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THE SCATTERING OF LIGHT
II. THE COMPLEX REFRACTIVE INDEX OF A MOLECULAR FLUID

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CONTENTS

We treat the complex refractive index of a finite molecular fluid on the basis of a classical many-body theory; the surface problem is handled through surface-dependent propagators. We develop a density expansion generalizing the Lorentz–Lorenz relation and sum all two-body terms to a closed form with intermolecular correlations determined by a Lennard-Jones pair potential; the dependence on density, temperature and frequency is discussed and the case when the frequency is near a molecular resonance is considered. The refractive index and the extinction coefficient are compared with experiments for gases.

We also derive a generalization of the macroscopic relation of Onsager and Böttcher from the many-body theory, essentially as an expansion in an effective polarizability of a molecule in the many-body system. Exact microscopic expressions for an effective polarizability and for a reaction field are identified, and it is shown that they are related like the Böttcher polarizability and the Onsager reaction field in a well-defined decorrelation approximation. The relation with, and validity of, the macroscopic formulae of Lorentz and Böttcher are analysed in depth.

1. INTRODUCTION

The present paper reports a theory of the complex refractive index; it is the second of a series of three papers on the optics of molecular fluids. The previous paper (Hynne & Bullough (1984), to be referred to as I) solved the problem of finding the response of a finite molecular fluid to incident light. The last paper in the series (Hynne & Bullough (1986), to be referred to as III) will treat external optical scattering.

The three papers treat the linear optical and dielectric properties of fluids of isotropically polarizable molecules within the scope described in I: a classical many-body theory in which a molecule can be considered the smallest unit of matter; a quasistatic approximation that ignores dynamical effects of molecular motion; and the dipole approximation, in which the polarization of a molecule is determined by the electric field at the centre of the molecule and the polarizability of the molecule.

The response theory, I, showed that the response of the molecular system to light is determined to a very good approximation by the geometry of the system plus a single parameter, the refractive index m, in almost complete agreement with macroscopic optics. Deviation from such continuum behaviour was found to be appreciable only within a distance of a few wavelengths from the surface. It is necessary to treat a finite system and the entire theory is complicated by surface-dependent integrals. We shall refer to the problem of understanding the meaning of the surface dependence and the calculational complexity caused by it as the surface problem.

The microscopic theory also demonstrated that the frequency-dependent dielectric constant, ϵ, equals the square of the refractive index, $\epsilon = m^2$ (again in agreement with macroscopic optics). It is therefore sufficient to develop the theory for the refractive index. The result of I for the refractive index (equation (I 5.25) in an obvious notation) will form the basis for the work of the present paper. We shall review the necessary background from I in §2 and in the beginning of §4.

We shall find that concepts first defined in macroscopic terms in two well-known models appear naturally in the microscopic theory; so the physical aspects of the theory are conveniently discussed through these ideas. We therefore first briefly discuss the two models, that of Lorentz and that of Onsager and Böttcher.

The most familiar model of macroscopic dielectric theory is the Lorentz model, which leads to the famous Lorentz–Lorenz relation

$$\left(\frac{m^2-1}{4\pi}\right)\left(\frac{3}{m^2+2}\right) = n\alpha \tag{1.1a}$$

between the refractive index m, the polarizability of a molecule α, and the density of molecules n. The quantity $\frac{1}{3}(m^2+2)$ is the Lorentz 'internal-field factor' and may be said to be due to distant dipoles, for it is well known that the result is found from macroscopic theory by excising a sphere of dielectric of *arbitrary* radius about the molecule whose polarization is being considered. The result (1.1 a) must therefore be corrected for the effect of close dipoles, the local field correction. This correction arises because, in general, the immediate surroundings of any given molecule are not uniformly polarized.

From (1.1 a), m is real if α is. Because of radiation reaction, however, the dipole moment induced in an isolated molecule is related to the field acting on it (the polarizing field) through a complex polarizability (I 2.7). So, arguably, (1.1 a) must be modified to

$$\left(\frac{m^2-1}{4\pi}\right)\left(\frac{3}{m^2+2}\right) = n\frac{\alpha}{1-s\alpha}, \tag{1.1b}$$

$$s = \tfrac{2}{3}\mathrm{i}k_0^3. \tag{1.1c}$$

This we refer to as the complex Lorentz–Lorenz relation. In (1.1 c) $k_0 = \omega/c$ is the wavenumber of light in empty space at the frequency ω considered.

Evidently, m from (1.1 a) depends on the single parameter $n\alpha$ but local field corrections modify this simple functional form. Another macroscopic theory, based on a model for polar fluids, devised by Onsager (1936) and extended to non-polar fluids by Böttcher (1942) suggests a complete revision of (1.1 a) to read

$$\left(\frac{m^2-1}{4\pi}\right)\left(\frac{2m^2+1}{3m^2}\right) = n\frac{\alpha}{1-\bar{s}\alpha} \tag{1.2a}$$

in which $\bar{s}$ is the coefficient of the Onsager reaction field,

$$\bar{s} = \frac{2}{a^3}\,\frac{m^2-1}{2m^2+1}. \tag{1.2b}$$

We shall refer to the expression $3m^2/(2m^2+1)$ in (1.2 a) as a cavity-field factor. The Onsager–Böttcher theory is reviewed in more detail in §5.

From (1.2), m is a function of the two parameters $n\alpha$ and $a^{-3}\,\alpha$ and, if a is viewed as a molecular diameter (as it is in the macroscopic theory), (1.2) is plainly in actual conflict with (1.1). We note, however, the formal similarity of the complex Lorentz–Lorenz relation and the Onsager–Böttcher relation; each contains a polarizability corrected by a self-field, either the radiation reaction or Onsager's reaction field. Also, I shows that there are infinitely many additional corrections to the Lorentz–Lorenz relation forming the total local-field correction. Thus the question arises whether these could serve to resolve this conflict, both in its conceptual and its numerical aspects. This, the 'local-field problem', is the main issue of the paper.

The (broadly affirmative) answer to this question is reached by developing the refractive-index theory in the paper along two distinct but parallel tracks. The two tracks associate very naturally with (1.1) and (1.2), respectively. One track leads to a generalization of (1.1 b) in terms of an infinite series in $n\gamma$: γ is the complex polarizability

$$\gamma = \frac{\alpha}{1-s\alpha}. \tag{1.3a}$$

The other leads to a generalization of (1.2 a) in the form essentially of a series in $n\beta$: β is an effective polarizability of a molecule within the many-body system and this was represented in the macroscopic model by an approximation to it, namely the Böttcher polarizability

$$\bar{\gamma} = \frac{\alpha}{1-\bar{s}\alpha}. \tag{1.3b}$$

The purpose of this paper is thus to provide a theory of the complex refractive index of molecular fluids which is exact within the scope defined above, which handles the surface problem and the transition to a translationally invariant description, and which solves the local field problem. To do this we find that the two alternative formulations (the development along the two tracks mentioned) are both needed because neither formulation can perform all these functions separately.

Each of the two developments of the theory relies on two basic processes: the propagation of the electromagnetic field radiated by an oscillating dipole; and the polarization of a molecule by a field. The differences between the two formulations are that the development associated with (1.1) employs elementary processes taking place 'in empty space' and uses the free-field propagator F (2.6) and the polarizability of an isolated molecule, γ; the formulation associated with (1.2) uses a screened (i.e. composite or dressed) propagator, $\mathscr{F}$, and an effective (also composite) polarizability β of a molecule embedded in the many-body system. Both of these composite processes are represented by infinite series, namely (4.1) for $\mathscr{F}$ and (6.9*b*) for β.

It can perhaps be seen from what we have already said, that the basic processes F, γ associate naturally with (1.1), and β, and arguably $\mathscr{F}$ and β, associate naturally with (1.2). But in practice we find it simpler first to develop the theory in terms of α together with F, the 'unscreened' formulation, or with $\mathscr{F}$, the 'screened' one. In these terms the results are unscreened or screened expansions in $n\alpha$ for the refractive index m. They are explicit to all orders and are rigorously equivalent. Subsequently γ and β will be introduced.

It is the unscreened theory which must be thought of as the fundamental one, however. It can be used for systematic developments such as a density expansion for m (actually given in §3) and it remains exact up to the point where we introduce well-defined approximations to ease numerical evaluation.

Even so, either of the exact theories is complicated by the surface problem. The unscreened expression for m, for example, depends formally on the geometry of the material medium at every order in $n\alpha$ beyond second order. Numerically this shape dependence is insignificant, but this fact in no way lightens the actual calculation of these surface dependent terms.

The surface dependence is handled in the screened theory at the expense of an approximation. The surface dependence is now contained in the screened propagator $\mathscr{F}$ and is associated with (multiple) reflections of spherical waves from the surface bounding the molecular system. Translationally invariant expressions for m are reached by approximating $\mathscr{F}$ by a closed form $\tilde{\mathsf{F}}$ (4.4); this ignores the reflected parts. This 'bulk approximation' introduces a technical divergence problem; and its use means, of course, that the screened and unscreened theories are no longer completely equivalent. The unscreened theory remains exact, however, so it is fundamental in this sense.

Because the originally equivalent unscreened and screened formulations finally result in generalizations of (1.1) and (1.2) respectively, we can make what we believe is a penetrating analysis of these macroscopic formulae and the concepts surrounding them, and so remove the many confusions which have grown up about them; we can show their inter-relationships and thus determine those features of each of them which can be said to be correct, and those which are inadequate. Within the whole analysis the effective polarizability β plays an important role. We do not introduce it until §6, where we define it from first principles and then identify it in the microscopic expressions for m. In this way we show that the generalized Lorentz–Lorenz relation actually contains corrections changing γ into β. Because other corrections change the

Lorentz internal-field factor towards the cavity-field factor, we conclude that the physics of the Onsager–Böttcher relation is the sounder starting point for a description of dielectric polarization.

Even so, we show that it is impossible to express the effective polarizability in terms of a reaction field without approximation; we therefore exhibit the approximation and discuss its implications. We conclude that an effective polarizability is actually a more valuable concept than Onsager's reaction field in the context of refractive-index theory. We show that the effective polarizability is used correctly in the simple Onsager–Böttcher relation and that the concept remains useful to an approximation beyond this. The analysis serves to stress the limitation of any macroscopic ideas based on a single molecule: intermolecular correlations always get in the way of any rigorous use of such ideas.

Throughout the work we pay special attention to the two-body terms. They are both the simplest and the most important non-trivial class of many-body terms, and they are summed and evaluated numerically in §3. They are invaluable as an example illustrating the effects of the approximations involved in the macroscopic approaches, and we use them as such.

It is worth stressing that the formal similarity between (1.1*b*) and (1.2*a*) is no accident. These similarities emerge in strictly parallel fashion in the two different formulations of the theory. Both of these involve the summation of two kinds of term concealed in integrals in I. One kind of term gives rise to the Lorentz internal-field factor in the unscreened theory and the cavity-field factor in the screened one. The other kind is summed to yield the complex polarizability in the unscreened theory and the effective polarizability in the screened one. The summation in the unscreened theory was carried out in I so we can start directly from this point in §3.

The rather technical nature of the derivations and an initial lack of physical motivation may make the argument difficult to follow. Therefore we include, in §2, a rather careful discussion of how the two kinds of term arise; then we discuss the physical meaning of them in later sections. We also call attention to an easy (heuristic) derivation of the simple Onsager–Böttcher relation from the microscopic theory in the summary of the paper in §9 (near (9.1)). Reference to this may help the reading of §§5 and 6; but §9 remains, we think, the best place for that easy derivation because it can there serve as a review.

Unfortunately, the systematic derivation of the generalized Onsager–Böttcher relation is complicated by a divergence problem which arises in the screened theory. This divergence becomes intrinsic to the translationally invariant approximation, and one is obliged to accept working with formally divergent expressions, particularly in the course of §5. Use of the exact effective polarizability eventually eliminates the divergences, however, and the final result of the screened theory, (7.19), is well defined if slightly approximate.

Historically, the result (1.1) was obtained by Lorentz (1880, 1909) and Lorenz (1880), and a predecessor in terms of the static dielectric constant is due to Mossotti (1850) and Clausius (1879). The question of the local-field corrections also goes back to Lorentz (1880) who considered a molecular crystal. A model similar to the one considered by Onsager (1936) and Böttcher (1942) had been used before by Bell (1931).

Microscopic treatment of the local-field problem for molecular fluids, usually in the context of a dielectric constant theory, was initiated by Keyes & Kirkwood (1931), Kirkwood (1936), and more systematically by Yvon (1936, 1937); see also Silberstein (1917). These early works already treat one particularly important term which lies at the heart of the conflict between the two macroscopic results (1.1) and (1.2).

Important contributions to the theory have also been made by Buckingham and co-workers (Buckingham & Pople 1955*a*, *b*; Buckingham & Steven 1957) who considered, in particular, the important two-body terms; by Mazur and co-workers (Mazur & Mandel 1956; Mazur 1958; Bedeaux & Mazur 1973); by Mead (1958*a*, *b*, 1960, 1962, 1968*a*, *b*, 1972), who was interested in the problem of spectral lines; by Linder & Hoernschemeyer (1967), who analysed certain concepts of the Onsager–Böttcher theory; by ourselves (Bullough 1962, 1967, 1968, 1970; Bullough *et al.* 1968; Bullough & Hynne 1968; Hynne 1970, 1974; Hynne & Bullough 1972); and by many others, see the references in I.

The present paper serves to give a complete and connected account of our work on the refractive index theory. Some of the results have been quoted as results simply, or have been derived in incomplete form, in our previous papers. Therefore in the present paper we exploit the firm base now developed in I to give all of the details of the derivations. From these we are able to give a more careful discussion of the results.

We now outline the organization of the paper. After the preliminary §2 we start in §3 by giving the unscreened expression for the refractive index first in the form of an expansion in $n\gamma$ generalizing the Lorentz–Lorenz relation, then rearranged as a density expansion. This is evaluated up to the quadratic term by summing all of the two-body terms with an approximate form for the propagator F. The case when the pair-correlation function is determined by a Lennard-Jones pair-potential is calculated analytically and numerically as a function of the temperature and, implicitly through γ, the frequency. Both the real refractive index and the extinction coefficient are calculated. The case where the frequency is near a molecular resonance is interpreted in terms of resonating pairs of molecules. In the simple case of a hard-sphere gas the refractive index is expressed in terms of elementary functions.

The screened theory is developed in §§4–7. Section 4 starts by reviewing the results of I for the screened theory and it goes on to treat the screened propagator $\mathscr{F}$, the significance of its surface dependence, its approximation in closed form, and the steps to a translationally invariant approximation for the refractive index. Section 5 contains a derivation of a formal expression of the Onsager–Böttcher type, and in §6 this is transformed into a physically acceptable form by introducing the effective polarizability. In §7 this result is extended to what is essentially a series in $n\beta$.

In §8 the relations between the two macroscopic expressions (1.1) and (1.2) are analysed, as well as the basis for each of them in the exact theory. From this we draw conclusions about the different validities of these well quoted formulae.

Section 9 constitutes a summary and conclusion to the whole paper.

2. Susceptibility kernel

We consider a system of N isotropically polarizable molecules at temperature T, contained in a region V of volume $|V|$. Incident upon the system is a coherent electromagnetic field $\boldsymbol{E}(\boldsymbol{x},\omega)$ of frequency ω. In I we solved the response problem for this system. We found the polarization and fields induced in response to the given external field. Through an argument in terms of the extinction theorem of Ewald (1912, 1916) and Oseen (1915) we determined the response in the form of two separate equations, (I 5.19) and (I 5.22).

One of these equations (I 5.22), determines the wave numbers of the fields in the medium, and hence the refractive index. It is this dispersion relation we shall be concerned with here.

The other equation determines the polarization and field apart from a parametric dependence upon the refractive index. In simplest geometry this second equation determines amplitudes of plane wave fields, as demonstrated in (I 6.17) and (I 6.19), for example.

In I the dispersion relation was recast in a more convenient form (I 5.25) in terms of a susceptibility kernel $\boldsymbol{\Lambda}$:

$$\frac{m^2(\omega)-1}{4\pi} = |V|^{-1}\,\mathrm{Tr}\int_V\int_V \boldsymbol{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\tilde{\mathsf{I}}(\boldsymbol{x}',\boldsymbol{x})\,\mathrm{d}\boldsymbol{x}\,\mathrm{d}\boldsymbol{x}'. \tag{2.1}$$

Here Tr denotes the trace of a tensor, and the kernel $\tilde{\mathsf{I}}$ takes one of the forms (I 5.26*a*, *b*)

$$\tilde{\mathsf{I}}(\boldsymbol{x}',\boldsymbol{x};m\boldsymbol{k}_0,\boldsymbol{u}) = \boldsymbol{u}\boldsymbol{u}\exp\left[\mathrm{i}m\boldsymbol{k}_0\cdot(\boldsymbol{x}'-\boldsymbol{x})\right], \tag{2.2a}$$

$$\tilde{\mathsf{I}}(\boldsymbol{x}',\boldsymbol{x};m\boldsymbol{k}_0) = \tfrac{1}{2}(\mathsf{U}-\hat{\boldsymbol{k}}_0\hat{\boldsymbol{k}}_0)\exp\left[\mathrm{i}m\boldsymbol{k}_0\cdot(\boldsymbol{x}'-\boldsymbol{x})\right]. \tag{2.2b}$$

Here $\hat{\boldsymbol{k}}_0$ denotes the unit vector in the direction of $\boldsymbol{k}_0$. The vector $\boldsymbol{k}_0$ has arbitary direction and length $k_0 = \omega/c$ which is the wave number of the incident light in empty space. The unit vector $\boldsymbol{u}$ has the character of a polarization vector. It is perpendicular to $\boldsymbol{k}_0$ but otherwise its direction is arbitary. In the refractive index theory it is immaterial which of the two forms (2.2*a*) and (2.2*b*) is used. A notation for the length of a vector and for a unit vector in the direction of a given vector similar to the one used for $\boldsymbol{k}_0$ here will be adopted subsequently in this paper.

The susceptibility kernel $\boldsymbol{\Lambda}$ is the key object and is defined through the relation between the average polarization $\boldsymbol{P}(\boldsymbol{x},\omega)$ and the average electric field $\boldsymbol{\mathscr{E}}(\boldsymbol{x},\omega)$ by (I 3.1*b*),

$$\boldsymbol{P}(\boldsymbol{x},\omega) = \int_V \boldsymbol{\Lambda}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{\mathscr{E}}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}'. \tag{2.3}$$

Thus, $\boldsymbol{\Lambda}$ originally determines a susceptibility or dielectric constant, $\epsilon(\omega)$, and it is possible to express the refractive index in terms of it because we have *derived* the relation

$$\epsilon(\omega) = m^2(\omega), \tag{2.4}$$

see the argument leading to (I 5.27). This means that the refractive index and the dielectric constant can be treated together. It is therefore sufficient to develop the theory of the refractive index, and we shall formulate it in terms of the susceptibility kernel $\boldsymbol{\Lambda}$.

The average electric field in (2.3) is itself defined in terms of $\boldsymbol{E}$ and $\boldsymbol{P}$ by (I 3.1*a*),

$$\boldsymbol{\mathscr{E}}(\boldsymbol{x},\omega) = \boldsymbol{E}(\boldsymbol{x},\omega) + \int_V \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{P}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}' \tag{2.5}$$

in which F is the dipole photon propagator which gives the field at $\boldsymbol{x}$ from any oscillatory dipole $\boldsymbol{p}(\omega)$ at $\boldsymbol{x}'$ as $\mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{p}(\omega)$. Explicitly, F is given by (I 2.2*a*),

$$\mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega) = (\nabla\nabla + k_0^2\,\mathsf{U})\frac{\exp(\mathrm{i}k_0 r)}{r}, \quad r = |\boldsymbol{x}-\boldsymbol{x}'| \tag{2.6}$$

or by the alternative forms (I 2.2*b*, *c*).

The integral in (2.5) is defined through the interpretation (I 3.4), namely

$$\lim_{v\to 0}\int_v \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\,\mathrm{d}\boldsymbol{x}' = -\tfrac{4}{3}\pi\mathsf{U} \tag{2.7}$$

in which v denotes a spherical region centred at $\boldsymbol{x}$, and the limit as the radius of the sphere goes to zero is taken. We shell refer to a contribution arising from the use of (2.7) as a 'Lorentz term'. Thus in (2.5) the definition (2.7) yields

$$\int_V \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{P}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}' = -\tfrac{4}{3}\pi\boldsymbol{P}(\boldsymbol{x},\omega)+\int_{V-v}\mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{P}(\boldsymbol{x}',\omega)\,\mathrm{d}\boldsymbol{x}' \qquad (2.8)$$

in which the integral over $V-v$ denotes the integral over the region V, treated as a principal value integral at the singular point $\boldsymbol{x}$: a small sphere about $\boldsymbol{x}$ is excluded from the region of integration and the limit as its radius goes to zero is taken. The definition (2.5) of the average electric field and the interpretation (2.7) were fully justified in the response theory I, see the discussion below (I 5.27). No error is introduced into the theory this way.

In (2.1) the integration with I yields the transverse part of the Fourier transform of the susceptibility kernel with the transformed variable set equal to the wave vector $m\boldsymbol{k}_0$. This means that (2.1) is actually an *equation in m*. The explicit dependence on m of the right side of (2.1), however, is in fact very weak. We shall therefore treat (2.1) as if it were an explicit expression. The understanding is that the value of m on the right side of (2.1) is actually supplied through iteration (if necessary).

We obtain, then, an explicit expression for the refractive index by substituting one of the series expansions obtained in I for $\mathbf{\Lambda}$. The fundamental expansion is (I 3.17), namely

$$\mathbf{\Lambda}_{10} = n\alpha\mathsf{U}\delta(\boldsymbol{x}_1-\boldsymbol{x}_0)+\sum_{p=1}^{\infty}(n\alpha)^{p+1}\int_V\cdots\int_V\mathsf{F}_{12}\cdot\mathsf{F}_{23}\ldots\mathsf{F}_{p0}H_{123\ldots p0}\,\mathrm{d}\boldsymbol{x}_2\ldots\mathrm{d}\boldsymbol{x}_p. \qquad (2.9)$$

We shall explain it shortly. In (2.9) and below we use a notation in which subscripts indicate positional variables. Thus, $\mathbf{\Lambda}_{10} = \mathbf{\Lambda}(\boldsymbol{x}_1,\boldsymbol{x}_0;\omega)$, for example. Note that, by definition, the first term of the sum over p in (2.9) is simply $(n\alpha)^2\,\mathsf{F}_{10}H_{10}$.

The intermolecular correlation functions H in (2.9) are given by (I 3.18) in general; explicitly the first few functions are

$$\left.\begin{aligned} H_{12} &= G_{12}-1,\\ H_{123} &= G_{123}-G_{12}-G_{23}+1,\\ H_{1234} &= G_{1234}-G_{123}-G_{234}-G_{12}G_{34}+G_{12}+G_{23}+G_{34}-1.\end{aligned}\right\} \qquad (2.10)$$

The functions G will be referred to as distribution functions to distinguish them from other intermolecular correlation functions. The function $G_{123\ldots p}$ is defined by (I 3.14) as the averaged product of the instantaneous density at the points $\boldsymbol{x}_1,\boldsymbol{x}_2,\ldots,\boldsymbol{x}_p$, divided by n^p. Explicitly, the first few distribution functions are

$$\left.\begin{aligned} G_{12} &= g_{12}+n^{-1}\delta_{12},\\ G_{123} &= g_{123}+n^{-1}[(\delta_{12}+\delta_{23})\,g_{13}+\delta_{13}g_{12}]+n^{-2}\delta_{12}\delta_{23},\\ G_{1234} &= g_{1234}+n^{-1}[(\delta_{12}+\delta_{13}+\delta_{14})\,g_{234}+(\delta_{23}+\delta_{24})\,g_{134}+\delta_{34}g_{123}]\\ &\quad +n^{-2}[\delta_{12}\delta_{23}+\delta_{12}\delta_{34}+\delta_{23}\delta_{34}+\delta_{13}\delta_{24}]\,g_{14}\\ &\quad +n^{-2}\delta_{14}[(\delta_{12}+\delta_{34})\,g_{23}+\delta_{23}g_{12}]+n^{-3}\delta_{12}\delta_{23}\delta_{34}.\end{aligned}\right\} \qquad (2.11)$$

The g are the ordinary distribution functions of the theory of fluids (Hill 1956) and

$\delta_{12} = \delta(\boldsymbol{x}_1 - \boldsymbol{x}_2)$ denotes a delta function. We shall explain the role of the delta functions when we have discussed the structure of the terms of $\mathbf{\Lambda}$ in general.

It is convenient to explain $\mathbf{\Lambda}$ in the context of (2.3), that is in its role as a susceptibility. As a typical example we may consider the third order term

$$\int_V \left[(n\alpha)^3 \int_V \mathsf{F}_{12} \cdot \mathsf{F}_{20} \, H_{120} \, \mathrm{d}\boldsymbol{x}_2 \right] \cdot \mathscr{E}_0 \, \mathrm{d}\boldsymbol{x}_0 \tag{2.12}$$

in which the function in square brackets is the third order contribution to $\mathbf{\Lambda}_{10}$. The term (2.12) may be said to represent the following process: first the average field induces a dipole in a molecule at $\boldsymbol{x}_0$, accounted for by one factor α and the $\mathscr{E}_0$. The dipole at $\boldsymbol{x}_0$ creates a field at $\boldsymbol{x}_2$ as described by F_{20}, and this field polarizes a molecule at $\boldsymbol{x}_2$ (giving a second factor α). The molecule at $\boldsymbol{x}_2$ then gives rise to a field at $\boldsymbol{x}_1$ (F_{12}) which polarizes a molecule there (a third factor α). The contribution from the configuration with molecules at $\boldsymbol{x}_1$, $\boldsymbol{x}_2$, and $\boldsymbol{x}_0$ is weighted by $n^2 H_{120} \, \mathrm{d}\boldsymbol{x}_2 \, \mathrm{d}\boldsymbol{x}_0$ and must be integrated over all positions $\boldsymbol{x}_2$ and $\boldsymbol{x}_0$ to obtain the complete third order contribution to the average dipole moment of a molecule at $\boldsymbol{x}_1$; there is an additional factor n in (2.12) because we calculate the dipole moment per unit volume (not per molecule).

