which approximately accounts for distortion effects replaces the idealization of a point dipole by a polarizability uniformly distributed throughout the molecular sphere. Such a model was used several years ago by Levine and McQuarrie[32] in a discussion of the pair polarizability of gases, and work is in progress to extend the present treatment along these lines.

With regard to the comparisons in Table II, we note that most of the molecules listed display considerable optical anisotropy, and hence the assumption of a scalar polarizability is untenable. Nonetheless, it is straightforward to show that the results for the *isotropic* Rayleigh ratio are unchanged when the formalism is generalized to molecules having an orientation-dependent point polarizability tensor with a spherical core,[33] provided the factor $f$ is expressed in terms of the dielectric constant in the manner employed above. As one expects, the Rayleigh ratio calculated in the Born approximation now contains, in addition, a depolarized component. Previous authors[12,14,15] have indicated that reasonable agreement with experimental depolarization ratios is only obtained when the local field models take into consideration nonsphericity of the molecular cores, although there is evidence[34] that polarizability distortion may also be a significant factor. This provides further motivation for investigating a model which can account for these distortion effects in dense fluids.

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