Roughly the weight H_{120} accounts for the probability (density) of the configuration $\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{x}_0$ of three molecules: it contains the ordinary three-body distribution function $n^2 g_{120}$, which gives the probability density that there is a molecule at $\boldsymbol{x}_2$ and another molecule at $\boldsymbol{x}_0$, given that there is a molecule at $\boldsymbol{x}_1$. But the weight H_{120} is a more complicated combination of correlation functions for two reasons. First of all the relation (2.3) describes the average polarization as a function of the average field $\mathscr{E}$ (rather than, for example, the external field $\boldsymbol{E}$). The structure of the correlation functions H reflects this fact. Second, it is always necessary to account for the possibility that the molecules which participate in the process need not all be distinct. It is precisely this situation the delta functions in G (and hence in H) take care of. They may therefore be said to describe self-correlations. We shall refer to functions like the H or G which include all self-correlations as generalized correlation (or distribution) functions.

As an illustration of the role of the self-correlations we may look at (2.12) again. The function H_{120} consists of four terms (see (2.10)); let us consider the contribution to (2.12) from G_{120}. From (2.11) we see that G_{120} includes four terms containing self-correlations in addition to the simple term g_{120}. From $n^{-1}\delta_{10} g_{12}$ we get

$$\left[n^2\alpha^3 \int_V \mathsf{F}_{12} \cdot \mathsf{F}_{21} \, g_{12} \, \mathrm{d}\boldsymbol{x}_2 \right] \cdot \mathscr{E}_1. \tag{2.13}$$

This term represents a process in which a dipole induced by $\mathscr{E}$ in a molecule at $\boldsymbol{x}_1$ creates a field acting on the molecule itself via a polarization of another molecule at a point $\boldsymbol{x}_2$, which can be anywhere in V. We call such a process a self-interaction (of the molecule at $\boldsymbol{x}_1$). The self-correlations contained in the generalized correlation functions take care of all the self-interactions of the theory. As we shall see, these play an important role in the theory of dielectric polarization.

The case in which a self-correlation connects two points directly across a propagator F is special. It describes a self-interaction not mediated by other molecules. This self-interaction is of fundamental quantum electrodynamical origin. Within the present essentially classical theory it is represented by the radiation reaction, introduced through the interpretation (I 2.26),

$$\int \mathsf{F}(\boldsymbol{x}, \boldsymbol{x}'; \omega) \, \delta(\boldsymbol{x} - \boldsymbol{x}') \, \mathrm{d}\boldsymbol{x}' = \tfrac{2}{3} \mathrm{i} k_0^3 \, \mathsf{U} \equiv s \mathsf{U}. \tag{2.14}$$

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Therefore, the remaining terms arising from G_{120} in (2.12) are

$$\tfrac{4}{3}\mathrm{i}k_0^3 n^2\alpha^3 \int_V \mathsf{F}_{10}\cdot\mathscr{E}_0\, g_{10}\,\mathrm{d}\boldsymbol{x}_0-\tfrac{4}{9}k_0^6 n\alpha^3\mathscr{E}_1 \tag{2.15}$$

besides the term containing g_{120}. The examples (2.13) and (2.15) show the terms arising from the self-correlations contained in G_{120}, which again is contained in the H_{120} of the third order term (2.12). There are similar contributions from the other terms of H_{120}.

The consistent treatment of all the self-interactions on an equal footing through self-correlations concealed in generalized correlation functions has resulted in a very economical notation. We shall continue to use this notation. The benefits are, for example, highly symmetrical expressions for a screened propagator and for an effective molecular polarizability introduced in (4.1) and (6.9*b*) below and an interesting extension of (2.14) to a 'screened self-interaction'. But to make detailed (numerical) evaluation it is necessary to write the terms out in all detail, as we shall do in §3; and in this situation it is preferable to handle radiation reaction separately through the use of the complex polarizability (I 2.7) already mentioned in (1.3*a*),

$$\gamma=\frac{\alpha}{1-\frac{2}{3}\mathrm{i}k_0^3\,\alpha}. \tag{2.16}$$

All self-correlations directly across F propagators must then be omitted.

It may be helpful if we also demonstrate the use of (2.7) in interpreting (2.12). Equation (2.7) means that we may view all integrals as principal value integrals at the singularities of the F propagators provided we add the 'contributions of the small spheres' as determined by (2.7). There are no such contributions from an F covered by a generalized distribution function G: for each term of G the integrand either vanishes at the singularity of F because an ordinary distribution function vanishes there, or else there is a delta function so that (2.14) applies. Thus the term from G_{120} in (2.12) has no contributions from small spheres. The terms in G_{12} and G_{20} have contributions solely from the F's not covered by a G. From these two terms we get

$$\tfrac{8}{3}\pi(n\alpha)^3\int_{V-v}\mathsf{F}_{10}\cdot\mathscr{E}_0\, G_{10}\,\mathrm{d}\boldsymbol{x}_0. \tag{2.17}$$

Note that the sign is positive because G_{12} and G_{20} appear with minus signs in H_{120}. The term from the $(+1)$ of H_{120} gives three contributions from the small spheres because the integral can be written

$$\int_V\int_V=\int_{V-v}\int_{V-v}+\int_v\int_{V-v}+\int_{V-v}\int_v+\int_v\int_v \tag{2.18}$$

in an informal notation with omission of the common integrand. The two cross terms are equal, and we get

$$-\tfrac{8}{3}\pi(n\alpha)^3\int_{V-v}\mathsf{F}_{10}\cdot\mathscr{E}_0\,\mathrm{d}\boldsymbol{x}_0+\tfrac{16}{9}\pi^2(n\alpha)^3\mathscr{E}_1. \tag{2.19}$$

The use of the definition (2.7) has simplified the series expansion of $\mathbf{\Lambda}$, and we shall continue to use this notation. But when we work with the refractive index we may choose to conceal all effects of small spheres in a Lorentz internal-field factor: the result (I 5.32) shows that we may omit all contributions from small spheres on the right side of (2.1) if we multiply the left side by a factor $3/(m^2+2)$, the inverse of the Lorentz internal-field factor. We shall use this form in §3.

In I we also derived an alternative expansion of the susceptibility kernel, (I 4.10), in terms of a screened propagator $\mathscr{F}$, which itself was given as an expansion (I 4.13) in terms of the usual propagator F. The screened propagator describes propagation in the medium, and the idea is to obtain a description which is more efficient by including partly summed entities in closed form with well-defined physical meaning. We shall summarize the results of I relevant to the screened formulation in §4.

We now develop the result (2.1) so obtaining expressions at low densities which can be evaluated numerically. Later we use the result in the discussion of the local-field problem.

3. Generalized Lorentz–Lorenz relation

In this section we shall analyse the refractive index as a function of the temperature and density of the fluid and (implicitly) of the frequency of the incident light. We shall work from (2.1) with the expansion (2.9). But we shall transfer the contribution of the small spheres to the left side as a factor $3/(m^2+2)$ by use of the result (I 5.32), and we shall handle radiation reaction through the complex polarizability (2.16) as we have said. We then get the generalized Lorentz–Lorenz relation

$$\left(\frac{m^2-1}{4\pi}\right)\left(\frac{3}{m^2+2}\right) = \sum_{p=1}^{\infty} L_p(n\gamma)^p, \tag{3.1a}$$

where γ is a function of the frequency ω, whereas the coefficients L_p depend on n and T as well as on ω; the coefficients up to fourth order are $L_1 = 1$ and

$$L_2 = |V|^{-1}\,\mathrm{Tr}\int_V \mathrm{d}x_1 \int_{-v} \mathrm{d}x_2\, \mathsf{F}_{12}\cdot\tilde{\mathsf{I}}_{21}(g_{12}-1), \tag{3.1b}$$

$$\begin{aligned} L_3 = |V|^{-1}\,\mathrm{Tr}\int_V \mathrm{d}x_1 \bigg[\int_{V-v} \mathrm{d}x_2 \int_{V-v} \mathrm{d}x_3\, \mathsf{F}_{12}\cdot\mathsf{F}_{23}\cdot\tilde{\mathsf{I}}_{31}(g_{123}-g_{12}-g_{23}+1) \\ +n^{-1}\int_V \mathrm{d}x_2\, \mathsf{F}_{12}\cdot\mathsf{F}_{21}\cdot\tilde{\mathsf{I}}_{11}\,g_{12}\bigg], \end{aligned} \tag{3.1c}$$

$$\begin{aligned} L_4 = |V|^{-1}\,\mathrm{Tr}\int_V \mathrm{d}x_1 \bigg[\int_{V-v} \mathrm{d}x_2 \int_{V-v} \mathrm{d}x_3 \int_{V-v} \mathrm{d}x_4\, \mathsf{F}_{12}\cdot\mathsf{F}_{23}\cdot\mathsf{F}_{34}\cdot\tilde{\mathsf{I}}_{41} \\ \times(g_{1234}-g_{123}-g_{234}-g_{12}g_{34}+g_{12}+g_{23}+g_{34}-1) \\ +n^{-1}\int_V \mathrm{d}x_2 \int_V \mathrm{d}x_3\, \mathsf{F}_{12}\cdot\mathsf{F}_{23}\cdot\mathsf{F}_{31}\cdot\tilde{\mathsf{I}}_{11}\,g_{123} \\ +n^{-1}\int_V \mathrm{d}x_2 \int_{V-v} \mathrm{d}x_3\, \mathsf{F}_{12}\cdot\mathsf{F}_{21}\cdot\mathsf{F}_{13}\cdot\tilde{\mathsf{I}}_{31}(g_{123}-g_{12}) \\ +n^{-1}\int_{V-v} \mathrm{d}x_2 \int_V \mathrm{d}x_3\, \mathsf{F}_{12}\cdot\mathsf{F}_{23}\cdot\mathsf{F}_{32}\cdot\tilde{\mathsf{I}}_{21}(g_{123}-g_{23}) \\ +n^{-2}\int \mathrm{d}x_2\, \mathsf{F}_{12}\cdot\mathsf{F}_{21}\cdot\mathsf{F}_{12}\cdot\tilde{\mathsf{I}}_{21}\,g_{12}\bigg]. \end{aligned} \tag{3.1d}$$

The integrations in (3.1) may always be taken as principal value integrals over the finite region V, but we have simplified the expression where possible. The integrations with respect to x_2 in (3.1b) and in the last term of (3.1d) may be extended over all space, but in (3.1b) the principal value prescription must be used at $x_2 = x_1$. The various terms in (3.1) arise from the H functions (2.10) with omission of self-correlations directly across F propagators (which have been summed and concealed in the complex polarizability γ). The leading term at each order contains simply the ordinary (non-generalized) correlation functions corresponding to the relevant H function, and is given by (2.10) with the G functions replaced by ordinary distribution functions g. The succeeding terms at each order arise from self-correlations not across F propagators contained in the generalized functions as discussed near (2.13).

At lowest order in $n\gamma$ equation (3.1) is just the complex Lorentz–Lorenz relation (1.1 *b*)

$$\left(\frac{m^2-1}{4\pi}\right)\left(\frac{3}{m^2+2}\right) = n\gamma. \tag{3.2}$$

The higher terms of (3.1 *a*) comprise the local-field correction, and the significance of this correction constitutes the main problem of this paper. In the following sections we shall see that the corrections are conceptually significant, and we now show that they can also be numerically important.

(*a*) *Density expansion*

We rearrange (3.1) as an expansion in powers of the density n,

$$\left(\frac{m^2-1}{4\pi}\right)\left(\frac{3}{m^2+2}\right) = \sum_{p=1}^{\infty} b_p(\omega, T)\, n^p, \quad b_1(\omega, T) = \gamma(\omega), \tag{3.3}$$

and investigate some experimental consequences at low densities. Notice that the series (3.1 *a*) as it stands is not a power series in $n\gamma$ because the coefficients depend on n; so m depends on n and γ separately. Thus $b_2 n^2$ gets contributions from all terms with $p \geqslant 2$ in (3.1) arising from self-correlations in the H-functions (2.10).

The term (3.1 *b*) is a two-body term because the integral involves two points. Similarly, the last term of each of (3.1 *c*) and (3.1 *d*) are two-body terms. All of the two-body terms contain an explicit factor n^2 and they contribute to the term $b_2 n^2$ in the density expansion (3.3). But notice that in each of these two-body terms the pair-distribution function g_{12} and the Fourier kernel T_{21} depend on n and must be expanded in powers of n (see, for example, Stell 1964).

$$g_{12} = e_{12}\left[1+n\int (e_{13}-1)\,(e_{23}-1)\,\mathrm{d}\boldsymbol{x}_3+\dots\right], \tag{3.4}$$

$$\mathsf{T}_{21} = \boldsymbol{uu}\exp\left(\mathrm{i}\boldsymbol{k}_0\cdot\boldsymbol{r}_{12}\right)\left[1+n(\mathrm{i}2\pi\gamma\boldsymbol{k}_0\cdot\boldsymbol{r}_{12})+\dots\right]. \tag{3.5}$$

Here

$$e_{12} = \exp\left[-\phi(r_{12})/k_{\mathrm{B}}T\right], \quad \boldsymbol{r}_{12} = \boldsymbol{x}_1-\boldsymbol{x}_2, \quad r_{12} = |\boldsymbol{r}_{12}|; \tag{3.6}$$

ϕ is the pair-potential, and k_{B} is Boltzmann's constant. We have assumed pairwise additivity in (3.4) but the higher terms of (3.4) contribute only to (3.3) for $p \geqslant 3$, and we do not calculate these quantities here.

It is plain that we get additional two-body terms from all orders $p \geqslant 2$ in (3.1); however, they can only come from the leading term $G_{123\dots p}$ of each $H_{123\dots p}$ function (2.10). The term (3.1 *b*) is special among the two-body terms in that it contains the correlation function $g_{12}-1$. All of the other two-body terms contain g_{12}, and these are conveniently classified according to whether the number of propagators F is even or odd. We may therefore write

$$b_2 = b_2^1(\omega, T)+b_2^{\mathrm{e}}(\omega, T)+b_2^{\mathrm{o}}(\omega, T) \tag{3.7 a}$$

in which, writing $\mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)$ as $\mathsf{F}(\boldsymbol{x}-\boldsymbol{x}')$,

$$b_2^1(\omega, T) = \gamma^2(\omega)\,\boldsymbol{uu}\colon \int_{-v} \mathsf{F}(\boldsymbol{r}) \exp\,(\mathrm{i}\boldsymbol{k}_0\cdot\boldsymbol{r})\,\{\exp\,[-\phi(r)/k_\mathrm{B}\,T]-1\}\,\mathrm{d}\boldsymbol{r}, \tag{3.7b}$$

$$b_2^\mathrm{e}(\omega, T) = \gamma(\omega)\,\boldsymbol{uu}\colon \sum_{p=1}^{\infty}\int [\gamma(\omega)\,F(\boldsymbol{r})]^{2p} \exp\,[-\phi(r)/k_\mathrm{B}\,T]\,\mathrm{d}\boldsymbol{r}, \tag{3.7c}$$

$$b_2^\mathrm{o}(\omega, T) = \gamma(\omega)\,\boldsymbol{uu}\colon \sum_{p=1}^{\infty}\int [\gamma(\omega)\,\mathsf{F}(\boldsymbol{r})]^{2p+1} \exp\,[\mathrm{i}\boldsymbol{k}_0\cdot\boldsymbol{r}-\phi(r)/k_\mathrm{B}\,T]\,\mathrm{d}\boldsymbol{r}. \tag{3.7d}$$

The integrations in (3.7) can be taken over all space except in the first term of the sum in (3.7*c*) which must be restricted to the finite region V. When the characteristic range l_0 of ϕ is small compared to k_0^{-1} we find by use of the explicit form (I 2.2*b*) of F

$$b_2^1(\omega, T) = \gamma^2(\omega)\left\{\tfrac{11}{15}k_0^2\int_0^\infty [\exp\,(-\phi(r)/k_\mathrm{B}\,T)-1]\,4\pi r\,\mathrm{d}r-\mathrm{i}\tfrac{4}{3}k_0^3\,B_2(T)\right\}[1+O(k_0^2\,l_0^2)], \tag{3.8a}$$

$$B_2(T) = -\frac{1}{2}\int_0^\infty \{\exp\,[-\phi(r)/k_\mathrm{B}\,T]-1\}\,4\pi r^2\,\mathrm{d}r, \tag{3.8b}$$

in which $B_2(T)$ is the usual second virial coefficient of the equation of state of the fluid. It is important to retain the real and imaginary parts according to their significance to Re(m) and Im(m) respectively. The first term of (3.8*a*) can be ignored therefore because it is $O(k_0^2\,l_0^2)$; but the second term, although $O(k_0^3\,l_0^3)$, must be retained because it is $O(1)$ relative to Im(m). As we shall see, a theory developed only up to b_2^1, like that derived by Hoek (1939) and Rosenfeld (1951), cannot give an adequate description of two-body contributions to Re(m).

To estimate the contribution of the remaining two-body terms we first approximate the propagator $\mathsf{F}(\boldsymbol{r})$ by its Coulomb part $\nabla\nabla r^{-1}$ and ignore the phase factors. The resulting contribution to (3.3) is

$$(n\gamma)^2\,h_2(\omega, T), \tag{3.9a}$$

$$h_2(\omega, T) = \tfrac{8}{3}\pi\int_0^\infty \left[\frac{1}{r^3-2\gamma(\omega)}-\frac{1}{r^3+\gamma(\omega)}\right]\exp\,[-\phi(r)/k_\mathrm{B}\,T]\,r^2\,\mathrm{d}r. \tag{3.9b}$$

This expression constitutes an exact summation of the series (3.7*c*, *d*) within the above-mentioned approximations. To derive it we note that the even and odd terms (3.7*c*) and (3.7*d*) combine when the phase factor is ignored. In the resulting sum over all powers of $\gamma\mathsf{F}$ (taken inside the integration) we write $(3\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}-\mathsf{U})$ as $2\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}-(\mathsf{U}-\hat{\boldsymbol{r}}\hat{\boldsymbol{r}})$. The two terms contribute independently because of orthogonality, and they give rise to the two fractions in square brackets in (3.9*b*) after a term proportional to r^{-3} has been added to the first term and subtracted from the second one inside the brackets. The result is satisfactory for the real part of m; but to treat the imaginary part correctly we need to include contributions of the radiation part of the propagator,

$$\mathsf{R}(\boldsymbol{x},\boldsymbol{x}';\omega) = \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)-\nabla\nabla|\boldsymbol{x}-\boldsymbol{x}'|^{-1}. \tag{3.10}$$

The first term of the series (3.7*c*) is surface dependent and must be treated separately. The two Fs there are written as a sum of Coulomb and radiation parts, and the contribution from the product of two Coulomb parts has already been included in h_2, whereas the two cross terms between Coulomb and radiation parts vanish to a good approximation. The contribution from the product of two radiation parts is $2\pi\frac{2}{3}\mathrm{i}k_0^3\, n^2\alpha^3$ as can be seen by all space Fourier transformation and use of Parseval's theorem (compare the imaginary part of the result (I 6.30) with $\boldsymbol{x}_0 = \boldsymbol{x}_1$). For the remaining terms of (3.7*c*) and for all terms of (3.7*d*) it is sufficient to include (in addition to $h_2(n\gamma)^2$) all contributions with one F in each term replaced by R and the remaining Fs replaced by $\nabla\nabla r^{-1}$. For simplicity we shall furthermore approximate R by its limit value $\frac{2}{3}\mathrm{i}k_0^3\,\mathsf{U}$ as $|\boldsymbol{x}-\boldsymbol{x}'|\to 0$ and again neglect phase factors. The result is the density expansion of the Lorentz–Lorenz relation up to second order in n

$$\left(\frac{m^2-1}{4\pi}\right)\left(\frac{3}{m^2+2}\right) = n\gamma + \left\{h_2 + \mathrm{i}\tfrac{2}{3}k_0^3\left[-2B_2 + 2\pi\gamma + \frac{\partial}{\partial\gamma}(\gamma^2 h_2)\right]\right\}(n\gamma)^2 + \dots. \tag{3.11}$$

Recall that the term $h_2(n\gamma)^2$ comes from the two-body terms (3.7*c*) and (3.7*d*) with Coulomb part propagators; inside the square brackets the term $-2B_2$ comes from (3.7*b*) and $2\pi\gamma$ comes from the first term of (3.7*c*) with (3.10); so the only term that remains to be explained in (3.11) is the last one in brackets, which comes from the effect of radiation parts (3.10) in the sum of two-body terms with at least three propagators. For this we note that a term with p propagators F gives rise to p equal terms in which one of the propagators is replaced by $\frac{2}{3}\mathrm{i}k_0^3\,\mathsf{U}$ to give $p\frac{2}{3}\mathrm{i}k_0^3(\nabla\nabla r^{-1})^{p-1}$. The result can obviously be expressed as a derivative with respect to γ as in the last term of (3.11). Note that the factor γ^2 inside the differentiation stems from the explicit factor γ^2 in the definition (3.9*a*, *b*) of h_2.

We have not been able to justify the approximations that have lead to (3.11) with complete rigour. But we shall see in III that (3.11) is consistent with a similar low-density result for the scattering obtained there provided that the frequency is far from a molecular resonance.

If we choose for $\phi(r)$ a Lennard-Jones potential (see, for example, Hirschfelder *et al.* 1954),

$$\phi(r) = k_\mathrm{B}\,T_0\left[\left(\frac{a}{r}\right)^{12} - 2\left(\frac{a}{r}\right)^{6}\right], \tag{3.12}$$

we obtain h_2 as the function

$$h_2(\omega, T) = h_\mathrm{LJ}\left(\frac{a^3}{\gamma}, \frac{T_0}{T}\right) = B\left(\frac{a^3}{\gamma}, \frac{T_0}{T}\right) - B\left(-\frac{a^3}{2\gamma}, \frac{T_0}{T}\right) \tag{3.13}$$

of the two dimensionless variables $z = a^3/\gamma$ and $w = T_0/T$. We have introduced the function

$$B(z,w) = \int_0^\infty \frac{\exp\left[w(2t^2-t^4)\right]}{t+z}\,\mathrm{d}t \tag{3.14}$$

of the real variable w and the complex variable z. Because $\gamma(\omega)$ has a positive imaginary part the integrand of (3.14) is non-singular at all frequencies $\omega > 0$.

If we choose instead a hard sphere potential for $\phi(r)$ so that the exponential in (3.9*b*) becomes a unit step function $\theta(r-r_0)$ with r_0 the hard sphere diameter, we then get the very simple closed form for h_2 (Hynne 1974):

$$h_2 = \tfrac{8}{9}\pi\,\ln\left(\frac{r_0^3+\gamma}{r_0^3-2\gamma}\right). \tag{3.15}$$

The result (3.15) is obtained directly by integration of (3.9*b*) with the hard-sphere potential. The logarithm in (3.15) is the principal branch defined on the complex plane cut along the negative real axis. We shall discuss the consequences of the results (3.13) and (3.15) below in this section.

For a discussion of the result (3.11) it is convenient to consider the real and imaginary parts of the refractive index separately. The real part is straightforward from (3.11) so we need only consider the imaginary part. We shall discuss it in the form of the extinction coefficient

$$\tau = 2k_0 \operatorname{Im}(m), \tag{3.16a}$$

which may conveniently be written

$$\tau = \frac{4\pi k_0}{\operatorname{Re}(m)} \operatorname{Im}\left\{\frac{m^2-1}{4\pi}\right\}. \tag{3.16b}$$

Denoting the right side of (3.11) by R we can omit the Lorentz factor from the left side of (3.11) if we divide the right side by $[1-\frac{4}{3}\pi\mathrm{R}]$. Expansion of this denominator up to terms quadratic in the density just adds a term $\frac{4}{3}\pi(n\gamma)^2$ to the right side. To obtain a true density expansion we must also expand the factor $[\operatorname{Re}(m)]^{-1} = 1-2\pi n\gamma+\dots$ from (3.16*b*) and retain linear and quadratic terms in the product. Except for frequencies so close to a molecular resonance ω_j that $\omega-\omega_j$ is comparable to the natural width of the spectral line, we may ignore the difference between α, $\operatorname{Re}(\gamma)$, and $|\gamma|$, for example, and we then have up to terms in n^2

$$\tau = \tfrac{8}{3}\pi k_0^4(n\alpha)^2\{1/n-2B_2+\tfrac{8}{3}\pi\alpha+[2\alpha\operatorname{Re}(h_2)+\tfrac{3}{2}k_0^{-3}\operatorname{Im}(h_2)]+\operatorname{Re}(2\gamma h_2+\gamma^2\,\partial h_2/\partial\gamma)\}+\dots. \tag{3.17}$$

The term $2\pi\gamma$ inside the brackets in (3.11) has been cancelled against a term from the expansion of $[\operatorname{Re}(m)]^{-1}$. In §4 we shall see how the factor $[\operatorname{Re}(m)]^{-1}$ is actually eliminated beyond the second order, see the discussion near (4.17). The term $n^{-1}-2B_2$ can now be identified as the beginning of an expansion of the isothermal compressibility κ_T of the fluid

$$\kappa_T k_{\mathrm{B}} T = n^{-1}[1-2B_2 n-(3B_3-4B_2^2)\,n^2+\dots], \tag{3.18}$$

in which B_p denotes the pth virial coefficient. Equation (3.18) can be obtained by differentiation of the virial equation of state. Actually, it arises here because of the expansion (3.4): if the full distribution function is retained the κ_T appears directly (see, for example, Hill 1956, p. 236). For a density expansion (3.17) is correct of course. But it is well known from the work of Einstein (1910) that τ is proportional to κ_T to a good approximation. We derive this result from the microscopic theory in III. We might also attempt to interpret the Lorentz term $\frac{8}{3}\pi\alpha$ in (3.17) as the beginning of an expression of a macroscopic factor such as $[\frac{1}{3}(m^2+2)]^2$. Factors like this appear in the scattering theory (see, for example, Fixman 1955). But we shall see in III that the term is naturally contained in the Einstein formula, which we prove there; in the density expansion it must appear explicitly in the quadratic terms, of course. We shall return to the result (3.17) in the subsection (*c*) below.

(*b*) *Dependence on temperature and molecular individuality*

We now discuss the two-body result (3.11) with h_2 given by (3.13) and (3.14) for a Lennard-Jones potential. We focus on the real part of the refractive index and its dependence on the temperature. It is therefore sufficient to consider

$$\left(\frac{m^2-1}{4\pi}\right)\left(\frac{3}{m^2+2}\right) = n\alpha+h_2(n\alpha)^2+\dots, \tag{3.19}$$

where m and h_2 mean their real parts. For argon, which has Lennard-Jones parameters

$T_0 = 119.8$ K, $a = 0.3822$ nm and polarizability $\alpha(\omega) = 1.667 \times 10^{-24}$ cm^3 at $\lambda = 2\pi c/\omega =$ 633 nm, we find at $T = 298.2$ K

$$z = a^3/\gamma = 33.5 - 3.64\mathrm{i} \times 10^{-8}, \quad w = T_0/T = 0.402. \tag{3.20}$$

This gives $h_2 = 0.517$ in agreement with the experimental value of 0.511 of Buckingham & Graham (1974). Table 1 gives theoretical values of h_2 for a few isotropically polarizable molecules and compares these with the experimental values which appear to be determined with sufficient accuracy. The values of h_2 in table 1 and figure 1 have been obtained by numerical integration of (3.14) with special care taken over the accuracy of the contributions from the regions near the singularities.

The first five rows of table 1 give the Lennard-Jones parameters and the reduced variables

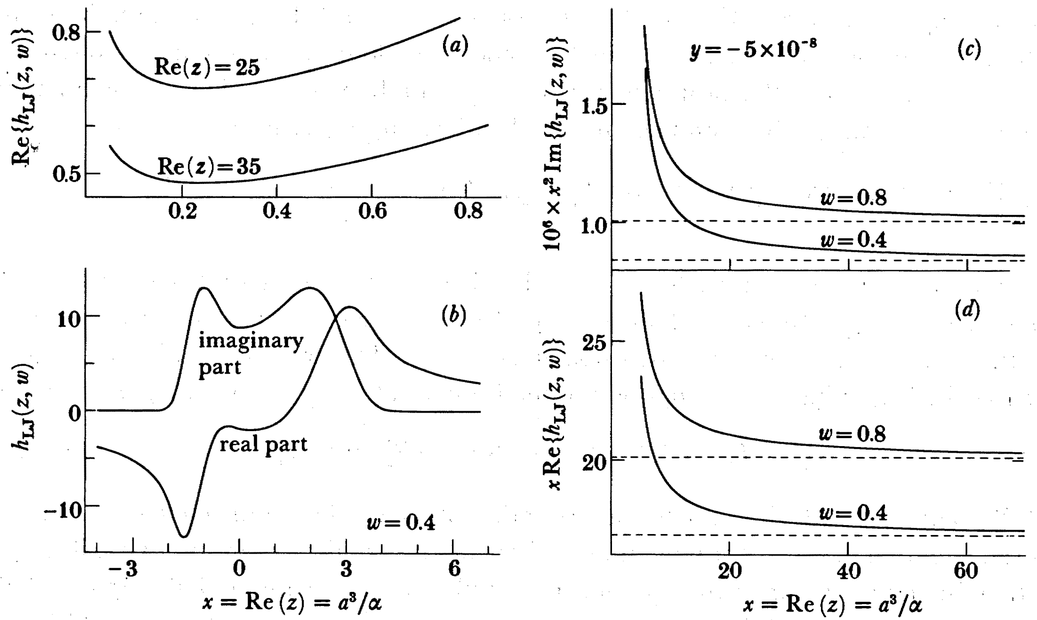

FIGURE 1. The two-body contribution to the complex refractive index as expressed by the function h_2 with a Lennard-Jones potential (parameters a and $k_B T_0$) as a function of the reduced inverse temperature and the reduced inverse polarizability. Note the scalings by x^2 and x in (*c*) and (*d*). Note also in (*b*) that the reliable regions are a tiny interval about $x = 0$ with exclusion of a still much smaller interval about $x = 0$; and furthermore the regions to the extreme left and right of the diagram.

TABLE 1. COMPARISON OF EXPERIMENTAL AND THEORETICAL VALUES OF THE TWO-BODY CONTRIBUTIONS TO THE REFRACTIVE INDEX TOGETHER WITH THE THEORETICAL TEMPERATURE COEFFICIENT

	argon	krypton	xenon	methane
$\alpha/(10^{-30}\ \mathrm{m}^3)$	1.668	2.484	4.045	2.616
$a/(10^{-10}\ \mathrm{m})$	3.822	4.04	4.60	4.285
$\mathrm{Re}(z) = a^3/\alpha$	33.5	26.6	24.1	30.1
T_0/K	119.8	171	221	148.2
$w = T_0/T$	0.402	0.574	0.741	0.497
$\mathrm{Re}(h_2)$	0.517	0.700	0.840	0.597
experimental	0.511[a]	0.60[b]	—	0.688[a]
$-(\partial h_2/\partial T)/(10^{-3}\ \mathrm{K}^{-1})$	0.211	0.588	1.065	0.385

[a] Buckingham & Graham (1974), $2\pi c/\omega = 633$ nm, $T = 299$ K.
[b] Orcutt & Cole (1967), $\omega \approx 0$, $T = 322$ K.

Re(z) and w used in the computations. The results are insensitive to Im(z) and -5×10^{-8} has been used for it. The temperature is 298.15 K in all theoretical results. The entry Re(h_2) determines the refractive index through (3.19) and together with the entry $\partial h_2/\partial T$ it determines the temperature coefficient through (3.22) and (3.23). The entry 'experimental' represents the quantity $\frac{4}{3}\pi B_r/A_r^2$ where A_r and B_r are the first and second refractivity virial coefficients as defined by, for example, Sutter (1972). It is this quantity that can be compared directly with Re(h_2) when any difference in temperature is accounted for through the temperature coefficient of h_2. This gives $h_2 = 0.686$ for krypton at 322 K. The experimental values for argon and methane in table 1 have been obtained (Buckingham & Graham 1974) directly from the variation of the refractive index with density using an accurate interferometric technique. The agreement with Re(h_2) is excellent for argon and reasonable for methane. The experimental value for krypton comes from a measurement of the dielectric constant at low frequency (Orcutt & Cole 1967), and the agreement is comparable to that of methane. For SF_6 (not shown in the table) the experimental values (Nelson & Cole 1971; Buckingham & Graham 1974) exceed the theoretical value by a factor of 2.6. In contrast, the light noble gases, helium and neon, are consistently found experimentally to have negative second refractivity (or dielectric) virial coefficients (and the same seems to apply to CF_4 (Blythe *et al.* 1960)); so these cases apparently cannot be described, even qualitatively, in the approximations of the present work. A number of mechanisms, most of them involving quantum features, have been considered to explain these experimental results (Michels *et al.* 1937; Ten Seldam & de Groot 1952; Jansen & Mazur 1955; Buckingham & Pople 1955*b*; Buckingham & Orr 1967; Heinrichs 1969; Lim *et al.* 1970; Certain & Fortune 1971; Buckingham *et al.* 1973; Buckingham & Watts 1973; O'Brien *et al.* 1973). The theory applies to isotropically polarizable molecules, and we have not attempted to adapt the results for a comparison with measurements on anisotropic molecules like N_2, CO_2, etc. (see, for example, Montixi *et al.* (1983) and the review by Sutter (1972)).

Figure 1 shows h_2 as a function of the inverse temperature, (*a*), and the inverse polarizability, (*b*), (*c*), and (*d*). The subscript LJ on h_{LJ} refers to the use of a Lennard-Jones potential. In figure 1*c*, *d* we plot both Re(h_2) and Im(h_2) as functions of $x = \mathrm{Re}(z) = a^3/\alpha$ for large x, with the choice $y = \mathrm{Im}(z) = -\frac{2}{3}(k_0 a)^3 = -5\times10^{-8}$, treated as a constant, and for the two values $w = T_0/T = 0.4$ and 0.8. We may view x as a measure of frequency ω but it should be noted that y also depends on ω; although Re(h_2) is always insensitive to variations in y, Im(h_2) is not when Im$(h_2) \ll 1$, and figure 1*b* can therefore only indicate the frequency dependence of Im(h_2). However, the primary purpose of these figures is to indicate the variation of h_2 from one substance to another. The scaling by x and x^2 is chosen to give non-zero horizontal aymptotes and hence improved numerical representation of the results. The asymptotic values correspond to the first term of the series b_2^c and were found for the real part by de Boer *et al.* (1953), by Buckingham & Pople (1955*a*), and for a hard sphere gas by Kirkwood (1936). It is seen that the correction from the higher terms is rather small at large x, that is for most substances well off resonance. Near a molecular resonance the higher terms are essential, however, as we shall show in subsection (*c*).

The temperature dependence of Re(h_2) is shown for $a^3/\alpha = 25$ and 35 in figure 1*a*. The temperature variation of m is conveniently expressed in terms of the dimensionless combination

$$L = \frac{1}{n\alpha}\left(\frac{m^2-1}{4\pi}\right)\left(\frac{3}{m^2+2}\right). \tag{3.21}$$

This quantity represents the molar refraction in units of the first refractivity virial coefficient, $A_r = \frac{4}{3}\pi N_A \alpha$, where N_A is Avogadro's constant (see, for example, Sutter 1972). We then find for the temperature variation

$$\left(\frac{\partial m}{\partial T}\right)_p = \frac{2\pi n\alpha}{m}\left(\frac{m^2+2}{3}\right)^2\left[\left(\frac{\partial L}{\partial T}\right)_p - \ell L\right], \tag{3.22}$$

where $\ell = V^{-1}(\partial V/\partial T)_p$ is the thermal expansivity. We therefore need only consider for the real part of the refractive index

$$\left(\frac{\partial L}{\partial T}\right)_p = \left(\frac{\partial L}{\partial T}\right)_n + \left(\frac{\partial n}{\partial T}\right)_p\left(\frac{\partial L}{\partial n}\right)_T = n\alpha\left[\frac{\partial h_2}{\partial T} - \ell h_2\right] + O(n^2), \tag{3.23}$$

which is the quantity often studied experimentally (see, for example, Beysens & Calmette 1977). We obtain the derivatives at constant density formally by setting $\ell = 0$ and replacing fixed p by fixed n in (3.22) and (3.23).

Figure 1*a* shows that h_2 has a minimum as a function of $w = T_0/T$ and hence $(\partial L/\partial T)_n$ has a zero as a function of T (still assuming sufficiently low densities). For argon this occurs at T = 497 K. Under ordinary conditions both terms in brackets in (3.23) are negative and the second term due to thermal expansion dominates. (It is nearly 90% of the total for argon.) Thus $(\partial L/\partial T)_p$ is usually negative (-8×10^{-8} K^{-1} for argon at room temperature and atmospheric pressure) and it becomes positive only at high temperatures. Table 1 shows $\partial h_2/\partial T$ for the selected gases; note the negative sign.

The low density region has been discussed also (for the static dielectric constant) by de Boer *et al.* (1953), who considered the first term of the series (3.7*c*), and by Buckingham & Pople (1955*a*) who considered an equivalent of the combined series (3.7*c*) and (3.7*d*) in a study of two molecules. Vezetti & Keller (1967) reported these terms in a many-molecule analysis. Note that these series sum to a divergent integral when radiation reaction is omitted, and because of this difficulty Buckingham & Pople actually calculate only the first term of (3.7*c*). We discuss the nature of the singularity shortly.

(*c*) *Dependence on frequency*

We now consider the complex refractive index (3.11) and in particular the extinction coefficient (3.17) as functions of frequency for either a Lennard-Jones gas or a hard-sphere gas at low densities using either (3.13) or (3.15) for h_2. That is to say we discuss the dependence of m or τ on ω through $\alpha(\omega)$ in several disconnected frequency regions where the fundamental approximations of the theory can be expected to apply.

Close enough to a resonance, $\omega_j, \alpha(\omega)$ can be approximated by

$$\alpha(\omega) \approx \frac{\chi_j}{\omega_j - \omega}, \quad \chi_j = \frac{e^2 f_j}{2m_e\,\omega_j}. \tag{3.24}$$

The proportionality factor χ_j is given by the quantum theory in terms of the oscillator strength of the resonance transition, f_j, and we have quoted it for easy reference; m_e denotes the electron mass. It is tempting now to interpret Re(z) essentially as frequency although it may be difficult in practice to observe the profile of h_2 by a frequency scan. Nevertheless, it is convenient to identify four distinct regions for which the labels owe something to spectral analysis:

(i) resonance regions $|\alpha| > \min(k_0^{-3}, (a^3/n)^{\frac{1}{2}})$,
(ii) line-wings regions $a^3 \ll |\alpha| \ll \min(k_0^{-3}, (a^3/n)^{\frac{1}{2}})$,
(iii) transition regions $|\alpha| \approx a^3$,
(iv) off-resonance regions $|\alpha| \ll a^3$.

We now compare the terms of (3.17) in square brackets, which come from $\mathrm{Im}(\gamma^2 h_2)$ with the last term, $\mathrm{Re}\{\partial(\gamma^2 h_2)/\partial\gamma\}$, which comes from terms with one radiation part propagator (3.10). Plainly, the two terms in $\mathrm{Re}\,(h_2)$ are equal. (We may treat γ as α here.) Comparison of $\partial h_2/\partial\gamma$ and $\mathrm{Im}\,(h_2)$, both calculated directly from the defining expression (3.13) shows that the term $\mathrm{Re}\,(\gamma^2\,\partial h_2/\partial\gamma)$ is equal to the term $\frac{3}{2}k_0^{-3}\,\mathrm{Im}\,(h_2)$ to a very good approximation in the off-resonance region but is small compared to that term in the line wings region.

To see this we look at $B(z, w)$ with $z = a^3/\gamma$ and we find

$$\mathrm{Re}\left(\gamma^2\frac{\partial B}{\partial\gamma}\right) = a^3\ \mathrm{Re}\int_0^\infty \frac{\exp\left[w(2t^2-t^4)\right]}{(t+z)^2}\,\mathrm{d}t, \tag{3.25a}$$

$$\tfrac{3}{2}k_0^{-3}\ \mathrm{Im}\,(B) = a^3\int_0^\infty \frac{\exp\left[w(2t^2-t^4)\right]}{|t+z|^2}\,\mathrm{d}t. \tag{3.25b}$$

From the other term $-B(-\frac{1}{2}z, w)$ of (3.13) we get the same result with an additional factor $\frac{1}{2}$, and with z replaced by $-\frac{1}{2}z$ in the denominators. So the two terms compared are very similar, but there is the difference that the former has a second order pole in the integrand just off the real axis whereas the latter has a pair of complex conjugate simple poles there. This difference is unimportant in the off-resonance region where the contributions from regions near the singularities are negligible because the exponential factor in (3.14) almost vanishes there, compare the discussion of the significance of the poles of h_2 below, but otherwise the contribution from a small region around $t = -1/\alpha$ or $t = 1/2\alpha$ completely dominates the integral (3.25b) or the similar one from $-B(-\frac{1}{2}z, w)$, whichever contains a near singularity within the region of integration. The same conclusion applies to (3.25a) only if the exponential function varies significantly with t near the singularity; and this is not the case in the line-wings regions.

From this analysis we see that in the off-resonance region (iv) the result (3.17) may be written

$$\tau = \tfrac{8}{3}\pi k_0^4(n\alpha)^2[1/n - 2B_2 + \tfrac{8}{3}\pi\alpha + 4\alpha\ \mathrm{Re}\,(h_2) + 3k_0^{-3}\ \mathrm{Im}\,(h_2)] + \dots. \tag{3.26}$$

We shall see in III that (3.26) agrees with a result for the total scattering from a low-density gas off resonance.

We now look at the other regions (i)–(iii). We are obliged to exclude the resonance regions (i) from consideration since (3.17) is inadequate there: in a rough sense γ contains a single particle resonance and all terms in $(n\gamma)^p$ in (3.1) also resonate there so 3-, 4-, and all p-body terms become important. The $(a^3/n)^{\frac{1}{2}}$ condition in the bound of the region (i) is a rough estimate of the region where many-body resonances are important and (3.17) fails. The estimate is based on the resonance of an approximate form of an effective polarizability for a molecule in the many-body system (see (5.22) with (5.13) below); we must refer to Hynne (1974) for details.

The magnitude of the resonance region is probably overestimated this way. So the estimate of the region of validity for the line-wings region, which is the one we are interested in here, is therefore conservative. The k_0^{-3} condition in (i) is a measure of the natural width introduced via radiation reaction through the resonance of $\gamma(\omega)$. Notice that a resonance region is narrow in terms of $\mathrm{Re}\,(z) = a^3/\alpha$, typically 10^{-3} at $n = 10^{15}\ \mathrm{cm}^{-3}$ according to (i).

The line wings regions exist at least for thin enough vapours and are still narrow on the $\mathrm{Re}\,(z)$ scale. The resonance region cannot be distinguished from the line wings region in figure 1, but the combined regions (i) and (ii) form a tiny interval around $\mathrm{Re}\,(z) = 0$ where $\mathrm{Im}\,(h_2)$ has a plateau. The transition regions (iii) are the broad regions around $\mathrm{Re}\,(z) = 2$ and $\mathrm{Re}\,(z) = -1$ connecting the line wings regions with the off-resonance regions (iv) to the right and left of the shoulders. These regions (iv) are characterized by the condition $\mathrm{Im}\,(h_2) \ll 1$. The curves for h_2 in figure 1*b* apply to $\mathrm{Im}\,(z) = -5\times10^{-8}$ and $w = T_0/T = 0.4$ and their extension to the right are given by the appropriate curves of figure 1*c*, *d*: notice the scalings by x and x^2 and the different scales of the ordinate axes.

The striking increase in the contribution of h_2 to τ when one passes from the off-resonance region into the combined regions (i), (ii), (iii) can be understood as follows. The integrand of (3.9) has singularities just off the real axis directly above or below the points given by

$$r^3 = 2\alpha(\omega) \tag{3.27a}$$

and

$$r^3 = -\alpha(\omega). \tag{3.27b}$$

For given frequency only one of these close singularities occurs within the region of integration. Close enough to actual resonance (3.24) will apply and we can solve (3.27) for ω to find

$$\omega = \omega_j - 2\chi_j r^{-3} = \omega_{\parallel}(r) \tag{3.28a}$$

or

$$\omega = \omega_j + \chi_j r^{-3} = \omega_{\perp}(r). \tag{3.28b}$$

These relations can be interpreted as the resonance frequencies for a *pair* of molecules separated by r with polarizations parallel to ($\parallel$) or perpendicular to ($\perp$) the intermolecular axis. The Boltzmann weight in (3.9) effectively limits the range of integration to some region $r > r_0$ (say). When contributions from resonating pairs occur in this effective range they actually dominate the integral, and this happens in the frequency interval

$$\omega_j - 2\chi_j r_0^{-3} < \omega < \omega_j + \chi_j r_0^{-3} \tag{3.29}$$

or for Re$\,(z)$ in the interval

$$-(a/r_0)^3 < \mathrm{Re}\,(z) < 2(a/r_0)^3, \tag{3.30}$$

which is independent of the approximation (3.24). Recall that a is the Lennard-Jones length parameter whereas r_0 is an effective hard-core diameter.

If we imagine the interval of Re$\,(z)$ of figure 1 scanned with increasing frequency (from right to left) we would see a gradual increase of $\mathrm{Im}\,(h_2)$ by several orders of magnitude when resonance distances solving (3.27*a*) (for axial polarizations) gradually move into regions accessible to molecular pairs. The shoulders are due to the enhanced probability of finding a (resonating) pair at the distance $r = a$ of the minimum of the pair potential. As the frequency passes the free-molecule resonance ω_j the resonance distance for axial polarization goes to infinity and resonances for perpendicular polarizations become possible for (infinitely) distant pairs of molecules. These resonances then replace the axial resonance. As the frequency is increased still further the resonance distance for perpendicular resonances decreases and ultimately moves into regions inaccessible to pairs of molecules with a drastic decrease of $\mathrm{Im}\,(h_2)$ as a result.

Because the main contribution to $\mathrm{Im}\,(h_2)$ in the line-wings region is from distant pairs of molecules the quasistatic theory is adequate (provided only that the Doppler effect can be ignored as it can sufficiently far from ω_j). On the other hand, the quasistatic theory may be inadequate in the transition region. Here the main contribution comes from close pairs of molecules for which molecular motion and quantal corrections may be important. In the off-resonance region h_2 gets relatively significant contributions from pairs of molecules for any $r > r_0$ and the quasistatic theory is expected to be adequate again.

In the line-wings region the situation is particularly simple. Here the approximation

$$h_2 \approx \tfrac{8}{9}\pi(-\ln 2 + \mathrm{i}\pi), \quad |\mathrm{Re}\,(z)| \ll 1, \tag{3.31}$$

applies (and applies particularly well to $\mathrm{Im}\,(h_2)$). Recall also that in region (ii) the derivative of h_2 in (3.17) is negligible compared to the term in $\mathrm{Im}\,(h_2)$. We therefore find the extinction coefficient in a line-wings region as

$$\tau = \tfrac{8}{3}\pi k_0 (n\alpha)^2 [(1/n - 2B_2)\, k_0^3 + \tfrac{8}{3}\pi (1 - \tfrac{4}{3} \ln 2)\, k_0^3 \alpha + \tfrac{4}{3}\pi^2] \tag{3.32}$$

at sufficiently low densities. The terms in $B_2 k_0^3$ and $k_0^3 \alpha$ can always be ignored in comparison with $\frac{4}{3}\pi^2$ at optical or lower frequencies and when the condition (ii) applies, so we have

$$\tau = \tfrac{8}{3}\pi k_0 \alpha^2 [k_0^3 n + \tfrac{4}{3}\pi^2 n^2]. \tag{3.33}$$

The first term in brackets is the one-body term, and this may be neglected except at densities comparable to k_0^3 or lower (corresponding to few molecules per cubic wavelength).

The result (3.33) may be compared with the experimental absorption of light in the wing of the caesium line at 852 nm ($f_j = 0.718$), for example. At densities where the one-body term may be neglected the extinction coefficient in units of $\frac{8}{3}\pi k_0 (n\alpha)^2$ has been found to be 15.4 by Gregory (1942) and 17.4 by Chen & Phelps (1968). These experimental results should be compared with the figure $\frac{4}{3}\pi^2 = 13.2$ of the present theory.

In the literature on spectral line shapes a result like (3.33) for the absorption (due to external scattering) in the wings of an absorption line is sometimes interpreted in terms of the width of the line on the assumption that the shape is Lorentzian. Interpreted this way the imaginary part of (3.31) gives the line width whereas the real part gives a shift of the resonance frequency, see the discussion by Hynne (1974). A result equivalent to (3.31) has also been obtained by Mead (1968*a*, *b*, 1972) precisely as a line width and shift. But we emphasize that the two-body terms are inadequate for a description of the resonance region (i), at least when the quasistatic approximation applies.

We now summarize the main results of this section. The refractive index depends at low densities essentially only on the three dimensionless parameters $n\gamma$, a^3/γ, and T_0/T, where a and $k_B T_0$ are the Lennard-Jones parameters. (The imaginary part of m has an additional explicit dependence on the frequency $\omega = ck_0$.) The main dependence is on the polarizability per unit volume as predicted by the Lorentz–Lorenz relation. But the corrections for intermolecular correlations are comparable to the effect of the Lorentz internal field factor: by expanding the Lorentz factor in (3.19) we find for the real part of m:

$$(m^2 - 1)/4\pi = n\alpha + (\tfrac{4}{3}\pi + h_2)\,(n\alpha)^2 + \dots. \tag{3.34}$$

Table 1 shows that h_2 is commonly 10–20 % of the Lorentz term $\frac{4}{3}\pi$, independently of density.

The broad features of the refractive index at low densities including effects of intermolecular correlations are represented in a simple way by (3.11) with the hard-sphere result (3.15). It contains the line-wings result (3.33) and describes off-resonance behaviour as well, except that it cannot account for the temperature dependence at constant density.

To recover the line-wings result it may be helpful to rewrite the logarithm in (3.15) as

$$\ln\left(\frac{r_0^{-3} + \alpha^{-1} - \frac{2}{3}\mathrm{i}k_0^3}{-2r_0^{-3} + \alpha^{-1} - \frac{2}{3}\mathrm{i}k_0^3}\right). \tag{3.35}$$

When α^{-1} can be neglected in comparison with r_0^{-3} (3.35) becomes independent of r_0 and equal to $-\ln 2+\mathrm{i}\pi$ to a very good approximation. We note also that the hard-sphere result (3.15) directly confirms the analysis made around (3.25).

To see in a simple way how the off-resonance behaviour is contained in (3.15), we may expand the logarithm in powers of γ/r_0^3. The first term of the expansion yields

$$8\pi n^2\gamma^3/(3r_0^3), \tag{3.36}$$

and this becomes identical with the term obtained by Kirkwood (1936) in the static limit. But the simple result (3.15) contains all but one of the infinity of two-body terms (the term $-\mathrm{i}\frac{4}{3}\pi k_0^3 B_2$ from (3.7b) appears separately in (3.11)).

The appearance of a length parameter a or r_0 with magnitude a molecular diameter signals the physical reality of the concepts underlying the Onsager–Böttcher result (1.2). In fact, it is easy to see that the Kirkwood term (3.36) is contained in (1.2), concealed in the Böttcher polarizability. We shall demonstrate in §5 how the Onsager–Böttcher relation is *entirely* contained in the microscopic theory when the many-body terms of all order are taken into account.

To achieve this goal we must develop the screened formulation of the theory for which the foundation was laid in §4 of I. We therefore start in the immediately following section by reviewing the relevant results from I.

4. SURFACE-DEPENDENT PROPAGATORS AND BULK APPROXIMATION

Equation (3.1) is the fundamental expression for the refractive index. It was obtained through the expansion (2.9) of the susceptibility kernel in terms of the polarizability α and the free field propagator F, and it therefore describes the refractive index in terms of elementary scattering processes taking place in vacuum: molecules are polarized as isolated molecules and fields propagate in empty space.

Unfortunately, there is the difficulty with the result (3.1) that certain of the integrals in the coefficients (3.1c), (3.1d), ... at each order p beyond the second depend on the geometry of the material system. This is the case with the last term of (3.1c) (the one containing $\mathsf{F}_{12}\cdot\mathsf{F}_{21}$), for example.

Conceptually this means that (3.1) determines a shape-dependent refractive index. The solution to this problem was sketched in I (see the discussion around (I 6.35)); and although the principle of solution indicated there was not in fact used to reach the result (3.1), we can infer from the discussion in I that the shape dependence of (3.1) must be entirely negligible as long as all linear dimensions of V are large compared to the wavelength of the incident light. Nevertheless, there remains the practical problem that the shape dependent integrals of the theory are difficult to compute analytically or numerically.

The surface problem is best treated through the screened formulation of the refractive index theory developed in I. The idea is to work with a 'screened' propagator $\mathscr{F}$ representing the propagation of fields in the medium rather than in empty space. The screened propagator was itself defined in I in terms of elementary scattering processes in vacuum, and the series representation (I 4.13),

$$\mathscr{F}_{10}=\sum_{p=1}^{\infty}(n\alpha)^{p-1}\int_V\cdots\int_V \mathsf{F}_{12}\cdot\mathsf{F}_{23}\ldots\mathsf{F}_{p0}\,G_{23\ldots p}\,\mathrm{d}\boldsymbol{x}_2\ldots\mathrm{d}\boldsymbol{x}_p \tag{4.1}$$

was derived for it. The first term of (4.1) equals F_{10} simply. The refractive index is obtained in terms of $\mathscr{F}$ through (2.1) by using the expansion (I 4.10) of Λ in terms of $\mathscr{F}$, namely

$$\Lambda_{10} = n\alpha\mathsf{U}\delta_{10} + \sum_{p=1}^{\infty} (n\alpha)^{p+1} \int_V \dots \int_V \mathscr{F}_{12} \cdot \mathscr{F}_{23} \dots \mathscr{F}_{p0}\, Y_{123\dots p0}\, \mathrm{d}\boldsymbol{x}_2 \dots \mathrm{d}\boldsymbol{x}_p. \tag{4.2}$$

Here the correlation functions Y are defined in (I 4.11*a*) and the first few functions are

$$Y_{12} = U_{12}, \quad Y_{123} = U_{123}, \quad Y_{1234} = U_{1234} + U_{13}\,U_{24}, \dots \tag{4.3a}$$

in terms of generalized Ursell functions,

$$U_{12} = G_{12} - 1, \quad U_{123} = G_{123} - G_{12} - G_{23} - G_{31} + 2, \dots, \tag{4.3b}$$

which themselves are defined in terms of the generalized distribution functions (2.11) by (I 4.12). The Ursell functions have the cluster property: they vanish rapidly whenever the distance between any two of its arguments goes to infinity.

This means that if all points of an integral are 'covered' by Ursell functions then all integrations can be extended to all space after the factor $|V|^{-1}$ and the integration with respect to $\boldsymbol{x}$ in (2.1) have been dropped. Such an integral is surface independent, and in general the surface dependence of integrals is most simply appreciated when the integrals are expressed in terms of Ursell functions. Therefore the expansion (4.2) is ideal for an analysis of the surface dependence. We shall see that the entire surface dependence is actually isolated in the propagators $\mathscr{F}$ this way, and we shall come to understand the physical meaning of the surface dependence in terms of the properties of $\mathscr{F}$.

It is convenient to use a diagrammatic notation, see figures 2 and 3. The basic element of a diagram is a set of black or white circles. Each circle indicates a factor $n\alpha$ and represents a point in space appearing as one argument of an integrand; broadly a circle represents a polarizable molecule. A line between two circles represents a propagator between the corresponding two points. A single line represents F and a double line represents $\mathscr{F}$. Intermolecular correlation functions are represented by loops of dotted lines, and a dotted line coinciding with a full line (or double line) adds a cross to the line. When only two circles are involved the loop degenerates to a line.

We use black or white circles to distinguish between correlation functions. In a diagram with white circles a dotted loop connecting p circles represents a generalized p-body Ursell function, $U_{123\dots p}$, defined in (I 4.12). A loop of dotted lines represents an ordinary p-body distribution function $g_{123\dots p}$ in a diagram with black circles. So it is important to distinguish the two kinds of diagrams. Notice in particular that diagrams in white circles conceal the terms arising from self-correlations. Such terms appear explicitly in the black circle notation as diagrams containing closed loops formed by chains of propagator lines as in figure 3. Such terms represent self-interactions and a closed loop of a single line, in particular, represents the radiation reaction (2.14). It should also be noted that a generalized Ursell function as well as an ordinary distribution function is symmetrical in all its variables although the representation by a loop of dotted lines cannot exhibit the full symmetry.

In any refractive index diagram we have a chain of circles connected by propagator lines, and each circle implies an integration of the corresponding point over the region V except when the circle carries a dot. In diagrams without dots a factor $|V|^{-1}\tilde{\mathsf{1}}_{p1}$ and the trace operation are understood, the factor $\tilde{\mathsf{1}}_{p1}$ connecting the first and last points of a chain. The spatial

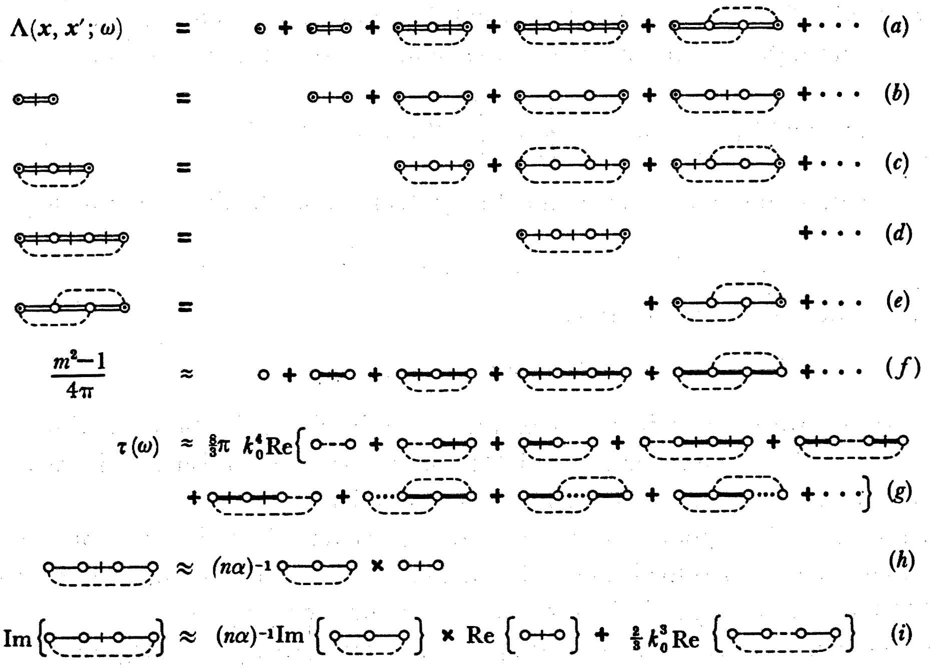

FIGURE 2. Diagrammatic representation of some results in the screened formulation. (*a*) The rigorously screened expansion (4.2) of $\mathsf{\Lambda}$. (*b*)–(*e*) Expansions of each term of (*a*) through (4.1), but expressed in terms of Ursell functions. (*f*) The refractive index from (*a*) in the bulk approximation. (*g*) The extinction coefficient in the bulk approximation. (*h*) Simplest example of the approximation involved in the use of $\tilde{\mathsf{F}}$ for $\mathscr{F}$. (*i*) The last term on the right is associated with damping in propagation as described by $\tilde{\mathsf{F}}$ in the second term of (*f*), but shown outside the bulk approximation.

arrangement of the circles in a diagram has no significance; it is usually convenient to draw a chain of propagator lines horizontally whereas simple closed loop diagrams are drawn as polygons. The slight modification which is needed to extend the diagram notation to describe optical scattering also will be explained in III.

Figure 2*a* shows the diagrammatic representation of the expansion (4.2) of $\mathsf{\Lambda}$. Equations (*b*)–(*e*) of figure 2 show the expansions of the successive terms of (*a*) arising through (4.1), expressed in terms of the generalized Ursell functions (white circle diagrams). We need this form in our discussion; but notice that the expansion of $\mathscr{F}$ is actually much simpler in terms of the generealized distribution functions G as (4.1) shows.

Although it is sometimes useful to view the expansion (4.2) as a compact representation of the unscreened series (2.9), the key to a deeper understanding of the refractive index is to regard $\mathscr{F}$ as an entity in (4.2). We now show that it can be approximated by the closed form

$$\tilde{\mathsf{F}}(\boldsymbol{x},\boldsymbol{x}';\omega) = (\nabla\nabla + m^2k_0^2\,\mathsf{U})\frac{\exp(\mathrm{i}mk_0|\boldsymbol{x}-\boldsymbol{x}'|)}{m^2|\boldsymbol{x}-\boldsymbol{x}'|}. \tag{4.4}$$

This is a generalization of (2.6) and describes the field at $\boldsymbol{x}$ from a dipole at $\boldsymbol{x}'$, propagated in a continuum of refractive index m. Because $\mathscr{F}$ clearly depends on the geometry we need an approximation which disregards surface effects.

We work from the equation (I 4.3) for $\mathscr{F}$, namely

$$\mathscr{F}_{10} = \mathsf{F}_{10} + \int_V\int_V \mathsf{F}_{12}\cdot\mathsf{\Lambda}_{23}\cdot\mathscr{F}_{30}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3. \tag{4.5}$$

The first step towards this 'bulk approximation' is to take the Fourier transform of (4.5) over all space, after having extended the integrations to all space. In this step we neglect the divergent parts from the surface terms which we want to eliminate. Denoting the Fourier transformed approximation to $\mathscr{F}(\boldsymbol{x},\boldsymbol{x}';\omega)$ by $\tilde{\mathsf{F}}(\boldsymbol{h},\omega)$ we find

$$\tilde{\mathsf{F}}(\boldsymbol{h},\omega) = \mathsf{F}(\boldsymbol{h},\omega)+\mathsf{F}(\boldsymbol{h},\omega)\cdot\Lambda(\boldsymbol{h},\omega)\cdot\tilde{\mathsf{F}}(\boldsymbol{h},\omega). \tag{4.6}$$

By arguments similar to the one leading to (I 5.20), $\Lambda(\boldsymbol{h},\omega)$, the Fourier transform of $\Lambda(\boldsymbol{x},\boldsymbol{x}';\omega)$, splits into longitudinal and transverse parts, and $\mathsf{F}(\boldsymbol{h},\omega)$ similarly splits:

$$\mathsf{F}(\boldsymbol{h},\omega) = \frac{4\pi k_0^2}{h^2-k_0^2}(\mathsf{U}-\hat{\boldsymbol{h}}\hat{\boldsymbol{h}})-4\pi\hat{\boldsymbol{h}}\hat{\boldsymbol{h}}. \tag{4.7}$$

Here k_0 is interpreted as $k_0+\mathrm{i}\delta$ with δ a positive infinitesimal. Thus (4.6) splits into independent equations determining the longitudinal and transverse parts of $\tilde{\mathsf{F}}(\boldsymbol{h},\omega)$ separately.

When the wavenumber $h = |\boldsymbol{h}|$ is small compared with a reciprocal correlation length, l^{-1}, $\Lambda(\boldsymbol{h},\omega)$ is a constant isotropic tensor to a good approximation which means that the longitudinal and transverse parts of $\Lambda(\boldsymbol{h},\omega)$ are nearly equal. Clearly, $\Lambda_{\parallel}(\boldsymbol{h},\omega)$ and $\Lambda_{\perp}(\boldsymbol{h},\omega)$ become equal in the limit $h\rightarrow 0$. Indeed, contributions from the leading term $n\alpha\mathsf{U}$ and from all terms of $\Lambda(\boldsymbol{x},\boldsymbol{x}';\omega)$ containing a delta function $\delta(\boldsymbol{x}-\boldsymbol{x}')$ as a factor (the self-interactions discussed in §6) are strictly isotropic and independent of h when the surface effect is neglected. And all terms with range of the order of a correlation length l are isotropic and independent of h up to a term $O((hl)^2)$ for small h. There are still terms at fourth and higher orders in $n\alpha$ which require the stricter condition $h \ll k_0$ rather than $h \ll l^{-1}$ for being constant and isotropic. But neglecting such terms we may use the result (2.1) to get

$$\Lambda_{\parallel}(h,\omega) \approx \Lambda_{\perp}(h,\omega) \approx (m^2-1)/4\pi \tag{4.8}$$

valid for $h \ll l^{-1}$. Note that the right side of (2.1) equals $\Lambda_{\perp}(mk_0,\omega)$ and that the wavevector from (2.2) satisfies the condition $mk_0 \ll l^{-1}$ at optical or lower frequencies and away from the critical point.

A crucial step now is to extend the relations (4.8) to all positive h. In this approximation we can readily solve the longitudinal and transverse equations from (4.6). The solutions combine in the result

$$\tilde{\mathsf{F}}(\boldsymbol{h},\omega) = \frac{4\pi}{m^2}\frac{m^2k_0^2\,\mathsf{U}-\boldsymbol{h}\boldsymbol{h}}{h^2-m^2k_0^2}, \tag{4.9}$$

which yields (4.4) by inverse Fourier transformation. The form (4.4) is a good approximation to the translationally invariant part of $\mathscr{F}$ at distances $|\boldsymbol{x}-\boldsymbol{x}'|$ large compared to a typical correlation length l (defined by (I 6.29) say).

The bulk photon propagator $\tilde{\mathsf{F}}$ satisfies the integral equation

$$\tilde{\mathsf{F}}(\boldsymbol{x},\boldsymbol{x}';\omega) = \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)+\frac{m^2-1}{4\pi}\int\mathsf{F}(\boldsymbol{x},\boldsymbol{x}'';\omega)\cdot\tilde{\mathsf{F}}(\boldsymbol{x}'',\boldsymbol{x}';\omega)\,\mathrm{d}\boldsymbol{x}'', \tag{4.10}$$

which can be obtained from (4.5) by approximating Λ as

$$\Lambda(\boldsymbol{x},\boldsymbol{x}';\omega) \approx \frac{m^2-1}{4\pi}\mathsf{U}\delta(\boldsymbol{x}-\boldsymbol{x}') \tag{4.11}$$

and extending the integration to all space. The approximation (4.11) views the medium as a continuum of refractive index m and ignores spatial dispersion.

The closed form (4.4) for a translationally invariant system will be used below to obtain a 'bulk approximation' to the refractive index. However, it is important to understand the surface dependence of $\mathscr{F}$. Intuitively, if $\mathscr{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{p}$ is viewed as the average field at $\boldsymbol{x}$ (in the medium) radiated from an oscillatory dipole probe at $\boldsymbol{x}'$, we must expect from macroscopic theory that $\mathscr{F}\cdot\boldsymbol{p}$ contains waves reaching $\boldsymbol{x}$ after reflections in the surface. To discuss this interpretation without appeal to macroscopic theory we consider a 'continuum approximation' $\tilde{\mathsf{F}}_V$ to $\mathscr{F}$ for the *finite* system by using (4.11) for Λ but retaining the finite region of integration. We then find for $\tilde{\mathsf{F}}_V$

$$\tilde{\mathsf{F}}_V(\boldsymbol{x},\boldsymbol{x}';\omega) = \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)+\frac{m^2-1}{4\pi}\int_V \mathsf{F}(\boldsymbol{x},\boldsymbol{x}'';\omega)\cdot\tilde{\mathsf{F}}_V(\boldsymbol{x}'',\boldsymbol{x}';\omega)\,\mathrm{d}\boldsymbol{x}''. \tag{4.12}$$

It is easy to show that the solution to (4.12) has the form

$$\tilde{\mathsf{F}}_V(\boldsymbol{x},\boldsymbol{x}';\omega) = \tilde{\mathsf{F}}(\boldsymbol{x},\boldsymbol{x}';\omega)+\tilde{\mathsf{f}}(\boldsymbol{x},\boldsymbol{x}';\omega), \tag{4.13}$$

where $\tilde{\mathsf{f}}$ as a function of $\boldsymbol{x}$ is analytic at $\boldsymbol{x}'\in V$; $\tilde{\mathsf{f}}$ satisfies an integral equation of the form

$$\tilde{\mathsf{f}}(\boldsymbol{x},\boldsymbol{x}';\omega) = \mathsf{q}(\boldsymbol{x},\boldsymbol{x}';\omega)+\frac{m^2-1}{4\pi}\int_V \mathsf{F}(\boldsymbol{x},\boldsymbol{x}'';\omega)\cdot\tilde{\mathsf{f}}(\boldsymbol{x}'',\boldsymbol{x}';\omega)\,\mathrm{d}\boldsymbol{x}''. \tag{4.14a}$$

Comparison of (4.14*a*) with (I 3.2) in the approximation (4.11) shows that for any dipole $\boldsymbol{p}$ we may describe $\tilde{\mathsf{f}}\cdot\boldsymbol{p}$ as the average electric field induced in the medium inside V in response to an externally incident field $\mathsf{q}\cdot\boldsymbol{p}$. The coefficient q is given by the explicit expression

$$\mathsf{q}(\boldsymbol{x},\boldsymbol{x}';\omega) = -\frac{m^2-1}{4\pi}\int_{-V} \mathsf{F}(\boldsymbol{x},\boldsymbol{x}'';\omega)\cdot\tilde{\mathsf{F}}(\boldsymbol{x}'',\boldsymbol{x}';\omega)\,\mathrm{d}\boldsymbol{x}'' \tag{4.14b}$$

in which $-V$ denotes the complement of V with respect to all space, that is V and $-V$ are disjoint and their union is all space. (When V is finite $-V$ is infinite, but terms oscillating with finite amplitude at infinity cancel against similar contributions neglected in $\tilde{\mathsf{F}}$.)

Now it is plain that $\tilde{\mathsf{f}}(\boldsymbol{x},\boldsymbol{x}';\omega)$ contains all of the surface dependence of $\tilde{\mathsf{F}}_V$. It has the character of a wave coming into the region V from the outside. In the case where V is the half-space $z > 0$, for example, we expect that $\tilde{\mathsf{f}}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{p}$ takes the form of a spherical wave reflected in the surface $z = 0$, formally emerging from an image dipole source at a point $\boldsymbol{x}''$ which is the mirror image of $\boldsymbol{x}'$ in the surface $z = 0$. Compare Tai (1971) and the solutions by Sommerfeld (1909, 1949) and Weyl (1919) to a similar problem in radio wave propagation discussed also by Stratton (1941). (We thank R. E. Collin for this reference.) Note that the x_1 dependence of the surface integral (I 6.30) evaluated in I fully agrees with this view. But otherwise we have not actually calculated $\tilde{\mathsf{F}}_V$ from (4.12) or $\tilde{\mathsf{f}}$ from (4.14) to confirm this interpretation. Nevertheless, we surely understand the nature of the surface dependence of $\mathscr{F}$, and we shall therefore now consider the surface dependence of the expression (2.1) for the refractive index and the question of obtaining a surface independent theory.

We propose to obtain a translationally invariant expression for the refractive index from (2.1) with (4.2)

$$\frac{m^2-1}{4\pi} = \sum_{p=1}^{\infty} M_p(n\alpha)^p, \quad M_1 = 1, \tag{4.15a}$$

$$M_p = \mathrm{Tr}\int\ldots\int \tilde{\mathsf{F}}_{12}\cdot\tilde{\mathsf{F}}_{23}\ldots\tilde{\mathsf{F}}_{(p-1)\,p}\cdot\mathsf{I}_{p1}\,Y_{123\ldots p}\,\mathrm{d}\boldsymbol{x}_2\ldots\mathrm{d}\boldsymbol{x}_p \tag{4.15b}$$

by replacing $\mathscr{F}$ by $\tilde{\mathsf{F}}$ and extending all integrations to all space. It is this prescription which we take finally to define what we call the bulk approximation. The result (4.15) is exhibited diagrammatically in figure 2 (*f*) where a heavy line represents $\tilde{\mathsf{F}}$. Equation (*f*) of figure 2 is similar to (*a*) except that heavy lines replace double lines. Also the dots in two circles in (*a*) indicating that $\Lambda(\boldsymbol{x},\boldsymbol{x}';\omega)$ has the two free variables $\boldsymbol{x}$ and $\boldsymbol{x}'$ are absent in (*f*) because the expression in m is a constant. Strictly speaking there is no integration with repect to $\boldsymbol{x}_1$ in (4.15). Originally in (2.1) there was an averaging over $\boldsymbol{x}$, and although this step is now superfluous the omission of a single dot in the diagrams of figure 2 (*f*) gives the most consistent notation.

The question remains if it is actually possible to extend all integrations to reach the bulk approximation in (4.15). It is clear that the integrals in (4.15) do not in general converge through the correlation functions. At the fourth order, for example, the correlation function Y_{1234} contains the term $U_{13}\,U_{24}$ as (4.3) shows; and from this term we get a contribution to M_4:

$$\operatorname{Tr}\int\dots\int\tilde{\mathsf{F}}_{12}\cdot\tilde{\mathsf{F}}_{23}\cdot\tilde{\mathsf{F}}_{34}\cdot\tilde{\mathsf{T}}_{41}\,U_{13}\,U_{24}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3\,\mathrm{d}\boldsymbol{x}_4. \tag{4.16}$$

Here configurations in which the distances $|\boldsymbol{x}_1-\boldsymbol{x}_3|$ and $|\boldsymbol{x}_2-\boldsymbol{x}_4|$ are both comparable to a correlation length will give a finite $U_{13}\,U_{24}$ no matter how large the distance between the two groups of points $\boldsymbol{x}_1,\boldsymbol{x}_3$ and $\boldsymbol{x}_2,\boldsymbol{x}_4$ is made. But nevertheless, the integral (4.16) converges because the product of the three propagators yields a factor $R^{-3}\exp(\mathrm{i}3mk_0R)$ asymptotically as the distance R between the two groups of points becomes large.

Quite generally the integrals in (4.15) are convergent through the *combination* of Ursell functions and propagators. In any integral of (4.15) there are always *at least three* propagators between any two groups of points not connected by Ursell functions. This conclusion follows from the explicit expression (I 4.11*a*) for the Y functions in terms of Ursell functions. For details see the discussion in §5 of Hynne (1975).

Returning for a moment to the rigorous expression for the refractive index, (2.1) with (4.2), we conclude that in this form the surface dependence has indeed been isolated in the screened propagators. In the continuum approximation where $\tilde{\mathsf{F}}_V$ replaces $\mathscr{F}$ the surface dependence arises entirely from the 'reflected parts' of the propagators $\tilde{\mathsf{F}}_V$, the $\tilde{\mathsf{T}}$s defined in (4.14).

Now that we fully understand the surface dependence of the refractive index theory we may ignore all surface effects: they are numerically insignificant. We shall therefore work from (4.15) in the following section.

We close the present section by noting a straightforward consequence of the screened expression (4.15) in relation to the unscreened theory of §3. We show how the factor $1/\operatorname{Re}(m)$ in the extinction coefficient (3.16*b*) is eliminated in the screened theory by an explicit factor $\operatorname{Re}(m)$ arising from the imaginary part of the propagator $\tilde{\mathsf{F}}$. We have

$$\operatorname{Im}\{\tilde{\mathsf{F}}(\boldsymbol{x},\boldsymbol{x}';\omega)\}=\tfrac{2}{3}\operatorname{Re}(m)\,k_0^3\,\mathsf{U}+O(k_0^2|\boldsymbol{x}-\boldsymbol{x}'|^2) \tag{4.17}$$

at small distances $|\boldsymbol{x}-\boldsymbol{x}'|$. Consequently we get a factor $\tfrac{2}{3}\operatorname{Re}(m)\,k_0^3$ from any $\operatorname{Im}(\tilde{\mathsf{F}})$ propagator covered by an Ursell function (which is short range). The result for τ is shown in figure 2*g* up to the fourth order in $n\alpha$ (terms containing three propagators $\tilde{\mathsf{F}}$).

It must be noted, however, that there are terms at fourth and all higher orders containing $\tilde{\mathsf{F}}$ propagators which are *not* covered by Ursell functions. For example, the last three terms shown in figure 2 (*g*) coming from (4.16) contain $U_{13}\,U_{24}$ which does not cover any of the three $\tilde{\mathsf{F}}$s.

We have introduced an auxilliary element of diagram notation *ad hoc*: a line in heavy dots represents $[\frac{2}{3}\,\mathrm{Re}\,(m)\,k_0^3]^{-1}\,\mathrm{Im}\,(\tilde{\mathsf{F}})$.

The simple result (4.17) actually assumes that m is real in $\tilde{\mathsf{F}}$. This assumption can be analysed in the unscreened theory by utilizing the exact equivalence of the screened and unscreened formulations. We first explain the precise consequences of the bulk approximation at the lowest order. Comparison with the rigorous expression for $\mathcal{F}$ shows that the bulk approximation means replacements like the one shown in figure 2*h* in addition to the neglect of surface effects: the action of the kernel $\mathbf{\Lambda}$ between F and $\mathcal{F}$ in (4.5) becomes replaced by a simple multiplication in (4.10). Now, the effect of an imaginary part of m shows up first in the term arising from the last one exhibited in figure 2*b* in its contribution to the imaginary part of the screened two-body term. In the bulk approximation this term is the product of two factors as figure 2*h* shows. The imaginary part is therefore a sum of the two terms shown in figure 2*i* in which the second one is shown outside the bulk approximation to exhibit its appearance in the unscreened theory.

The second term of figure 2*i* is associated with an $\mathrm{Im}\,(m)$ in the propagator $\tilde{\mathsf{F}}$. To see this, note that an $\mathrm{Im}\,(m)$ in $\tilde{\mathsf{F}}$ must come from the factor $\frac{1}{4}(m^2-1)/\pi$ in (4.10), which itself comes from $\mathbf{\Lambda}$ in (4.5). From the iterative expansion of (4.5) it is now clear that the middle of the three propagators in the last term of figure 2*b* comes from $\mathbf{\Lambda}$, and the last term of figure 2*i* contains the imaginary part of precisely this middle propagator. The last term of figure 2*i* is therefore associated with damped propagation. It is intimately related to real multiple scattering as we show in III, and it plays an important role in the derivation of the Einstein light scattering equation discussed there. In III we shall give a more careful discussion of damped propagation, and we shall show that the terms associated with damping really do not participate in the elimination of the factor $[\mathrm{Re}\,(m)]^{-1}$.

5. Cavity field and Onsager reaction field

Unfortunately the expansion (4.15) is still not yet well defined. We need expressions for the contributions from small spheres and from self-correlations associated with an $\tilde{\mathsf{F}}$ propagator corresponding to the definitions (2.7) and (2.14) for F. The generalization of (2.7),

$$\lim_{v\to 0}\int_v \tilde{\mathsf{F}}(x,x';\omega)\,\mathrm{d}x' = (-\tfrac{4}{3}\pi/m^2)\,\mathsf{U} \tag{5.1}$$

is immediate, but the generalization of (2.14),

$$\int \tilde{\mathsf{F}}(x,x';\omega)\,\delta(x-x')\,\mathrm{d}x' = \tilde{s}(\omega)\,\mathsf{U} \tag{5.2}$$

is not so clear; we shall return to it shortly. We shall refer to a contribution arising from the use of (5.1) as a 'screened Lorentz term' and to one from (5.2) as a 'screened self-interaction'.

For the moment we recall the effect of the small spheres and the self-correlations across F propagators in the unscreened formulation, (2.1) with (2.9). The terms from (2.7) and (2.14) sum to yield the Lorentz–Lorenz relation with a complex polarizability, (3.2). The small spheres provide the Lorentz internal-field factor $\frac{1}{3}(m^2+2)$ (appearing as the reciprocal quantity on the left side of (3.2)) and the self-correlations directly across F propagators sum to the complex polarizability (2.16), which accounts for the effect of radiation reaction.

In the screened formulation, (2.1) with (4.2), the corresponding contributions, (5.1) and (5.2), have a similar effect: indeed we shall show that these terms sum to yield the Onsager–Böttcher relation (1.2). We shall find that the small spheres give a cavity-field factor $3m^2/(2m^2+1)$ and the self-correlations directly across $\tilde{\mathsf{F}}$ propagators provide an effective polarizability like (1.3*b*). Thus the use of small spheres and self-correlations may have appeared to be a purely technical artifice but now we see that these terms have actual physical significance. Consequently we shall need to discuss several issues in this section.

First, we must review the model of Onsager and Böttcher in order to identify the concepts it involves at a macroscopic level. These concepts are subsequently used for comparisons at microscopic level. Next we must scrutinize the integral (5.2) in order to give it its proper meaning. Then finally we can demonstrate that the contributions arising from (5.1) and (5.2) sum to a relation of the Onsager–Böttcher form (1.2).

We now briefly describe the macroscopic model of dielectric polarization due to Onsager and Böttcher (see also Böttcher 1973; Böttcher & Bordewijk 1978). Onsager (1936) calculated the local field on a molecule for a model in which a reference molecule is placed at the centre of a spherical cavity of radius $\bar{a}$ in a dielectric continuum of dielectric constant $\epsilon = m^2$. The local field is here the sum of the field $\boldsymbol{E}_{\mathrm{c}}$ in the empty cavity and the reaction field $\boldsymbol{E}_{\mathrm{r}}$ of the dipole which actually is present in the cavity. If the electric field in the medium far from the cavity is uniform and equal to $\boldsymbol{\mathscr{E}}$, and if the actual dipole moment of the reference molecule is denoted by $\boldsymbol{p}$, we then have

$$\boldsymbol{E}_{\mathrm{c}} = \frac{3m^2}{2m^2+1}\boldsymbol{\mathscr{E}}, \tag{5.3}$$

$$\boldsymbol{E}_{\mathrm{r}} = \frac{2}{\bar{a}^3}\frac{m^2-1}{2m^2+1}\boldsymbol{p} = \bar{\mathfrak{s}}\boldsymbol{p}. \tag{5.4}$$

Onsager used the model to treat a polar fluid in which the distinction between the contributions $\boldsymbol{E}_{\mathrm{c}}$ and $\boldsymbol{E}_{\mathrm{r}}$ is essential. Böttcher (1942) applied Onsager's model to a fluid of polarizable nonpolar molecules and by eliminating $\boldsymbol{E}_{\mathrm{c}}$, $\boldsymbol{E}_{\mathrm{r}}$, and $\boldsymbol{p}$ from the equations,

$$\boldsymbol{p} = \alpha(\boldsymbol{E}_{\mathrm{c}}+\boldsymbol{E}_{\mathrm{r}}), \tag{5.5}$$

$$n\boldsymbol{p} = \frac{m^2-1}{4\pi}\boldsymbol{\mathscr{E}}, \tag{5.6}$$

he obtained the relation

$$\left(\frac{m^2-1}{4\pi}\right)\left(\frac{2m^2+1}{3m^2}\right) = n\frac{\alpha}{1-\bar{\mathfrak{s}}\alpha}, \tag{5.7}$$

which we call the Onsager–Böttcher relation. It compares with the complex Lorentz–Lorenz relation (3.2), but the Lorentz internal field is replaced by a cavity field, and the radiation reaction in the complex polarizability is replaced by the Onsager reaction field.

Before we derive (5.7) from the microscopic theory we must discuss (5.2). As it stands, the integral is certainly divergent at the singularity $\boldsymbol{x}' = \boldsymbol{x}$ of $\tilde{\mathsf{F}}(\boldsymbol{x},\boldsymbol{x}';\omega)$. However, by use of (4.10) we may rewrite (5.2) as

$$\bar{\mathfrak{s}}(\omega)\,\mathsf{U} = \int \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\,\delta(\boldsymbol{x}-\boldsymbol{x}')\,\mathrm{d}\boldsymbol{x}' + \frac{m^2-1}{4\pi}\int \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\tilde{\mathsf{F}}(\boldsymbol{x}',\boldsymbol{x};\omega)\,\mathrm{d}\boldsymbol{x}'. \tag{5.8}$$

The first term is the radiation reaction given by (2.14). To evaluate the integral in the second term, we split each of F and $\tilde{\mathsf{F}}$ into longitudinal (Coulomb) and transverse (radiation) parts

$$\mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega) = \nabla\nabla|\boldsymbol{x}-\boldsymbol{x}'|^{-1}+\mathsf{R}(\boldsymbol{x},\boldsymbol{x}';\omega), \tag{5.9a}$$

$$\tilde{\mathsf{F}}(\boldsymbol{x},\boldsymbol{x}';\omega) = m^{-2}\nabla\nabla|\boldsymbol{x}-\boldsymbol{x}'|^{-1}+\tilde{\mathsf{R}}(\boldsymbol{x},\boldsymbol{x}';\omega) \tag{5.9b}$$

and observe that the cross-terms between Coulomb parts and radiation parts in the integral in (5.8) vanish by orthogonality in $\boldsymbol{k}$-space (or $\boldsymbol{h}$-space in the notation of (4.7)). The contribution of the radiation parts can be evaluated by Parseval's theorem. It combines with the radiation reaction from the first term of (5.8) to give a screened radiation reaction (compare with Doniach 1963)

$$\tfrac{2}{3}imk_0^3\,\mathsf{U}. \tag{5.10}$$

The contribution of the Coulomb parts is divergent; but we may write the complete self-interaction (5.8) symbolically as

$$\mathfrak{s} = \tfrac{2}{3}imk_0^3+\frac{2(m^2-1)}{m^2}\int_0^\infty r^{-4}\,\mathrm{d}r. \tag{5.11}$$

The divergence problem arises because $\mathscr{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\cdot\boldsymbol{p}$ describes the average field at $\boldsymbol{x}$ from a dipole $\boldsymbol{p}$ at $\boldsymbol{x}'$, averaged without restriction on the molecular configuration in relation to the two points. But physically only molecular dipoles appear in the theory and all self-interactions are either radiation reaction or self-interactions of a molecule via surrounding molecules. And in such processes the repulsive forces between molecules prevent any surrounding molecule from getting close to the reference molecule and hence prevents divergences like that in (5.11). Thus the divergences are due to the 'probe' character of $\mathscr{F}$ and in the rigorous theory the divergencies must always cancel exactly. It is when the bulk approximation is applied that the trouble is introduced: the replacement of $\mathscr{F}$ by $\tilde{\mathsf{F}}$ evidently destroys the perfect balance of the compensating parts. We therefore see that (4.15) is only a formal series: it contains divergent terms and is presumably divergent as a whole.

On the other hand looking at (5.11) it is plain that it fails to account for the correlations between the reference molecule and its surroundings, namely the fact that any molecule makes itself a 'cavity' into which it prevents other molecules from penetrating. We shall see in §6 how this effect appears naturally in the rigorous theory. But we may here introduce the exclusion effect in (5.11) simply by excluding a spherical region about $\boldsymbol{x}$ from the region of integration. The radius of the excluded region must equal a molecular diameter; we may denote it by $\bar{a}$ as in the macroscopic model. We then get (compare Mead 1960, 1962)

$$\mathfrak{s} = \tfrac{2}{3}imk_0^3+\frac{2}{\bar{a}^3}\,\frac{m^2-1}{3m^2}. \tag{5.12}$$

We see immediately that the second term in (5.12) is almost identical with the coefficient of the Onsager reaction field, in (5.4). The only difference is that the denominator in (5.4), $2m^2+1$, is replaced by $3m^2$ in (5.12).

The result (5.12) confirms that $\mathfrak{s}$ can be regarded as a generalization of the Onsager reaction field, but the molecular diameter $\bar{a}$ is as yet undetermined. The exclusion effect is naturally described in terms of correlations, and the natural way to introduce it in (5.11) is by inserting a pair-correlation function in the integral

$$\tilde{s} = \tfrac{2}{3}\mathrm{i}mk_0^3 + \frac{2(m^2-1)}{m^2}\int_0^\infty r^{-4}g_2(r)\,\mathrm{d}r. \tag{5.13}$$

This expression implicitly defines an effective molecular diameter as

$$\bar{a} = \left[3\int_0^\infty r^{-4}g(r)\,\mathrm{d}r\right]^{-\frac{1}{3}} \tag{5.14}$$

so that (5.13) and (5.14) together give (5.12). We see that $\tilde{s}$ generalizes both the radiation reaction (2.14) and the static Onsager reaction field (5.4). Even so these manipulations of the divergent integral (5.2) are made only to motivate a rigorous microscopic definition of the Onsager reaction field which we give in §6. The final result will not depend on $\tilde{s}$.

For the moment we think of $\tilde{s}$ as defined by (5.13). We now wish to sum all of the (pure) screened Lorentz terms and self-interactions. These come from the terms of the correlation functions Y, which are either constant or contain one or several delta functions each connecting consecutive arguments. The actual summation will be carried out quite easily in what follows by using an integral relation among the appropriate kernels. (See also the simplified argument around (9.1) in the summary of results.) But to exhibit the kind of terms we are dealing with and their origin we first note the contributions from the lowest orders. At orders $p = 2$, 3 and 4 in (4.15) the relevant terms arise from the following terms of the functions Y_{12}, Y_{123}, and Y_{1234}

$$\left.\begin{aligned}&n^{-1}\delta_{12}-1,\\&n^{-2}\delta_{12}\,\delta_{23}-n^{-1}(\delta_{12}+\delta_{23})+2,\\&n^{-3}\delta_{12}\,\delta_{23}\,\delta_{34}-n^{-2}(\delta_{12}\,\delta_{23}+\delta_{12}\,\delta_{34}+\delta_{23}\,\delta_{34})+2n^{-1}(\delta_{12}+\delta_{23}+\delta_{34})-5.\end{aligned}\right\} \tag{5.15}$$

(Note that, for example, the term $n^{-1}\delta_{13}$ from Y_{123} is not included here because the delta function is not directly across any $\tilde{\mathsf{F}}$ propagator.) The terms (5.15) substituted for Y_{12}, Y_{123}, Y_{1234}, ... in the relevant terms of the series (4.15) give rise to the following contributions

$$\left.\begin{aligned}&u+t,\\&u^2+2ut+2t^2,\\&u^3+3u^2t+6ut^2+5t^3,\\&\ldots\ldots\end{aligned}\right\} \tag{5.16}$$

apart from a common factor $n\alpha$. The notation is $u \equiv \tilde{s}\alpha$ and $t \equiv (\frac{4}{3}\pi/m^2)\,n\alpha$.

We now denote by W the sum of all these terms multiplied by the factor $n\alpha$ together with the first term of (4.15*a*), $n\alpha$ itself. We then have

$$(m^2-1)/4\pi = W + C \tag{5.17}$$

in which C denotes what remains from the series (4.15),

$$C = m_2^0(n\alpha)^2 + m_3^0(n\alpha)^3 + C_3\,n^2\alpha^3 + [(16\pi/3m^2)\,n\alpha + 2\tilde{s}\alpha]\,m_2^0(n\alpha)^2 + \ldots, \tag{5.18a}$$

$$m_2^0 = \mathrm{Tr}\int_{-v}\tilde{\mathsf{F}}_{12}\cdot\tilde{\mathsf{T}}_{21}(g_{12}-1)\,\mathrm{d}\boldsymbol{x}_2, \tag{5.18b}$$

$$m_3^0 = \mathrm{Tr}\int_{-v}\int_{-v}\tilde{\mathsf{F}}_{12}\cdot\tilde{\mathsf{F}}_{23}\cdot\tilde{\mathsf{T}}_{31}(g_{123}-g_{12}-g_{23}-g_{31}+2)\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3, \tag{5.18c}$$

$$C_3 = \mathrm{Tr}\int\tilde{\mathsf{F}}_{12}\cdot\tilde{\mathsf{F}}_{21}\cdot\tilde{\mathsf{T}}_{11}(g_{12}-1)\,\mathrm{d}\boldsymbol{x}_2. \tag{5.18d}$$

The notation for the coefficients is the following: the superscript zero signifies principal value integral; the lower case signifies that the self-correlations in M_p are omitted in m_p. Note that C contains contributions of powers of u and t mixed with terms containing correlation functions. Now actually to sum the terms like (5.16) we use (I 4.9),

$$\mathbf{\Lambda}_{10} = \mathbf{Л}_{10} - \int_V \int_V \mathbf{\Lambda}_{12} \cdot \mathscr{F}_{23} \cdot \mathbf{\Lambda}_{30} \, \mathrm{d}x_2 \, \mathrm{d}x_3. \tag{5.19}$$

Now refer to (2.1): we form the expression on the right side there in two different ways by using $\mathbf{\Lambda}_{10}$ from the left side of (5.19) for one way and the expression on the right side of (5.19) for the other. We thus have an identity. We now use the screened expansions (in terms of $\mathscr{F}$) for each kernel and take the bulk approximation (replacing $\mathscr{F}$ by $\tilde{\mathsf{F}}$ and V by all space). Because we have an identity the sums of terms like (5.16) on either side of that identity must be equal. The left side provides W simply. The right side has two terms. In the term derived from the integral in (5.19) the propagator $\mathscr{F}_{23}$ becomes $\tilde{\mathsf{F}}$ in bulk approximation and simply gives a factor $(-\frac{4}{3}\pi/m^2)\,\mathsf{U}$. Then the remaining product of two $\mathbf{\Lambda}$s gives a factor W^2. So the integral in (5.19) ultimately provides $(\frac{4}{3}\pi/m^2)\,W^2$.

The contribution from the term $\mathbf{Л}_{10}$ in (5.19) is more difficult. We offer a proper analysis in the next section so we just sketch the argument here. The polarization propagator $\mathbf{Л}_{10}$ is given explicitly in terms of F by (I 3.13) and this is reproduced in (6.2) below. We evidently need an expansion in terms of $\mathscr{F}$, that is formally in $\tilde{\mathsf{F}}$. However, from the fact that the unscreened expansion (6.2) is recovered from the screened one through expansion of each $\mathscr{F}$ by use of (4.1) we infer from the unscreened expansion (6.2) that a term of $\mathbf{Л}_{10}$ with p propagators $\tilde{\mathsf{F}}$ yields precisely one term, namely $n\alpha\,(\tilde{s}\alpha)^p$. (There cannot arise any other type because the first and last points, x_1 and x_0, are always correlated in any term of $\mathbf{Л}_{10}$.)

The sum of all terms like (5.16) from $\mathbf{Л}_{10}$ together with the term $n\alpha$ is then clearly $n\alpha/(1-\tilde{s}\alpha)$. So from (5.19) we see finally that the sum W of all pure contributions from (5.1) and (5.2) must satisfy

$$W = n\alpha/(1-\tilde{s}\alpha) + (\tfrac{4}{3}\pi/m^2)\,W^2, \tag{5.20a}$$

or

$$W[1-(4\pi/3m^2)\,W] = n\alpha/(1-\tilde{s}\alpha). \tag{5.20b}$$

Now solve (5.17) for W and substitute the result in (5.20b). This yields

$$\left(\frac{m^2-1}{4\pi}\right)\left(\frac{2m^2+1}{3m^2}\right) = n\frac{\alpha}{1-\tilde{s}\alpha} + \frac{m^2+2}{3m^2}C + \frac{4\pi}{3m^2}C^2. \tag{5.21}$$

The formula (5.21) is evidently a generalized form of the Onsager–Böttcher relation. When truncated at the first term on the right it is precisely of the form of (5.7). The left side contains the inverse of the cavity-field factor: the leading term on the right is of the form $n\tilde{\gamma}$ and $\tilde{\gamma}$ is an effective polarizability

$$\tilde{\gamma} = \frac{\alpha}{1-\tilde{s}\alpha}. \tag{5.22}$$

Evidently $\tilde{\gamma}$, in which $\tilde{s}$ has been temporarily interpreted by (5.13), is a natural generalization of both the complex polarizability (2.16) for an isolated molecule and of the static polarizability (1.3b). Thus (5.21) generalizes the Onsager–Böttcher relation by including correction terms in C: these corrections are of order $O((n\alpha)^2)$ because C is. The result (5.21) is then, in a sense to be explained, ‘exact’.

The result (5.21) is actually an exact consequence of the 'bulk appproximation' (4.15) (some of whose terms are exhibited in figure 2 (*f*)). However, it is not usable because the starting point (4.15) is purely formal. As explained, the bulk approximation introduces divergences into the separate terms of the theory. Indeed, recalling that (5.13) was put into the theory 'by hand', a divergence really appears at leading term in (5.21), namely in $n\tilde{\gamma}$, where $\tilde{s}$ is not defined.

To make sense of (5.21) we first show, in §6, that in the exact theory the first term of (5.21), $n\tilde{\gamma}$, is replaced by $n\beta$ with β a well-defined and wholly natural effective polarizability. We also obtain a natural microscopic definition of an Onsager reaction field s and show that in a well defined decorrelation approximation s is related to β as $\bar{s}$ to $\bar{\gamma}$ in the macroscopic theory, (1.3*b*). In this fashion we show how the Onsager–Böttcher relation (1.2) is contained in the microscopic theory. In §7 we shall deal with the higher terms of (5.21). Our general procedure is to use the formal result (5.21) as a guide and as far as is possible replace its right side by appropriate expressions in terms of β, because β does not involve the bulk approximation.

6. Effective polarizability

In the previous section the generalized Onsager–Böttcher relation (5.21) was derived through the identity based on (5.19): the effective polarizability $\tilde{\gamma}$, (5.22), arose from the term $\mathcal{J}_{10}$ in (5.19). The result was formal because the reaction field $\tilde{s}$ was not well defined, though (5.13) was used to show what sort of expression it surely ought to be.

Fortunately, the kernel $\mathcal{J}_{10}$ in (5.19) does actually contain a microscopic expression for an effective polarizability with all the physical properties we expect from such a quantity. However, to see this we must analyse the *unscreened* expressions (I 3.12) and (I 3.13) for $\mathcal{J}^{\text{in}}_{10}$ and $\mathcal{J}_{10}$, namely

$$\mathcal{J}^{\text{in}}_{10} = n^{\text{in}}_1 \alpha \mathsf{U}\delta_{10} + \sum_{p=1}^{\infty} \alpha^{p+1} \int_V \ldots \int_V \mathsf{F}_{12}\cdot\mathsf{F}_{23}\ldots\mathsf{F}_{p0}\, n^{\text{in}}_1 n^{\text{in}}_2 \ldots n^{\text{in}}_p n^{\text{in}}_0 \,\mathrm{d}\boldsymbol{x}_2 \ldots \mathrm{d}\boldsymbol{x}_p, \tag{6.1}$$

$$\mathcal{J}_{10} = n\alpha \mathsf{U}\delta_{10} + \sum_{p=1}^{\infty} (n\alpha)^{p+1} \int_V \ldots \int_V \mathsf{F}_{12}\cdot\mathsf{F}_{23}\ldots\mathsf{F}_{p0}\, G_{123\ldots p0} \,\mathrm{d}\boldsymbol{x}_2 \ldots \mathrm{d}\boldsymbol{x}_p. \tag{6.2}$$

The polarization kernel $\mathcal{J}^{\text{in}}$ applies to an instantaneous configuration $\{\boldsymbol{x}^{\text{in}}_j\}$ of the molecular system with molecules at sites $\boldsymbol{x}^{\text{in}}_j, j = 1, 2, \ldots, N$, for N molecules, and

$$n^{\text{in}}(\boldsymbol{x}) = \sum_j \delta(\boldsymbol{x} - \boldsymbol{x}^{\text{in}}_j) \tag{6.3}$$

is the instantaneous density of molecules. The kernel $\mathcal{J}^{\text{in}}$ gives the polarization induced in the many-body system in response to an external field $\boldsymbol{E}(\boldsymbol{x}, \omega)$ as the linear relation (I 2.31),

$$\boldsymbol{P}^{\text{in}}(\boldsymbol{x}, \omega) = \int_V \mathcal{J}^{\text{in}}(\boldsymbol{x}, \boldsymbol{x}'; \omega)\cdot \boldsymbol{E}(\boldsymbol{x}', \omega)\,\mathrm{d}\boldsymbol{x}'. \tag{6.4}$$

The kernel $\mathcal{J}$ is the average value of $\mathcal{J}^{\text{in}}$ and, evidently, it determines the average polarization induced in response to $\boldsymbol{E}$.

We now *define* the effective polarizability of a given molecule in the many-body system in fixed configuration as the coefficient in a linear relation that determines the dipole moment induced in a molecule as a result of an external field acting on that molecule. In this definition the external field is applied only to the chosen molecule. Note, nevertheless, that this 'external field' may still embrace effects of other molecules: in the macropscopic model it is exactly in this sense that the cavity field acts as an external field to the reference molecule.

To obtain the effective polarizability of a molecule at $x_j^{\rm in}$ from (6.1) we simply omit $n_1^{\rm in}$, $n_0^{\rm in}$, and δ_{10}, and set $x_1 = x_0 = x_j^{\rm in}$. These changes ensure that an applied field acts on the molecule at $x_j^{\rm in}$ and that the result is the polarization of that same molecule. The result can be written

$$\beta_{\rm j}^{\rm in}(\omega) = \alpha(\omega)\,\mathsf{U} + \alpha^2(\omega)\,\mathscr{F}^{\rm in}(x_j^{\rm in}, x_j^{\rm in};\omega) \tag{6.5}$$

in terms of the screened propagator for the system in an instantaneous state, defined by (I 4.1),

$$\mathscr{F}^{\rm in}_{10} = \mathsf{F}_{10} + \int_V\int_V \mathsf{F}_{12}\cdot\mathbf{\Pi}^{\rm in}_{23}\cdot\mathscr{F}^{\rm in}_{30}\,{\rm d}x_2\,{\rm d}x_3 \tag{6.6a}$$

and given explicitly by the iterative solution,

$$\mathscr{F}^{\rm in}_{10} = \sum_{p=1}^{\infty} \alpha^{p-1}\int_V\cdots\int_V \mathsf{F}_{12}\cdot\mathsf{F}_{23}\cdots\mathsf{F}_{p0}\,n_2^{\rm in}\,n_3^{\rm in}\cdots n_{\rm p}^{\rm in}\,{\rm d}x_2\cdots{\rm d}x_p. \tag{6.6b}$$

The first term of the sum in (6.6*b*) is F_{10} by definition. Plainly, the average value of $\mathscr{F}^{\rm in}_{10}$ is $\mathscr{F}_{10}$ as given by (4.1). The kernel $\mathbf{\Pi}^{\rm in}$ in (6.6*a*) is defined by $\mathbf{\Pi}^{\rm in}_{10} = n_1^{\rm in}\,\alpha\mathsf{U}\delta_{10}$ (see (I 2.30)) and so it is essentially a polarizability density (because it is strictly local).

It is now natural to define the effective polarizability of a molecule at an arbitrary point x as

$$\beta^{\rm in}(x,\omega) = n^{-1}\sum_j \beta_j^{\rm in}(\omega)\,\delta(x - x_j^{\rm in}) \tag{6.7}$$

and we may then express $\mathfrak{P}^{\rm in}$ in terms of $\beta^{\rm in}(x,\omega)$ as

$$\mathfrak{P}^{\rm in}(x,x';\omega) = n\beta^{\rm in}(x,\omega)\,\delta(x-x') + \alpha^2\mathscr{F}^{\rm in}(x,x';\omega)\sum_j\sum_{i\neq j}\delta(x-x_j^{\rm in})\,\delta(x'-x_i^{\rm in}). \tag{6.8}$$

This result shows that $\beta^{\rm in}$ is essentially the sum of all those terms of $\mathfrak{P}^{\rm in}_{10}$ which have a self-correlation connecting x_1 and x_0 plus the polarizability of an isolated molecule (contained in the first term of $\mathfrak{P}^{\rm in}_{10}$). The higher terms of $\beta^{\rm in}$ correct the polarizability for all interactions of a molecule with itself via surrounding molecules or through empty space (radiation reaction).

From (6.7) we finally obtain the average effective polarizability of a molecule at x as

$$\beta(x,\omega) = \langle\beta^{\rm in}(x,\omega)\rangle = n^{-1}\langle\sum_j \beta_j^{\rm in}(\omega)\,\delta(x-x_j^{\rm in})\rangle \tag{6.9a}$$

or explicitly

$$\beta(x_1,\omega) = \alpha\mathsf{U} + \alpha^2\sum_{q=1}^{\infty}(n\alpha)^{q-1}\int_V\cdots\int_V \mathsf{F}_{12}\cdot\mathsf{F}_{23}\cdots\mathsf{F}_{q1}\,G_{123\ldots q}\,{\rm d}x_2\cdots{\rm d}x_q. \tag{6.9b}$$

This is now the quantity we shall normally refer to as the 'effective polarizability': it is well defined and owes nothing to the bulk approximation: the first term of the sum multiplying α^2 is $\mathsf{F}_{11} = \frac{2}{3}{\rm i}k_0^3\,\mathsf{U}$.

We shall now find it instructive to introduce a microscopic expression for a reaction field of Onsager's type, although the result will not figure as such in our final expressions in §7. The objective is to find the relation between the reaction field and the effective polarizability, and in particular to see whether the macroscopic relation (1.3*b*) applies. The result will help us in assessing the validity of the macroscopic models introduced in §1, which is one purpose of the paper.

To define such a reaction field we have to analyse the instantaneous situation and (6.7) still further. It may be helpful therefore if we first consider the expansion of the macroscopic expression (1.3*b*) namely

$$\alpha/(1-\bar{s}\alpha) = \alpha+\alpha^2\bar{s}+\alpha^3\bar{s}^2+\ldots \tag{6.10}$$

in the context of the macroscopic model. From (5.4) and (5.5) we may write the dipole moment induced in the reference molecule

$$\boldsymbol{p} = \frac{\alpha}{1-\bar{s}\alpha}\boldsymbol{E}_{\mathrm{c}} = (\alpha+\alpha^2\bar{s}+\alpha^3\bar{s}^2+\ldots)\cdot\boldsymbol{E}_{\mathrm{c}}. \tag{6.11}$$

Equation (6.11) states that the dipole moment induced in the reference molecule equals the effective polarizability times the cavity field. Note that $\boldsymbol{E}_{\mathrm{c}}$ is the field in the empty cavity so it may be said to act as an external field on the reference molecule (compare the remarks surrounding the definition of the effective polarizability below (6.4)).

We may think of the polarization of the reference molecule according to (6.11) as taking place in stages. First there is the direct effect of the cavity field on the molecule which produces a dipole $\alpha\boldsymbol{E}_{\mathrm{c}}$. This dipole creates a field which polarizes the surrounding dielectric, and this polarization in turn gives rise to a field $\bar{s}\alpha\boldsymbol{E}_{\mathrm{c}}$ on the molecule, the reaction field of the initial dipole $\alpha\boldsymbol{E}_{\mathrm{c}}$. This reaction field $\bar{s}\alpha\boldsymbol{E}_{\mathrm{c}}$ induces an additional dipole moment $\alpha\bar{s}\alpha\boldsymbol{E}_{\mathrm{c}} = \alpha^2\bar{s}\boldsymbol{E}_{\mathrm{c}}$ in the molecule. But this additional dipole creates its own additional reaction field $\bar{s}\alpha\bar{s}\alpha\boldsymbol{E}_{\mathrm{c}}$ on the reference molecule which leads to yet an additional dipole moment, $\alpha^3\bar{s}^2\boldsymbol{E}_{\mathrm{c}}$. This sequence of processes sums to the closed form given in (6.11) which contains the effective polarizability.

Note that $\bar{s}$ may be said to describe the reaction field of a *fixed* oscillatory molecular dipole. Indeed, the idea of a reaction field was conceived by Onsager for the static equivalent of this dipole in a theory of the dielectric constant for polar molecules. When a fixed molecular dipole is replaced by a *polarizable* reference molecule the reaction field acts as a positive feedback enhancing the polarization of the molecule, and this mechanism gives rise to the concept of an effective polarizability.

The series in (6.10) for the effective polarizability is actually more in the spirit of the molecular description than is the closed form to which it sums: we now show that (6.5) contains a series expression of the same form.

In the processes involved in the effective polarizability, it is apparently important to distinguish the selected molecule from all the molecules that surround it. We therefore write the instantaneous density (6.3) as a sum of two terms:

$$n^{\mathrm{in}}(\boldsymbol{x}) = n_j^{\mathrm{in}}(\boldsymbol{x})+n_J^{\mathrm{in}}(\boldsymbol{x}), \tag{6.12a}$$

$$n_j^{\mathrm{in}}(\boldsymbol{x}) = \delta(\boldsymbol{x}-\boldsymbol{x}_j^{\mathrm{in}}), \quad n_J^{\mathrm{in}}(\boldsymbol{x}) = \sum_{i\neq j}\delta(\boldsymbol{x}-\boldsymbol{x}_i^{\mathrm{in}}). \tag{6.12b}$$

Thus, $n_J^{\mathrm{in}}(\boldsymbol{x})$ represents the density of molecules when the molecule at $\boldsymbol{x}_J^{\mathrm{in}}$ has been removed, whereas $n_j^{\mathrm{in}}(\boldsymbol{x})$ is the molecular density of a system consisting of the isolated reference molecule.

We shall also need to split the kernel $\mathbf{\Pi}^{\mathrm{in}}$ similarly:

$$\mathbf{\Pi}^{\mathrm{in}}(\boldsymbol{x},\boldsymbol{x}';\omega) = \mathbf{\Pi}_j^{\mathrm{in}}(\boldsymbol{x},\boldsymbol{x}';\omega)+\mathbf{\Pi}_J^{\mathrm{in}}(\boldsymbol{x},\boldsymbol{x}';\omega); \tag{6.13a}$$

$$\mathbf{\Pi}_j^{\mathrm{in}}(\boldsymbol{x},\boldsymbol{x}';\omega) = n_j^{\mathrm{in}}(\boldsymbol{x})\,\alpha(\omega)\,\mathsf{U}\delta(\boldsymbol{x}-\boldsymbol{x}'), \tag{6.13b}$$

$$\mathbf{\Pi}_J^{\mathrm{in}}(\boldsymbol{x},\boldsymbol{x}';\omega) = n_J^{\mathrm{in}}(\boldsymbol{x})\,\alpha(\omega)\,\mathsf{U}\delta(\boldsymbol{x}-\boldsymbol{x}'). \tag{6.13c}$$

Further, we introduce a propagator $\mathscr{F}_J^{\text{in}}$ for the system in fixed configuration with the molecule at $\boldsymbol{x}_j^{\text{in}}$ removed. Comparison with (6.6*a*) for $\mathscr{F}^{\text{in}}$ shows that $\mathscr{F}_J^{\text{in}}$ must satisfy the integral equation

$$\mathscr{F}_J^{\text{in}}(\boldsymbol{x},\boldsymbol{x}';\omega) = \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)+\int_V\int_V \mathsf{F}(\boldsymbol{x},\boldsymbol{x}'';\omega)\cdot\boldsymbol{\Pi}_J^{\text{in}}(\boldsymbol{x}'',\boldsymbol{x}''';\omega)\cdot\mathscr{F}_J^{\text{in}}(\boldsymbol{x}''',\boldsymbol{x}';\omega)\,\mathrm{d}\boldsymbol{x}''\,\mathrm{d}\boldsymbol{x}'''. \tag{6.14}$$

It is related to $\mathscr{F}^{\text{in}}$ by the integral equation

$$\begin{aligned}\mathscr{F}^{\text{in}}(\boldsymbol{x},\boldsymbol{x}';\omega) &= \mathscr{F}_J^{\text{in}}(\boldsymbol{x},\boldsymbol{x}';\omega)\\ &\quad+\int_V\int_V \mathscr{F}_J^{\text{in}}(\boldsymbol{x},\boldsymbol{x}'';\omega)\cdot\boldsymbol{\Pi}_j^{\text{in}}(\boldsymbol{x}'',\boldsymbol{x}''';\omega)\cdot\mathscr{F}^{\text{in}}(\boldsymbol{x}''',\boldsymbol{x}';\omega)\,\mathrm{d}\boldsymbol{x}''\,\mathrm{d}\boldsymbol{x}'''.\end{aligned} \tag{6.15}$$

To prove (6.15), substitute the right side of (6.14) for $\mathscr{F}_J^{\text{in}}$ in (6.15) and reduce the resulting equation by use of (6.15) itself. By combining the terms $\boldsymbol{\Pi}_j^{\text{in}}$ and $\boldsymbol{\Pi}_J^{\text{in}}$ by means of (6.13*a*) we then see that $\mathscr{F}^{\text{in}}$ as defined by (6.15) with (6.14) satisfies (6.6*a*), which can be assumed to have a unique solution.

We now *define* the instantaneous reaction field coefficient of a molecule at $\boldsymbol{x}_j^{\text{in}}$ as

$$\varsigma_j^{\text{in}}(\omega) = \mathscr{F}_J^{\text{in}}(\boldsymbol{x}_j^{\text{in}},\boldsymbol{x}_j^{\text{in}};\omega). \tag{6.16}$$

From this we may then define an average reaction field coefficient for a molecule at an arbitrary point $\boldsymbol{x}$ corresponding to $\bar{\varsigma}$ in the Onsager–Böttcher model as

$$\varsigma(\boldsymbol{x},\omega) = n^{-1}\langle\sum_j \varsigma_j^{\text{in}}(\omega)\,\delta(\boldsymbol{x}-\boldsymbol{x}_j^{\text{in}})\rangle \tag{6.17a}$$

or explicitly, from the iterative solution of (6.14),

$$\varsigma(\boldsymbol{x}_1,\omega) = \sum_{q=1}^{\infty}(n\alpha)^{q-1}\int_V\cdots\int_V \mathsf{F}_{12}\cdot\mathsf{F}_{23}\ldots\mathsf{F}_{q1}\,G_{1;23\ldots q}\,\mathrm{d}\boldsymbol{x}_2\ldots\mathrm{d}\boldsymbol{x}_q \tag{6.17b}$$

in which the first term is $\mathsf{F}_{11} = \frac{2}{3}ik_0^3\,\mathsf{U}$. Thus, $\varsigma(\boldsymbol{x},\omega)\cdot\boldsymbol{p}$ is the average reaction field of a *molecular* dipole $\boldsymbol{p}$ at $\boldsymbol{x}$. The correlation function $G_{1;23\ldots q}$ is defined by

$$G_{1;23\ldots q} = n^{-q}\langle\sum_j\delta(\boldsymbol{x}_1-\boldsymbol{x}_j^{\text{in}})\sum_{k\neq j}\delta(\boldsymbol{x}_2-\boldsymbol{x}_k^{\text{in}})\ldots\sum_{l\neq j}\delta(\boldsymbol{x}_q-\boldsymbol{x}_l^{\text{in}})\rangle. \tag{6.17c}$$

It can be obtained from the distribution function $G_{123\ldots q}$ which appears in (6.9*b*) for $\boldsymbol{\beta}$ by omitting those self-correlations that connect the point $\boldsymbol{x}_1$ with any of the other points $\boldsymbol{x}_2, \boldsymbol{x}_3, \ldots, \boldsymbol{x}_q$.

It is important to realize that ς does not include all self-interactions of a molecular dipole. Classically, it may be thought of as representing the self-interaction of a fixed, oscillatory, molecular dipole, a generalization of the self-interaction of the permanent, static, molecular dipole considered by Onsager. Although the generalization is not easily realized physically it is important for understanding the macroscopic model.

We now show how the effective molecular polarizability $\boldsymbol{\beta}$ (which contains *all* self-interactions) can almost be expressed in terms of ς. By substituting (6.15) in (6.5) and using (6.5) in the result we get

$$\begin{aligned}\boldsymbol{\beta}_j^{\text{in}} &= \alpha\mathsf{U}+\alpha^2[\varsigma_j^{\text{in}}+\alpha^{-1}\varsigma_j^{\text{in}}\cdot(\boldsymbol{\beta}_j^{\text{in}}-\alpha\mathsf{U})]\\ &= \alpha\mathsf{U}+\alpha\varsigma_j^{\text{in}}\cdot\boldsymbol{\beta}_j^{\text{in}}.\end{aligned} \tag{6.18}$$

Equation (6.18) can be solved for $\boldsymbol{\beta}_j^{\text{in}}$ to give

$$\boldsymbol{\beta}_j^{\text{in}}(\omega) = \alpha(\omega)\,[\mathsf{U} - \boldsymbol{\sigma}_j^{\text{in}}(\omega)\,\alpha(\omega)]^{-1}. \tag{6.19}$$

The result (6.19) has the form of the macroscopic Böttcher polarizability (1.3*b*), but it applies to an instantaneous situation. We wish to obtain a corresponding relation between the average values $\boldsymbol{\beta}$ and $\boldsymbol{\sigma}$.

We first note that $\boldsymbol{\beta}(\boldsymbol{x},\omega)$ and $\boldsymbol{\sigma}(\boldsymbol{x},\omega)$ are actually surface dependent and may depend on the position of the point $\boldsymbol{x}$ in relation to the surface of the region V containing the molecular system. This surface dependence may be said to be inherited from the propagator $\mathscr{F}$ (although the average of $\mathscr{F}^{\text{in}}$ does not appear as such in $\boldsymbol{\beta}$ or $\boldsymbol{\sigma}$). We therefore understand the surface effect of $\boldsymbol{\beta}$ and $\boldsymbol{\sigma}$ qualitatively in terms of 'reflected waves' from the analysis of $\mathscr{F}$ and its approximation $\tilde{\mathsf{F}}_V$ in §4. Physically it is quite natural that the reaction field from an oscillatory molecular dipole in a *finite* many-body system must contain waves reflected in the surface; but the situation differs from the one discussed in §4 because we consider the radiation from a *molecular* dipole here, and we cannot expect any simple macroscopic approximation to apply in detail. The important point is, however, that we almost certainly can neglect the surface effects of $\boldsymbol{\beta}(\boldsymbol{x},\omega)$ and $\boldsymbol{\sigma}(\boldsymbol{x},\omega)$ for all points $\boldsymbol{x}$ well away from the surface of V.

When this condition applies $\boldsymbol{\beta}(\boldsymbol{x},\omega)$ and $\boldsymbol{\sigma}(\boldsymbol{x},\omega)$ must therefore be isotropic tensors, independent of $\boldsymbol{x}$, to a good approximation. We expect from the analysis near (I 6.30) that we need only exclude a surface layer of a few wavelengths thickness, and this is negligible in volume in comparison with $|V|$ except for extraordinary geometries. We may therefore define $\boldsymbol{x}$-independent scalar quantities $\beta(\omega)$ and $\sigma(\omega)$† by averaging over the region V and over directions. These quantities depend formally on the shape of V, but numerically the dependence is negligible. We therefore have

$$\boldsymbol{\beta}(\boldsymbol{x},\omega) \approx \beta(\omega)\,\mathsf{U}, \quad \beta(\omega) = \tfrac{1}{3}|V|^{-1}\operatorname{Tr}\int_V \boldsymbol{\beta}(\boldsymbol{x},\omega)\,\mathrm{d}\boldsymbol{x}, \tag{6.20a}$$

$$\boldsymbol{\sigma}(\boldsymbol{x},\omega) \approx \sigma(\omega)\,\mathsf{U}, \quad \sigma(\omega) = \tfrac{1}{3}|V|^{-1}\operatorname{Tr}\int_V \boldsymbol{\sigma}(\boldsymbol{x},\omega)\,\mathrm{d}\boldsymbol{x}. \tag{6.20b}$$

We now come to the question of whether there exists a relation between the averaged quantities (6.20) which is like (6.19) for the instantaneous ones. We therefore try

$$\beta \approx \frac{\alpha}{1-\sigma\alpha} = \sum_{p=0}^{\infty} \alpha^{p+1}\sigma^{p} \tag{6.21}$$

as an approximation. To assess this approximation we expand the right side of (6.19) and substitute the series into the expression (6.9*a*) for $\boldsymbol{\beta}$. The result is the expansion

$$\boldsymbol{\beta}(\boldsymbol{x},\omega) = \sum_{p=0}^{\infty} \alpha^{p+1}(\omega)\,\langle \boldsymbol{\sigma}^{\text{in}\,p}(\boldsymbol{x},\omega)\rangle, \tag{6.22a}$$

in which

$$\langle \boldsymbol{\sigma}^{\text{in}\,p}(\boldsymbol{x},\omega)\rangle = n^{-1}\langle \sum_j [\boldsymbol{\sigma}_j^{\text{in}}(\omega)]^p\,\delta(\boldsymbol{x}-\boldsymbol{x}_j^{\text{in}})\rangle. \tag{6.22b}$$

The terms of the expansion (6.22*a*) are shown in diagrammatic notation in figure 3 (*a–d*) apart from a trivial factor. We see that $\langle \boldsymbol{\sigma}^{\text{in}\,p}(\boldsymbol{x},\omega)\rangle$ is represented by the series of all diagrams with precisely p closed loops of chains of propagators emerging from the common first and last

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† The typeface distinguishes scalar (σ) and tensor ($\boldsymbol{\sigma}$); it is also clear which is which from the context.

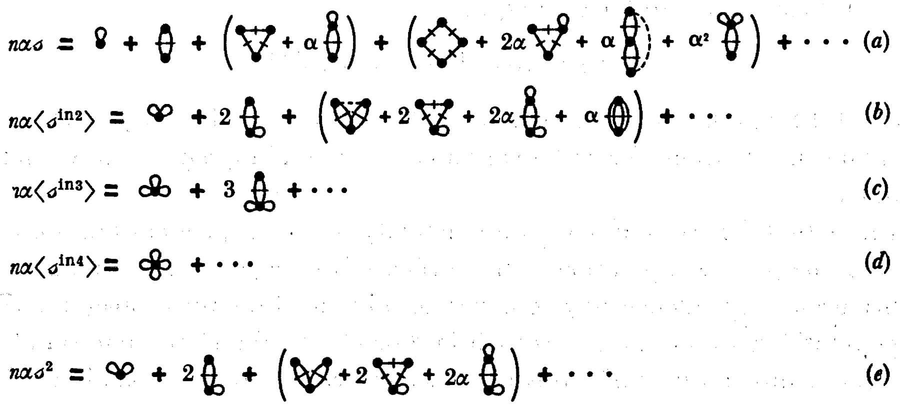

FIGURE 3. (*a*)–(*d*) Self-interactions contained in the effective polarizability β, as given by (6.22). (*e*) The term in σ^2 from the expansion of the approximate form (6.21) to be compared with the corresponding term of the exact expansion of β shown in (*b*).

point representing the reference molecule. In particular, $\sigma(\boldsymbol{x}, \omega) = \langle \sigma^{\mathrm{in}}(\boldsymbol{x}, \omega) \rangle$ is the sum of all diagrams with precisely one such closed loop. It is plain that the approximation (6.21) must involve a decorrelation in which, broadly, the average of a power of $\sigma^{\mathrm{in}}(\boldsymbol{x}, \omega)$ is replaced by the power of the average of $\sigma^{\mathrm{in}}(\boldsymbol{x}, \omega)$.

We can see an example of this decorrelation approximation by comparing, for example, $\langle \sigma^{\mathrm{in}2}(\boldsymbol{x}, \omega) \rangle$ and $\langle \sigma^{\mathrm{in}}(\boldsymbol{x}, \omega) \rangle^2$, given in (*b*) and (*e*) of figure 3. The similarity of structure is obvious, but we note a significant difference in the terms with four propagators: the three-body distribution function in the term with two 'two-body loops' in (*b*) is replaced by a product of two pair-distribution functions in (*e*). Moreover, the last term shown in (*b*) appears to be completely absent in (*e*). The approximation (6.21) can thus be characterized succinctly as the neglect of all correlations between different closed loops. (Note that the last term of (*b*) has four propagators F not two $\mathscr{F}$s.)

A more physical interpretation of (6.22) will make the meaning of this result clear. The polarization of a molecule in a many-body system may be viewed as a sequence of more elementary processes precisely as in the discussion of the macroscopic relation (6.11). First there is a direct polarization of the reference molecule, as described by the polarizability α. The field of the resulting dipole polarizes the surrounding molecules, and this results in a field on the reference molecule, the reaction field of the dipole. This reaction field polarizes the reference molecule further, and the additional dipole moment in turn gives rise to an additional reaction field via surrounding molecules etc. For a molecule at $\boldsymbol{x}$ in a many-body system in fixed configuration, this sequence of processes is described correctly by the expansion of the right side of (6.19) or by the closed form (6.19) itself.

When we take the average value to obtain $\beta(\boldsymbol{x}, \omega)$ we observe that two surrounding molecules participating in two elementary self-interactions of the reference molecule are correlated; for example, they cannot come arbitary close to each other. Actually, they need not be distinct: one molecule may participate in several elementary self-interactions. This situation may also be described as a consequence of correlation, namely self-correlation. This correlation explains why the average effective polarizability cannot rigorously be expressed in terms of an average reaction field, as the macroscopic model of Onsager and Böttcher supposes. We discuss the implications of this observation in §8.

We introduced the average reaction field $\mathscr{s}$, (6.17 *a*, *b*) with (6.20 *b*), because of its importance in macroscopic theory and because it has enabled us to show that the effective polarizability β, defined through (6.9 *a*, *b*) and (6.20 *a*) 'makes sense'. For β is defined naturally in terms of a dipole moment induced by an external field on a molecule; it contains corrections for all self-interactions; and in a well defined decorrelation approximation it can be expressed in terms of $\mathscr{s}$ in the way that macroscopic theory suggests.

Nevertheless, the most important fact about $\beta(\omega)$ is that $\boldsymbol{\beta}(\boldsymbol{x}, \omega)$ is actually contained as such in $\mathfrak{M}$ as the average of (6.8) shows; it is therefore contained term by term in $\mathbf{\Lambda}$ and so by (2.1), $\beta(\omega)$ is contained term by term in $\frac{1}{4}(m^2-1)/\pi$ (to neglect of any surface dependent anisotropy). It is also exact and owes nothing to bulk approximation. Thus we can use it as a part of our programme of transforming the formal result (5.21) into a well defined expression.

Now it is already plain what went wrong in the derivation of the Onsager–Böttcher relation in §5, and how $\beta(\omega)$ should be used in (5.21). The formal polarizability $\tilde{\gamma} = \alpha/(1-\tilde{s}\alpha)$ in (5.21) derived from $\mathfrak{M}$ in (5.19) simply failed to include all of the self-interactions contained in $\mathfrak{M}$ and the missing ones remain in the term C. Thus β, which contains all self-interactions in which a chain of $\tilde{\mathrm{F}}$ propagators begins and ends at the same point, has to replace $\tilde{\gamma}$ in (5.21) and the corresponding self-interactions must then be omitted from C. Thus terms like C_3, (5.18 *d*), are to be omitted from the series expression (5.18 *a*) for C. Indeed, because β contains all self-interactions in which a chain of $\tilde{\mathrm{F}}$ propagators begins and ends at the same point and contains no other terms, all such terms but only these must be omitted from C: C will therefore still contain self-interactions without this property and will need further correction a programme which is carried out in part in the next §7.

We now have the result

$$\left(\frac{m^2-1}{4\pi}\right)\left(\frac{2m^2+1}{3m^2}\right) = n\beta + \frac{m^2+2}{3m^2}C' + \frac{4\pi}{3m^2}C'^2 \tag{6.23}$$

instead of (5.21). The $n\beta$ is exact, and the prime on C reminds that self-interactions are removed from it by the procedure just described: C' is exact in the formal sense that it contains all the terms now remaining in the bulk approximation once the self-interactions are removed.

This way we can account completely for the simple Onsager–Böttcher relation (5.7) by dropping the terms in C'. Then

$$\left(\frac{m^2-1}{4\pi}\right)\left(\frac{2m^2+1}{3m^2}\right) = n\beta. \tag{6.24}$$

Expressed in terms of orders of small parameters this step is justified only to neglect of $O((n\alpha)^2)$. On the other hand $n\beta$ sums an infinity of two-body terms of order $O((n\alpha)^2)$ (including all odd orders in a small parameter α/a^3, where a is some effective molecular diameter). Similarly, $n\beta$ sums infinite classes of three-body terms, four-body terms, etc. which are $O((n\alpha)^3)$, $O((n\alpha)^4)$, etc. For the real part of the refractive index the first significant correction to (6.24) comes at order $O((n\alpha)^2) \times O((\alpha/a^3)^2)$ provided the correlation length is small compared to the wavelength (neglecting terms of relative order of magnitude $O((k_0 l)^2)$).

In the next section, §7 we shall show we can improve on (6.24) to some extent. We are able to take a partial account of the additional terms contained in (6.23). But to do it we are obliged to make a decorrelation approximation comparable to that for (6.21). We then correct this in part by taking account of the more important terms still remaining.

7. GENERALIZED ONSAGER–BÖTTCHER RELATION

To extend (6.24) we work from (4.15), and first sum *all* terms involving $\tilde{s}$ including those depending on intermolecular correlations; we show that we may rewrite (4.15) as

$$\frac{m^2-1}{4\pi} = \sum_{p=1}^{\infty} m_p(n\tilde{\gamma})^p + Q, \tag{7.1a}$$

$$m_p = \mathrm{Tr}\int\dots\int \tilde{\mathsf{F}}_{12}\cdot\tilde{\mathsf{F}}_{23}\dots\tilde{\mathsf{F}}_{(p-1)\,p}\cdot\tilde{\mathsf{I}}_{p1}\,y_{123\dots p}\,\mathrm{d}\boldsymbol{x}_2\dots\mathrm{d}\boldsymbol{x}_p. \tag{7.1b}$$

Here $\tilde{\gamma}$ is the (formal) effective polarizability (5.22), and $y_{123\dots p}$ is the ordinary correlation function, which can be derived from the generalized function $Y_{123\dots p}$ by omitting all self-correlations (terms containing one or more delta functions). It is given by (4.3*a*) when the generalized Ursell functions are replaced by the ordinary ones. In (7.1*a*) the term Q is the sum of all terms of the series in (4.15) with at least one delta function not directly across a propagator $\tilde{\mathsf{F}}$. (There is of course a degree of freedom in writing products of delta functions because, for example, $\delta_{12}\delta_{23} = \delta_{12}\delta_{13}$. But it is to be understood that if a set of points are 'covered' by a product of delta functions these must be written in such a way that each delta function connects consecutive points of the set with the ordering determined by the chain of propagators.)

To prove (7.1) we first derive a relation showing how the Y functions behave when two consecutive points approach each other,

$$Y_{123\dots p} = n^{-1}\delta(\boldsymbol{x}_j-\boldsymbol{x}_{j-1})\,Y_{123\dots(j-1)\,(j+1)\dots p}+Z^{(j)}_{123\dots p} \tag{7.2}$$

in which the function $Z^{(j)}_{123\dots p}$ is continuous at $\boldsymbol{x}_{j-1}$ as a function of $\boldsymbol{x}_j$. The generalized distribution function $G_{123\dots p}$ satisfies a relation similar to (7.2) in which the corresponding G functions replace the Y functions and Z is replaced by another function with the same continuity property. The relation (7.2) can now be proved by induction from a recurrence relation for the Y functions in terms of the G functions, equation (4.2) of Hynne (1975). (Note that a p-body correlation function there is printed in script fount because it contains an additional factor n^p.)

From (7.2) we infer that $Y_{123\dots p}$ contains a term with q delta functions, each connecting a pair of consecutive points at 'positions' $j_1, j_2, \dots, j_q$ and no other delta functions, and that the term has the form

$$n^{-q}\delta_{j_1(j_1-1)}\,\delta_{j_2(j_2-1)}\cdots\delta_{j_q(j_q-1)}\,y_{12\dots(j_s-1)\,(j_s+1)\dots p}. \tag{7.3}$$

Here the function y depends on the points $\boldsymbol{x}_1, \boldsymbol{x}_2, \dots, \boldsymbol{x}_p$ with $\boldsymbol{x}_{j_1}, \boldsymbol{x}_{j_2}, \dots, \boldsymbol{x}_{j_q}$ omitted; and $Y_{123\dots p}$ contains no other term with precisely the same set of delta functions.

By using the result (7.3) we may now write the coefficient M_p of the series (4.15) as

$$M_p = \sum_{q=0}^{p-1}\binom{p-1}{q} m_{p-q}\,n^{-q}\,\tilde{s}^q + Q_p \tag{7.4}$$

in which Q_p is the sum of all contributions coming from terms of $Y_{123\dots p}$ with at least one delta function not connecting consecutive points. The binomial coefficient in (7.4) arises because we get the same term irrespective of which set of q out of $p-1$ propagators $\tilde{\mathsf{F}}$ is covered by delta functions (and yielding factors $\tilde{s}$ through (5.2)).

By substituting the result (7.4) in (4.15*a*) and defining

$$Q = \sum_{p=1}^{\infty} Q_p(n\alpha)^p \tag{7.5}$$

we get
$$\frac{m^2-1}{4\pi}=\sum_{p=1}^{\infty}(n\alpha)^p\sum_{q=0}^{p-1}\binom{p-1}{q}m_{p-q}\,n^{-q}\,\tilde{\zeta}^q+Q. \tag{7.6}$$

We may rearrange the double sum in (7.6) as a sum over q with $p-q$ fixed followed by a sum over $p-q$. If we rename $p-q$ as p we then obtain

$$\begin{aligned}\frac{m^2-1}{4\pi}&=\sum_{p=1}^{\infty}m_p(n\alpha)^p\sum_{q=0}^{\infty}\binom{p+q-1}{q}(\tilde{\zeta}\alpha)^q+Q\\&=\sum_{p=1}^{\infty}m_p\left(\frac{n\alpha}{1-\tilde{\zeta}\alpha}\right)^p+Q,\end{aligned} \tag{7.7}$$

which proves (7.1) with $\tilde{\gamma}$ defined by (5.22). For the second equality of (7.7) we have used the identity

$$\binom{p+q-1}{q}=(-1)^q\binom{-p}{q}. \tag{7.8}$$

The argument of §5 now brings (7.7) into the Onsager–Böttcher form; for the sum of all pure screened Lorentz terms of the series (7.7) is precisely the W introduced at (5.17) because the self-interactions arising from (5.2) are already summed in $\tilde{\gamma}$. We may therefore write (7.7) as

$$\frac{m^2-1}{4\pi}=W+C^0+Q \tag{7.9}$$

in which C^0 is the series from (7.1) with the pure Lorentz terms omitted,

$$C^0=m_2^0(n\tilde{\gamma})^2+[m_3^0+(16\pi/3m^2)\,m_2^0]\,(n\tilde{\gamma})^3+\dots; \tag{7.10}$$

the coefficients m_p^0 are exhibited in (5.18). The series (7.10) compares with (5.18), but the term in $\tilde{\zeta}$ shown in (5.18a) is now concealed in $m_2^0(n\tilde{\gamma})^2$ and the term in C_3 is included in Q. Comparison of (7.9) and (5.17) now shows that

$$C=C^0+Q. \tag{7.11}$$

By solving (7.9) for W and substituting in (5.20b) we therefore get (5.21) with C replaced by C^0+Q, namely

$$\left(\frac{m^2-1}{4\pi}\right)\left(\frac{2m^2+1}{3m^2}\right)=n\tilde{\gamma}+\frac{m^2+2}{3m^2}(C^0+Q)+\frac{4\pi}{3m^2}(C^0+Q)^2. \tag{7.12}$$

The result is that, apart from Q, the right side of (5.21) becomes a power series in $n\tilde{\gamma}$. Now we saw in §6 that β should replace $\tilde{\gamma}$ in the first term of (5.21) and at the same time all those self-interactions in which the chain of propagators $\tilde{\mathsf{F}}$ began and ended at x_1 (i.e. at the reference molecule) should be omitted from C. All of these terms are necessarily in Q. This of course now suggests that we replace $\tilde{\gamma}$ by β in all of the higher terms of the series C^0 making the necessary omissions in Q.

We must say immediately that such a procedure cannot produce an exact result like the one obtained for the linear term. But by accepting a simple decorrelation we reach a formula this way which we believe is a good aproximation and which could prove of real practical value. In any case, the analysis that follows provides valuable insight into the character of the corrections to the simple Onsager–Böttcher relation. These insights should help with any future work which attempts to give a more exact analysis based directly on the unscreened formulations. We sketch the beginning of such an approach near the end of this section.

To assess the possibility of replacing $\tilde{\gamma}$ by β in the series C^0 we must see whether Q contains terms that eliminate the divergences of the powers of $\tilde{\gamma}$ and produces powers of β. As far as the divergences are concerned this problem is analogous to the one discussed previously (Hynne & Bullough 1972) for the linear term, and we shall not discuss the problem here. However, Q contains corrections of a different character as shown in the Appendix. These corrections account for correlations between self-interaction loops belonging to effective polarizabilities associated with different molecules.

As we indicate in that Appendix these correlations between loops contained in divergent terms of Q are probably rather unimportant numerically. But there are terms in Q which (broadly) represent such high degree of (self-)correlation between loops of effective polarizabilities at different molecules that no part is contained in powers of $\tilde{\gamma}$. These terms are wholly contained in Q and therefore convergent.

The idea is therefore, as an approximation, to replace powers of $\tilde{\gamma}$ by powers of β in (7.12), to omit the divergent terms from Q (which compensate the divergences of the $\tilde{\gamma}^p$), and retain the convergent terms of Q. This procedure represents a weak decorrelation because the weak correlations 'between different β' are ignored this way; but the strong correlations are retained through the convergent terms of Q. This procedure leads to a useful formula although we cannot provide complete justification for it. We quote it below when we have considered the simplest of the convergent terms of Q.

At order p in $n\alpha$ the contributions to Q arise from those terms of $Y_{123\ldots p}$, which contain at least one delta function δ_{rs} connecting non-consecutive points x_r and x_s, and which do not contain δ_{1p}. At order p one term, as referred to here, is the complete contribution from $Y_{123\ldots p}$ with a given product of delta functions, and we are interested in those giving a convergent integral when substituted for $Y_{123\ldots p}$ in (4.15*b*). We shall consider the two-body terms contained in Q in detail: these are first defined and so can be identified in their unscreened forms; so we are concerned with the expressions (3.7*b*), (3.7*c*), and (3.7*d*) after restoring the pair-correlation function $g(r)$ there. We first note that all the *even* two-body terms (3.7*c*) are contained in the $n\beta$ that replaces the first term of (5.21), because all the terms of (3.7*c*) represent pure self-interactions of the reference molecule, and β contains all of those. Furthermore, the term (3.7*b*) is evidently contained in m_2 because $\tilde{\mathsf{F}}$ contains F.

On the other hand we now show that all of the *odd* two-body terms (3.7*d*) are contained in Q. To see this we first consider the fourth order term of (4.15) which is governed by the correlation function

$$\begin{aligned} Y_{1234} &= U_{1234} + U_{13}\,U_{24} \\ &= G_{1234} - G_{123} - G_{234} - G_{124} - G_{134} - G_{12}\,G_{34} - G_{14}\,G_{23} \\ &\quad + 2(G_{12} + G_{23} + G_{34} + G_{14}) + G_{13} + G_{24} - 5 \end{aligned} \tag{7.13}$$

in terms of the generalized Ursell functions (4.3*b*) or the generalized distribution functions (2.11). All terms from (7.13) with one or more delta function not connecting consecutive points are contained in the term Q in (7.1). We consider the contribution from Y_{1234} with a product of two delta functions connecting x_3 with x_1 and x_4 with x_2. From (2.11) we see that there is only one such term contained in G_{1234}, namely

$$n^{-2}\delta_{13}\,\delta_{24}\,g_{12} \tag{7.14}$$

and none of the other terms of (7.13) contains this combination of delta functions.

So the contribution from (7.14) substituted for Y_{1234} in (4.15) gives

$$n^2\alpha^4\ \mathrm{Tr}\int \tilde{\mathsf{F}}_{12}\cdot\tilde{\mathsf{F}}_{21}\cdot\mathsf{F}_{12}\cdot\mathsf{T}_{21}\,g_{12}\,\mathrm{d}x_2. \tag{7.15a}$$

We then see that (7.15*a*) contains the two-body term

$$n^2\alpha^4\ \mathrm{Tr}\int \mathsf{F}_{12}\cdot\mathsf{F}_{21}\cdot\mathsf{F}_{12}\cdot\mathsf{T}_{21}\,g_{12}\,\mathrm{d}x_2, \tag{7.15b}$$

which is essentially the last term of (3.1*d*) or the first term of the series (3.7*d*). We shall therefore refer to (7.15*a*) or (7.15*b*) as two-body terms even though they are not strictly proportional to n^2 (as (3.4), (3.5), and (4.4) all show).

To understand the role of the two-body term (7.15) we first interpret a more normal term, the one for $p = 2$ in the sum of (7.1) with $\tilde{\gamma}$ replaced by β:

$$(n\beta)^2\ \mathrm{Tr}\int \tilde{\mathsf{F}}_{12}\cdot\mathsf{T}_{21}(g_{12}-1)\,\mathrm{d}x_2. \tag{7.16}$$

This term describes a process in which a molecule at x_2 in the medium is first polarized by some field (contained in T_{21}), as accounted for by one factor β. The field from the dipole propagates through the medium from x_2 to x_1 (the factor $\tilde{\mathsf{F}}_{12}$) and polarizes a molecule at x_1 in the medium (the second factor β). For short this scheme can be labelled '$\beta\tilde{\mathsf{F}}\beta$'.

Now (7.15*b*) may be viewed as a process of the same general character. First the dipole initially induced in a molecule at x_2 (factor α) interacts with itself via a molecule at x_1 as described by $\alpha^2\mathsf{F}_{21}\cdot\mathsf{F}_{12}$. This self-interaction is part of the polarization of the molecule at x_2 in the medium as described by an effective polarizability β. The dipole arising from the self-interaction then creates a field which propagates from x_2 to x_1 (left factor F_{12}) and polarizes a molecule there (the last factor α which is the lowest order contribution to an effective polarizability). So superficially the process (7.15*b*) is part of the '$\beta\tilde{\mathsf{F}}\beta$' processes.

The important point now is that the self-interaction of the molecule at x_2 is not independent of the propagation from x_2 to x_1 because both processes involve the *same* molecule at x_1. It is therefore impossible to describe this process in terms of quantities like β and $\tilde{\mathsf{F}}$ (or $\mathscr{F}$), which are *separately* averaged. Replacing $\tilde{\gamma}$ by β (and omitting Q) in (7.1) would therefore involve a decorrelation approximation very similar to the one implied by expressing β in terms of a reaction field as in (6.21) where the comparison of (*b*) and (*e*) in figure 3 was instructive.

The process (7.15*b*) can equally well be described as first a propagation from x_2 to x_1 (the factor F_{12} to the right) and subsequently a self-interaction of a molecule at x_1 through the one at x_2. It is interesting that the two interpretations correspond to one and the same process in contrast to the situation when the self-interaction is through a third molecule.

The result for (7.15) may now be extended to show that all the remaining of the odd two-body terms in the series (3.7*d*) are also contained in Q. From the general expression (I 4.11) for the

Y functions in terms of generalized Ursell functions we find that each even order Y function beyond (7.13) starts with two terms similar to those of Y_{1234}

$$Y_{123456} = U_{123456} + U_{135}\,U_{246} + \ldots, \tag{7.17a}$$

$$Y_{123\ldots8} = U_{123\ldots8} + U_{1357}\,U_{2468} + \ldots, \tag{7.17b}$$

$$\vdots$$

(see figure 2 of Hynne (1975) for Y_{123456}). Taken together, the two terms exhibited for each Y function contain

$$n^{-4}\,\delta_{13}\,\delta_{35}\,\delta_{24}\,\delta_{46}\,g_{12}, \tag{7.18a}$$

$$n^{-6}\,\delta_{13}\,\delta_{35}\,\delta_{57}\,\delta_{24}\,\delta_{46}\,\delta_{68}\,g_{12}, \tag{7.18b}$$

$$\vdots$$

and the remaining terms not shown in (7.17) do not contain further terms with the combination of delta functions of (7.18); this follows from the definition (I 4.11) of the Y functions. The terms (7.18) reduce the 6, 8, ... order terms of (4.15) to well defined two-body terms similar to (7.15a) with 5, 7, ... propagators $\tilde{\mathsf{F}}$ transmitting fields back and forth between molecules at $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$. And by definition these terms are all in Q because they arise from delta functions not directly across $\tilde{\mathsf{F}}$ propagators.

It is plain that the higher of the odd two-body terms have the general character that can be described as follows: multiple self-interaction of a molecule at $\boldsymbol{x}_2$ via one at $\boldsymbol{x}_1$; propagation from $\boldsymbol{x}_2$ to $\boldsymbol{x}_1$; multiple self-interaction of the molecule at $\boldsymbol{x}_1$ via the one at $\boldsymbol{x}_2$. And several equivalent interpretations (corresponding to the two interpretations of (7.15)) are possible, all describing one and the same physical process. But as with (7.15) the processes cannot be described adequately in terms of β.

With this as a background we can now return to the question of finding the 'correct' interpretation of the formal result (7.12). It is plain from the discussion that a term $\tilde{\gamma}^p$ is divergent because it lacks contributions contained in Q that naturally belong to it. This divergence problem stems from the use of the screened propagator $\mathscr{F}$, as described below (5.11). These compensating divergences must of course be transferred from Q to reach a final result.

If all the relevant terms are transferred from Q to $\tilde{\gamma}^p$ we would get something like a p-body (or p-centre) effective polarizability. As an approximation we transfer the compensating divergences with neglect of weak correlations by replacing $\tilde{\gamma}^p$ by β^p in the series C^0, and we keep the strong correlations by retaining the convergent terms of Q explicitly. If the resulting series are denoted by $\mathscr{C}$ and $\mathscr{Q}$ respectively, we get

$$\left(\frac{m^2-1}{4\pi}\right)\left(\frac{2m^2+1}{3m^3}\right) = n\beta + \frac{m^2+2}{3m^2}\,(\mathscr{C}+\mathscr{Q}) + \frac{4\pi}{3m^2}\,(\mathscr{C}+\mathscr{Q})^2 \tag{7.19a}$$

in which
$$\mathscr{C} = m_2^0(n\beta)^2 + [m_3^0 + (16\pi/3m^2)\,m_2^0]\,(n\beta)^3 + \ldots \tag{7.19b}$$

and the first few terms of $\mathscr{Q}$ will be

$$\begin{aligned}\mathscr{Q} = {} & n^2\alpha\,\mathrm{Tr}\sum_{p=1}^{\infty}\int(\alpha\tilde{\mathsf{F}}_{12})^{2p+1}\cdot\tilde{\mathsf{T}}_{21}\,g_{12}\,\mathrm{d}\boldsymbol{x}_2 + \ldots \\ & + n^3\alpha^5\,\mathrm{Tr}\iint\tilde{\mathsf{F}}_{12}\cdot\tilde{\mathsf{F}}_{23}\cdot\tilde{\mathsf{F}}_{31}\cdot\tilde{\mathsf{F}}_{12}\cdot\tilde{\mathsf{T}}_{21}(g_{123}-g_{12})\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3 + \ldots \\ & + n^3\alpha^6\,\mathrm{Tr}\iint\tilde{\mathsf{F}}_{13}\cdot\tilde{\mathsf{F}}_{31}\cdot\tilde{\mathsf{F}}_{12}\cdot\tilde{\mathsf{F}}_{23}\cdot\tilde{\mathsf{F}}_{32}\cdot\tilde{\mathsf{T}}_{21}\,g_{123}\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3 + \ldots.\end{aligned} \tag{7.19c}$$

In $\mathscr{C}$ the coefficients m_p^0 are given by (7.1 *b*) with the small spheres omitted; thus all integrals of (7.1 *b*) are interpreted as principal value integrals yielding m_p^0 (not m_p). Note that at $O((n\beta)^3)$ and beyond, the coefficients in $\mathscr{C}$ depend on m^2, a feature we have not been able to sum away.

The series $\mathscr{Q}$ is the sum of all *convergent* terms arising from (4.15) through correlation functions containing at least one delta function not directly across a propagator $\tilde{\mathsf{F}}$ but without any delta function connecting the first and last points, called x_1 and x_p in the notation of (4.15 *b*). Equation (7.19 *c*) displays all of the two-body terms of $\mathscr{Q}$ (the odd ones) and two typical three-body terms proportional to α^5 and α^6 respectively: they are exhibited again in figure 4.

FIGURE 4. Diagrammatic representation of the series (7.19 *c*) showing the first term of the series of odd two-body terms and the two typical three-body terms exhibited in (7.19 *c*).

Thus we have reached a well-defined result (7.19) for the generalized Onsager–Böttcher relation. It is evidently approximate; but we have laboriously built up a picture that indicates to the order of terms explicitly exhibited in (7.19 *b*) and (7.19 *c*) that (7.19 *a*) is a good approximation. Even so, the methods of summation and approximation used make it impossible to put a precise number or order expression on the error made in reaching (7.19 *a*).

The result (7.19) is the best possible 'practical' formula we have been able to provide (although for any real practical calculation we will still need some approximation for β, and we have no better closed form than (5.22) with (5.13) as alternative to the unscreened series (6.9 *b*)). However, because of the uncertainties surrounding the precise status of (7.19) one would still like to have an exact expression from which it would be possible, in principle, to construct an exact dispersion relation of a generalized Onsager–Böttcher form, utilizing the insights gained through the derivation of (7.19) for that purpose.

An exact relation must build on an unscreened expression such as (3.1). We may sum all terms of (3.1) in which the chain of propagators F begins and ends at the reference molecule (index 1 in (3.1)) to get $n\beta$. So we have

$$\left(\frac{m^2-1}{4\pi}\right)\left(\frac{3}{m^2+2}\right) = n\beta + \sum_{p=2}^{\infty} L_p'(n\gamma)^p. \tag{7.20a}$$

Here the coefficients L_p' are given by (3.1 *b*), (3.1 *c*), ... with omission of the closed loop terms mentioned. Explicitly, L_p' is given by

$$L_p' = |V|^{-1}\,\mathrm{Tr}\int_V\int_{V-v}\cdots\int_{V-v}\mathsf{F}_{12}\cdot\mathsf{F}_{23}\ldots\mathsf{F}_{(p-1)p}\cdot\tilde{\mathsf{T}}_{p1}H_{123\ldots p}'\,\mathrm{d}\boldsymbol{x}_1\ldots\mathrm{d}\boldsymbol{x}_p \tag{7.20b}$$

in which the correlation function $H_{123\ldots p}'$ by definition is obtained from $H_{123\ldots p}$ (given by (I 3.18) or (2.10)) by omitting all terms with delta functions connecting cyclically consecutive points.

Equation (7.20) has an effective polarizability on the right side but a Lorentz internal-field factor on the left. We know from (7.19) that a cavity-field factor goes with the term $n\beta$ on the right. On the other hand, the appearance of macroscopic factors containing m and the *square* of $(\mathscr{C}+\mathscr{Q})$ in the higher terms of (7.19) suggests that the cavity-field factor associates naturally with the linear term $n\beta$ *only* (and not with the higher terms). This conclusion agrees with the picture that the higher terms of (7.19) involve multicentre effective polarizabilities for which a simple spherical cavity is plainly inappropriate.

So working from (7.20) we must aim at deriving an expression of the form

$$\frac{m^2-1}{4\pi} = \frac{3m^2}{2m^2+1}n\beta + \text{corrections}. \tag{7.21}$$

Evidently it is unlikely that we can derive a form like (7.21) in any simple way; but from the steps of the derivation of (7.19) we may already infer what types of contributions contained in the higher terms of (7.20) are responsible for the change of the Lorentz factor towards a cavity-field factor. For example, the term

$$(n\gamma)^3 |V|^{-1}\,\mathrm{Tr}\int_V \int_{V-v} \int_{V-v} \mathsf{F}_{12}\cdot\mathsf{F}_{23}\cdot\mathsf{T}_{31}(g_{13}-1)\,\mathrm{d}\boldsymbol{x}_1\,\mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3 \tag{7.22}$$

is typical of the terms which must be important contributors. For the self-correlation term associated with it has gone into β and (7.22) itself contributes to the elimination of the reaction field of a Lorentz sphere which accounts for the difference between the Lorentz and cavity-field factors as we show in §8. The $g_{13}-1$ provides a sphere of molecular size about $\boldsymbol{x}_1$ and local environment in the integration with respect to $\boldsymbol{x}_3$; and the excursion into a smooth dielectric on the two-coordinate is characteristic of a reaction field. So corrections like (7.22) are finally responsible for the Onsager cavity-field factor as modified by the actual local environment. We have not carried out this direct approach to the Onsager–Böttcher relation through (7.20) and the unscreened theory in much more detail than this. Our 'best' result to date remains (7.19). But we shall discuss the significance of the change of the internal-field factor in macroscopic terms and this is done in §8.

It remains tantalizing that the result (7.12) is formally exact yet cannot be used until the divergences are matched away whereas (7.20) is both exact and well defined but formally surface dependent and therefore difficult to work with. The approximate formula (7.19) (supported by the possibility of the exact expression (7.20)) therefore constitutes our final result for the refractive index: it is our best possible compromise between practical utility and exactness for fluids outside the low density region; the systematic density expansion (3.3) remains the best approach for gases.

It is discouraging that we have not been able to obtain a result that is both exact and useful for numerical work. A way out of the dilemma of the surface problem against the divergence problem may be to screen only the transverse part of the propagator F, and this may be the best approach for computational purposes. However, the quite deep understanding of the mechanism of dielectric polarization we have built up at microscopic level would not have been obtained by such an approach; we now use this understanding in a comparison of the two strictly macroscopic formulae, the Lorentz–Lorenz formula (1.1) and the Onsager–Böttcher formula (1.2) in §8.

8. Evaluation of macroscopic models

We are now in a position to compare the two *macroscopic* expressions introduced at the start of this paper. These are the Lorentz–Lorenz equation (1.1) and the Onsager–Böttcher equation (1.2). These macroscopic relations are generalized by the microscopic theory as the formulae (3.1) and (7.19) respectively.

We first discuss the Lorentz–Lorenz relation and note that the generalized relation (3.1) contains the term $n\beta$ on the right side: only $n\alpha$ or $n\gamma$ appears in the simple form (1.1). The presence of $n\beta$ in (3.1) was pointed out at (7.20). It is in (3.1) because it is in (2.1) and because $n\beta$ contains no Lorentz terms and so cannot have contributed to the Lorentz internal-field factor on the left of (3.1). The presence of $n\beta$ in (2.1) is evident from the expansion (I 3.16) of $\mathbf{\Lambda}$ which starts with the kernel **Л**, (which itself contains $n\beta$ as (6.8) and (6.9) show).

Thus, the correction terms to the simple Lorentz–Lorenz relation (the higher terms of (3.1)) change the $n\gamma$ of (1.1 *b*) into $n\beta$: the simple Lorentz–Lorenz relation lacks all of the self-interactions corresponding to the second term of (6.5). We shall show below how other correction terms of (3.1) change the Lorentz internal-field factor on the left side of (1.1) to the cavity-field factor that appears in (1.2). The two sets of correction together mean that the Onsager–Böttcher relation forms a better starting point for a description of the refractive index although it itself needs correction as (7.19) shows.

Although it is a trivial consequence of (3.1) it is worth stressing that the simple Lorentz–Lorenz relation (1.1) also lacks all of the two-body terms, the $b_2(\omega, T)\, n^2$ of (3.3) with b_2 given by the infinite sum (3.7). Of course, the inverse Lorentz factor on the left of (1.1) takes account of distant dipoles, but all effects of correlations between pairs of molecules are missing. This results in systematic error already at low densities as we have discussed near (3.34).

We now turn to the Onsager–Böttcher relation (1.2). Evidently (1.2) does account for the self-interactions of the reference molecule, in so far as it contains the macroscopic polarizability (1.3 *b*). The discussion of §6 shows precisely what this means in microscopic terms; we shall exemplify the consequences by accounting for the important two-body terms.

We first note that the Onsager–Böttcher relation with the exact polarizability $n\beta$ includes all of the even two-body terms (3.7 *c*) but no other two-body terms. The remaining ones are of course contained in the correction terms of (7.19) to the simple Onsager–Böttcher relation. All the odd two-body terms (3.7 *d*) are contained in $\mathscr{Q}$ as (7.19 *c*) shows. And the single term (3.7 *b*) is contained in m_2^0, given by (5.18 *b*). (Note that to lowest order in $n\alpha$ the factor $\frac{1}{3}(m^2+2)/m^2$ of $\mathscr{C}$ in (7.19 *a*) becomes unity and the propagator $\tilde{\mathsf{F}}$ in (5.18 *b*) becomes F.)

So the Onsager–Böttcher relation with the exact polarizability contains all the even two-body terms (3.7 *c*) but not the odd ones (3.7 *d*) or (3.7 *b*), and from this we may get to the macroscopic relation in two stages. First we approximate the effective polarizability β by (6.21) in terms of an *exact* reaction-field coefficient $\mathscr{s}$, given by the microscopic expression (6.17 *b*) and shown in figure 3 *a*. Then we replace the exact $\mathscr{s}$ by the macroscopic form of it (1.2 *b*).

Already in the first step, the approximation (6.21), we lose all of the even two-body terms (3.7 *c*) beyond the first. The reason is that these terms all contain multiple closed loops and such terms become approximated by powers of the single-loop two-body term shown as the second term in figure 3 *a*; and these powers do not have the character (density dependence) of the true two-body terms they approximate.

The further step of replacing the exact reaction-field coefficient $\mathscr{s}$ by the approximate macroscopic form (1.2 *b*) cannot be followed in such minute details, but the results (5.12)–(5.14) throw some light on the approximation.

Certainly the screened radiation reaction $\frac{2}{3}imk_0^3$ is missing in (1.2 *b*) and, although this imginary term is small compared to the real reaction field, it is essential to the extinction coefficient and to the internal consistency of the theory.

It is satisfactory that the modified formal reaction field (5.12) (or (5.13) with (5.14)) otherwise resembles the macroscopic expression (1.2 *b*) so closely. We can see how the concept of a cavity introduced in the macroscopic theory is actually contained in the exact microscopic expression (6.17*b*) for the reaction field (compare with Linder & Hoernschemeyer 1967). We see that in the integrations in (6.17*b*) the integrands vanish when any of the integration variables come closer to the point $\boldsymbol{x}_1$ than some molecular (hard core) diameter. So in each term an effective cut-off is introduced by the appropriate many-body correlation function. This set of correlation functions replace the simple pair-correlation function introduced heuristically in (5.13). But the main effect is the same: the reference molecule makes itself a cavity into which it prevents other molecules from penetrating, and this is the reason why some molecular diameter must play an important role in the theory.

We may summarize our analysis of the two macroscopic models as follows. The Lorentz–Lorenz relation lacks all self-interactions and all two-body terms. The Onsager–Böttcher relation contains the self-interactions in approximate form, but it lacks all but one of the two-body terms. However, the single two-body term included,

$$n^2\alpha^3\tfrac{1}{3}|V|^{-1}\,\mathrm{Tr}\int_V \mathrm{d}\boldsymbol{x}_1\int_V \mathrm{d}\boldsymbol{x}_2\,\mathsf{F}_{12}\cdot\mathsf{F}_{21}\,g_{12} \tag{8.1}$$

(essentially the term considered already by Kirkwood (1936) and Yvon (1936, 1937) is in fact numerically the most important of the two-body terms except near a resonance (compare with §3). So the Onsager–Böttcher relation does give a satisfactory description for low density gases for which it is definitely better than the Lorentz–Lorenz relation.

We still have to explain the change of the Lorentz internal-field factor in (3.1) into the cavity-field factor of (7.19) through the higher terms of (3.1). Related questions are why the screened Lorentz terms sum to a cavity-field factor and what these terms mean physically.

Recall first that in the Lorentz model the internal field on a molecule can be obtained as the average field $\mathscr{E}$ minus the field inside a sphere of uniform polarization $\boldsymbol{P}$,

$$\boldsymbol{E}_{\mathrm{L}} = \mathscr{E} - (-\tfrac{4}{3}\pi\mathsf{U})\cdot\boldsymbol{P}. \tag{8.2}$$

The cavity field, on the other hand, equals the Lorentz internal field minus the reaction field of a polarized Lorentz sphere,

$$\boldsymbol{R}_{\mathrm{L}} = \left(\frac{2}{\bar{a}^3}\,\frac{m^2-1}{2m^2+1}\right)\left(\frac{4\pi}{3}\bar{a}^3\boldsymbol{P}\right) = \tfrac{8}{3}\pi\,\frac{m^2-1}{2m^2+1}\boldsymbol{P} \tag{8.3}$$

and can therefore be written

$$\boldsymbol{E}_{\mathrm{c}} = \mathscr{E} - (-\tfrac{4}{3}\pi\boldsymbol{P} + \boldsymbol{R}_{\mathrm{L}}) \tag{8.4}$$

or

$$\boldsymbol{E}_{\mathrm{c}} = \mathscr{E} - \left(-\frac{4\pi}{2m^2+1}\mathsf{U}\right)\cdot\boldsymbol{P}. \tag{8.5}$$

The expression (8.5) for the cavity field has the same form as the Lorentz internal field (8.2) but the Lorentz term (2.7) is replaced by

$$-\frac{4\pi}{2m^2+1}\mathsf{U}, \tag{8.6}$$

which almost equals the screened Lorentz term (5.1). Again the model has denominator $2m^2+1$ rather than $3m^2$ as in the (5.1) (compare (1.2*b*) with (5.12)). This similarity between the macroscopic model and the microscopic theory is not accidental.

To see this we use the integral equation (4.10) to rewrite (5.1) as

$$\int_v \tilde{\mathsf{F}}(\boldsymbol{x},\boldsymbol{x}';\omega)\,\mathrm{d}\boldsymbol{x}' = \int_v \mathsf{F}(\boldsymbol{x},\boldsymbol{x}';\omega)\,\mathrm{d}\boldsymbol{x}' + \frac{m^2-1}{4\pi}\int \mathrm{d}\boldsymbol{x}''\int_v \mathrm{d}\boldsymbol{x}'\mathsf{F}(\boldsymbol{x},\boldsymbol{x}'';\omega)\cdot\tilde{\mathsf{F}}(\boldsymbol{x}'',\boldsymbol{x}';\omega), \qquad (8.7)$$

where v is understood to mean the limit of a vanishing small sphere centred on $\boldsymbol{x}$ (not $\boldsymbol{x}''$ in the last term on the right side as our convention would imply). The first term of (8.7) is by definition the usual Lorentz term (2.7) and equals the first term in brackets in (8.4) apart from the factor $\boldsymbol{P}$. The second term (upon multiplication by $\boldsymbol{P}$) almost has the form of a reaction field of a small polarized sphere. It evidently corresponds to the second term in brackets in (8.4). It is not quite the reaction field of a polarized Lorentz sphere because $\tilde{\mathsf{F}}$ in (8.7) is the propagator for a uniform system rather than for one having a cavity, and the integration with respect to $\boldsymbol{x}''$ in (8.7) includes the sphere. Nevertheless the similarity is striking whereas the differences explain the denominators $3m^2$ and $2m^2+1$. It is remarkable that the contributions of the screened Lorentz terms (5.1) in the screened theory nevertheless sum to produce precisely a cavity-field factor, despite the differences just discussed. (Briefly, the explanation is that we sum contributions (5.1) from a set of terms in the screened theory that differs from the one for which the terms (2.7) are summed in the unscreened theory.)

We may view this result as stating that the corrections of (3.1) to the simple Lorentz–Lorenz relation (1.1) eliminate the reaction field of the Lorentz sphere. Plainly, this artificial reaction field must be replaced by the true reaction field of a *molecule* which as we have seen is indeed present in the higher terms of (3.1).

The terms of (3.1) that eliminate the reaction field of the Lorentz sphere can be identified by using the expansion generated by (4.1) in (4.2) and (2.1), compare with (7.22). In this way it becomes clear that the conceptual framework of the Onsager–Böttcher model is indeed the physically natural starting point of an understanding of dielectric polarization.

The idea of a molecular cavity, with the cavity field created by the external field in the presence of the surrounding molecules plus the reaction field of the molecular dipole in the cavity is in complete accord with the microscopic theory apart from the decorrelation approximation (6.21). Conceptually, the main limitation of the model is that it treats the surroundings of any molecule as a continuum. The approximation of the effective polarizability in terms of the Onsager reaction field is a consequence of this feature: it is impossible to treat multiple interactions with a specific group of surrounding molecules unless the surroundings are represented by discrete molecules.

9. Summary and conclusion

The present paper is part of a unified theory of the optical processes in molecular fluids exposed to externally incident light. The foundation of the theory was laid in the previous paper in this series, I, on the optical response of a finite molecular fluid. From results obtained there we have developed a theory of the complex refractive index m of a fluid of isotropically polarizable molecues. The theory also applies to the frequency dependent dielectric constant $\epsilon(\omega)$ through the relation $\epsilon(\omega) = m^2(\omega)$ derived from the microscopic theory in I.

From this theory we derive expressions for the real part of the refractive index and for the extinction coefficient τ. We investigate their dependence on the density of molecules, the temperature, and the frequency, and we solve the conceptual aspects of the local field problem in an analysis of the conflicting macroscopic formulae of Lorentz and Böttcher. These results are obtained through the interplay of two formulations of the refractive index theory, the unscreened theory developed in §§2 and 3 from the expansion (2.9) of the susceptibility kernel, and the screened theory developed in §§4–7 from the expansion (4.2).

The unscreened theory is the fundamental one. It is exact within the scope defined in the introduction, and it is in keeping with the idea of explaining the propagation of light in a medium as the result of elementary scattering processes taking place in empty space.

The fundamental formula for the refractive index is therefore the expansion (3.1) in $n\gamma$ generalizing the Lorentz–Lorenz relation (1.1). The coefficients L_p are known to all orders, determined by the H functions, (I 3.18) and (2.10), with omission of self-correlations directly across propagators F.

The series (3.1) is then arranged as a density expansion so that the dependence of the refractive index on the thermodynamic state of the fluid and the frequency of the incident light can be investigated. The coefficients have to be calculated term by term, and we evaluate the first two by summing the infinity of two-body terms (3.7). The result therefore applies to gases at sufficiently low densities, and the dependence on density, n, temperature, T, and frequency, ω, is given by the ω and T dependent coefficients, the refractivity virial coefficients (or dielectric virial coefficients).

The second refractivity virial coefficient is calculated in an approximation described around (3.9) and (3.10). The result is (3.11) for the refractive index, which splits into (3.19) for the real part and (3.17) for the extinction coefficient, τ. These results are expressed in terms of a function h_2, given by (3.9*b*), which is calculated for two choices of intermolecular potential. For the Lennard-Jones potential (3.12), h_2 is given by (3.13) in terms of the integral (3.14). It is a function of the dimensionless variables a^3/γ and T_0/T only, with a and $k_B T_0$ the Lennard-Jones parameters. We show that the refractive index then essentially depends only on $n\gamma$, a^3/γ, and T_0/T. For a hard-sphere gas h_2 takes the very simple form (3.15), which nevertheless describes many features correctly, as discussed near (3.35) and (3.36).

The second refractivity coefficient is calculated numerically for a Lennard-Jones gas; the results are summarized in table 1 and figure 1. We note in particular that the correction is typically 10–20% of the contribution of the Lorentz internal-field factor (see (3.34)), and that the temperature coefficient of the refractive index, given by (3.22) with (3.21) and (3.23), is usually negative at room temperature, whether it refers to constant density or to constant pressure.

The result (3.11) applies in disconnected frequency regions, namely far from any molecular resonance and in the wings of resonance absorption lines. Off resonance the extinction coefficient is given by (3.26); in line wings (3.33) applies. Both expressions are special cases of the more general result (3.17).

Physically the line-wing frequency regions are characterized by distant pairs of molecules resonating at frequencies given by (3.28). These resonance conditions appear in the theory from singularities just off the real axis in the integral (3.9*b*).

The screened theory, §§4–7, provides a framework for a conceptual analysis of the mechanism of dielectric polarization. The main conclusion is that the Onsager–Böttcher relation is wholly contained in the microscopic expressions for the refractive index. This follows from (5.19) substituted in (2.1) through a simple approximation; thus

$$\mathbf{\Lambda} = \mathbf{J} - \iint \mathbf{\Lambda} \cdot \mathscr{F} \cdot \mathbf{\Lambda} \, \mathrm{d}\boldsymbol{x}_2 \, \mathrm{d}\boldsymbol{x}_3 \qquad (9.1\,a)$$

yields
$$\frac{m^2-1}{4\pi} \approx n\beta - \left(\frac{-4\pi}{3m^2}\right)\left(\frac{m^2-1}{4\pi}\right)^2. \tag{9.1b}$$

The average of (6.8) shows that $\mathfrak{I}$ contains $n\beta$; and in the bulk approximation $\mathscr{F}$ becomes $\tilde{\mathsf{F}}$ and the integral of this propagator contains $(-4\pi/3m^2)$ through (5.1). Then each $\boldsymbol{\Lambda}$ yields approximately $(m^2-1)/4\pi$ through (2.1), and (9.1*b*) follows if what remains of $\mathfrak{I}$ and from the integration of $\mathscr{F}$ is ignored. Simple algebraic rearrangement finally brings (9.1*b*) into the Onsager–Böttcher form with an exact effective polarizability β.

The argument we have just given serves to identify the key steps of the systematic derivation of the Onsager–Böttcher relation (6.23), given in §§5 and 6, whereas (9.1*a*) and (9.1*b*) exhibited together reveal structural relations between the microscopic and macroscopic expressions. But to justify (9.1*b*) as an approximation and to extend it to the final result (7.19) requires the very much more elaborate argument given in the main text.

The derivation of the generalized Onsager–Böttcher relation (7.19) is important not the least for the physical insight it provides, namely a thorough understanding of the significance of macroscopic concepts within the microscopic theory, and namely and particularly of the effective polarizability, the Onsager reaction field, the cavity field, and the Lorentz internal field.

The effective polarizability is defined below (6.4), and we find the exact expansion (6.9*b*) for it. It has the form of the polarizability of an isolated molecule corrected by all possible self-interactions of the molecule, see (6.22*a*) with figure 3. It is contained in the polarization kernel $\mathfrak{I}$, as we mentioned below (9.1), and it appears on the right side of (3.1). So the generalized Lorentz–Lorenz relation contains $n\beta$, not just $n\gamma$, as (7.20) shows.

The reaction-field coefficient is defined in the microscopic theory by (6.17*a*) with (6.16), and it is given explicitly by the expansion (6.17*b*) with (6.17*c*). This definition is wholly in the spirit of Onsager's original macroscopic definition for a static dipole.

The effective polarizability can be expressed in terms of the reaction field coefficient by the relation (6.21) in agreement with Böttcher's macroscopic polarizability (1.3*b*). But in the molecular theory this relation is only an approximation. It neglects correlations between molecules participating in different self-interactions of a reference molecule. As a consequence, one loses all but one of the two-body terms contained in β in the approximation (6.21). The problem is solely associated with intermolecular correlations: we derive the exact relation (6.19) for a fixed (instantaneous) configuration of molecules.

The conclusion is that an effective polarizability, not a reaction field, is the fundamental concept in the refractive index theory or in general for fluids of non-polar molecules; for the low-frequency dielectric constant of polar fluids the Onsager reaction field remains fundamental.

The effective polarizability goes together with a cavity field, which appears in the microscopic theory through (5.1) as (9.1) has just recalled. The physical meaning is explained in §8: the term (5.1) (upon multiplication by the average polarization $\boldsymbol{P}$) represents essentially the field from a 'polarized Lorentz sphere' *without its reaction field*. When this field (in its macroscopic version (8.6)) is subtracted from the average field $\mathscr{E}$, one obtains the cavity field (8.5).

In the Lorentz model the internal field has the well-known form (8.2) of the average field minus the field from the polarized Lorentz sphere, $-(\frac{4}{3}\pi)\,\boldsymbol{P}$. But in the microscopic theory the reaction field from the polarized Lorentz sphere becomes replaced by the reaction field of a molecule as contained in the effective polarizability β, so the cavity field factor remains on the left side of (7.19) whereas the term $n\beta$ appears explicitly on the right. The macroscopic cavity factor is further corrected for intermolecular correlations by the higher terms on the right side of (7.19).

One conclusion surely is that the Onsager–Böttcher model is physically more satisfactory than the Lorentz model. We have argued elsewhere that there are also didactic advantages from using it in elementary dielectric theory (Hynne (1983); note that the simplified diagrammatic notation used there differs considerably from the one used here). The Onsager–Böttcher relation has its own shortcomings: we explain these in §8 with special reference to the two-body terms.

The ideas we have just discussed appear directly in the macroscopic models. In addition to these, there appears in the microscopic theory another concept of macroscopic significance, the screened propagator $\mathscr{F}(\boldsymbol{x},\boldsymbol{x}';\omega)$, defined in I and given by the expansion (4.1). Physically it describes the electromagnetic field from an oscillatory dipole propagating in the material medium. We show in §4 that $\mathscr{F}$ can be approximated by a 'macroscopic' form $\tilde{\mathsf{F}}_V$, which consists of two parts, $\tilde{\mathsf{F}}_V = \tilde{\mathsf{F}} + \tilde{\mathsf{f}}$, a translationally invariant part, $\tilde{\mathsf{F}}$, given by the natural closed form (4.4), and a surface dependent part, $\tilde{\mathsf{f}}$, that has the character of reflected waves, and which we believe can be represented as the sum of all multiply reflected parts of a primary spherical wave described by $\tilde{\mathsf{F}}$. The derivation shows that the approximation of $\mathscr{F}(\boldsymbol{x},\boldsymbol{x}';\omega)$ by $\tilde{\mathsf{F}}(\boldsymbol{x},\boldsymbol{x}';\omega)$ is best when $|\boldsymbol{x}-\boldsymbol{x}'|$ is large compared to a typical intermolecular correlation length, and we give an example to illustrate the approximation involved, see figure 2*h*.

A result of the theory on a more technical level is the solution of the surface problem. The refractive index as given for example by (3.1) depends on the shape of the region V containing the molecular system. The solution of the problem employs (2.1) with the expansion (4.2) and utilizes the approximation $\tilde{\mathsf{F}}_V$ for $\mathscr{F}$ just mentioned. We show that the surface dependence stems from the reflected part $\tilde{\mathsf{f}}$ of the propagator $\tilde{\mathsf{F}}_V$, and that it can be neglected in short range integrals because amplitudes of spherical waves decrease as the inverse distance from a source. A bulk approximation which replaces $\mathscr{F}$ by $\tilde{\mathsf{F}}$ and extends integrations to all space can therefore be applied to reach the manifestly shape independent expression for the refractive index (4.15).

The final result of the screened theory is the generalized Onsager–Böttcher relation (7.19). It is the natural starting point for approximations extending the low-density result (3.11) to higher densities; but we have not yet explored its numerical consequences. The result (7.19) has much of the character of an expansion in $n\beta$ although the numerically important terms of $\mathscr{Q}$ must appear separately: the neglect of these terms means an approximation comparable to the decorrelation approximation (6.21) for the effective polarizability. Although (7.19) is evidently approximate (already through the use of $\tilde{\mathsf{F}}$) the term $n\beta$ on the right side is entirely correct; but the powers of $n\beta$ represent an approximation. The discussion below (7.19) explains why.

An important feature of the theory is that it is developed along two tracks, the unscreened and screened formulations. This dichotomy is actually a virtue because many of our results depend on both tracks. It is unfortunate, however, that the unscreened theory is encumbered with the surface dependence and the screened theory with the divergence problem. The surface problem cannot be avoided because any exact theory must have it although in numerical work the problem may be managed artificially through the use of a convergence factor on the propagator F.

The divergence problem can be avoided in several ways, but it is not obviously possible to derive all the results obtained here from such alternative formulations; and the very simple structure of the unified theory exhibited in I would undoubtedly be lost if the screened theory is modified. The most promising way of eliminating the surface dependence without introducing a divergence problem is to screen only the *transverse* part of the propagator F. How this might be carried out in practice can be seen from the solution of a similar problem in connection with macroscopic multiple scattering in the paper III.

The refractive index theory we have presented here is of course incomplete in several ways, first of all as regards numerical evaluation. Obvious extensions within the present framework could sum the two-body terms with the full propagator F or sum the three-body terms in an approximation similar to the one used to obtain (3.11). Approximations to the effective polarizability improving on the form (5.22) with (5.12) would also be very useful. On the conceptual side of the local field problem the present work has perhaps achieved more. Still a number of problems remain, such as providing an actual proof from the microscopic theory that the 'reflected part' of the propagator $\tilde{\mathsf{F}}_V$ has the proposed form.

APPENDIX

In this Appendix we shall indicate the role of the divergent terms of Q (introduced in (7.1)) by analysing a specific example. We look at a contribution coming from the term $M_6(n\alpha)^6$ of (4.15). We consider the contribution to Q from the terms of Y_{123456} containing the product of two delta functions $\delta_{13}\,\delta_{46}$ and no other. The delta functions reduce the sixth order term to a four-body term, and if we relabel the resulting variables as $\boldsymbol{x}_1$, $\boldsymbol{x}_2$, $\boldsymbol{x}_3$, and $\boldsymbol{x}_4$ (see figure 5) we then get

$$n^4\alpha^6\,\mathrm{Tr}\iiint \mathrm{d}\boldsymbol{x}_2\,\mathrm{d}\boldsymbol{x}_3\,\mathrm{d}\boldsymbol{x}_4\,\tilde{\mathsf{F}}_{13}\cdot\tilde{\mathsf{F}}_{31}\cdot\tilde{\mathsf{F}}_{12}\cdot\tilde{\mathsf{F}}_{24}\cdot\tilde{\mathsf{F}}_{42}\cdot\mathsf{T}_{21}$$
$$\times\,(g_{1234}-g_{123}-g_{124}-g_{13}\,g_{24}+g_{12}+g_{13}+g_{24}-1). \qquad \text{(A 1)}$$

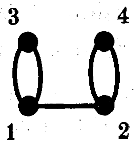

FIGURE 5. Numbering of coordinates $\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{x}_3, \boldsymbol{x}_4$ in the integral expression (A 1) analysed in the Appendix. No correlation functions are marked on this figure.

The factor n^4 arises because each delta function carries a factor n^{-1} with it. The contribution (A 1) to Q may be compared with the first term of the series $\mathscr{C}$, (7.19*b*), namely

$$m_2^0(n\beta)^2 = (n\beta)^2\,\mathrm{Tr}\int_{-v}\tilde{\mathsf{F}}_{12}\cdot\mathsf{T}_{21}(g_{12}-1)\,\mathrm{d}\boldsymbol{x}_2. \qquad \text{(A 2)}$$

The integral (A 1) diverges when $\boldsymbol{x}_3$ approaches $\boldsymbol{x}_1$ and when $\boldsymbol{x}_4$ aproaches $\boldsymbol{x}_2$; it converges at infinite distances between the points because of the *combination* of correlation functions and propagators. The divergences of (A 1) partly compensate the divergences of the term $m_2^0(n\tilde{\gamma})^2$ and thus partly justify the replacement of the formal polarizability $\tilde{\gamma}$ by β; but the divergences do not match in pairs and the bookkeeping is very complicated. So for details of the analysis of this problem we refer to Hynne & Bullough (1972) where an analogous but simpler case is treated.

Here we are primarily interested in the goodness of the approximation involved in using powers of β in the step from C^0 to $\mathscr{C}$. We therefore consider the contributions to the integrals (A 1) where the points $\boldsymbol{x}_3$ and $\boldsymbol{x}_4$ are widely separated from the points $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$. The correlation function in (A 1) then behaves asymptotically as $g_{12}(g_{34}-1)$, whereas the two sets of points are connected by four propagators ensuring convergence. It is convenient to write this combination of correlation functions as

$$g_{12}(g_{34}-1) = (g_{12}-1)(g_{34}-1)+(g_{34}-1). \tag{A 3}$$

The contribution of (A 1) through the first term on the right of (A 3) can be associated with a part of the term (A 2) namely that coming from two-body loops from each of the two factors β. In (A 2) these two loops are of course totally uncorrelated. But by adding the first term of (A 3) to the correlation function of (A 2) we get $(g_{12}-1)\,g_{34}$ and this accounts for the fact that the two molecules at $\boldsymbol{x}_3$ and $\boldsymbol{x}_4$ in the two loops cannot penetrate each other. Plainly, by using β^2 in $\mathscr{C}$ instead this exclusion effect is not properly accounted for so a 'fluctuation term' should be retained in Q to account for the difference. We believe that fluctuation terms of this sort are small enough so that they can actually be neglected. (This argument does not account for the difference between the screened and unscreened propagators used in Q and $\mathscr{C}$ so the argument needs to be taken still further.)

The second term on the right of (A 3) generates a contribution that may be compared with the last three-body term of (7.19*c*). To the short-range correlation function $(g_{34}-1)$ connecting the two loop-molecules in (A 3) there corresponds a self-correlation $n^{-1}\delta_{34}$ in (7.19*c*): the two molecules are replaced by one. Asymptotically the contribution from the last term of (A 3) equals the three-body term of (7.19*c*) apart from a factor

$$(n\kappa_T k_B T-1) = -2B_2 n+\dots. \tag{A 4}$$

(For this factor we have used the compressibility theorem of the grand ensemble (see, for example, Hill 1956, p. 236) and the expansion (3.18). Thus, except for quite dense fluids, we may neglect the four-body term in comparison with the three-body term exhibited in (7.19*c*).)

In summary, we have analysed the term (A 1), a typical divergent term from Q. We know from the exact (unscreened) theory that the divergences of Q must exactly eliminate the divergences from the powers of $\tilde{\gamma}$ in C^0, apart from the artificial mismatch introduced by the replacement of $\mathscr{F}$ by $\tilde{\mathrm{F}}$. Suppose now for a moment that elimination of divergences replaces powers of $\tilde{\gamma}$ by powers of β so that the term $m_2^0(n\tilde{\gamma})^2$ becomes (A 2). We then find that the term (A 2) is further corrected by a fluctuation term from (A 1) that accounts for the fact the self-interactions contained in the two factors β in β^2 are actually correlated. Such correlations are neglected in the step from (7.12) to (7.19). The neglected terms are considered numerically insignificant: it does not matter much that two different loop-molecules exclude each other from a small part of the entire region available. On the other hand, it is important to retain terms in which two loop-molecules are in fact identical; the three-body term shown as the last one in (7.19*c*) is important on that account. As figure 4 illustrates (contrast the last term shown with figure 5) this three-body term may be said to have two two-body self-interactions of two different molecules through the *same* third molecule.

This is as far as we can reasonably go here towards indicating the significance of the divergent terms of Q and justifying the neglect of them.

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