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## The Onsager reaction field as a screened self-interaction in refractive index theory

F HYNNE† and R K BULLOUGH‡

† Chemistry Laboratory III, HC Ørsted Institute, Universitetsparken 5, DK 2100 Copenhagen Ø, Denmark

‡ Department of Mathematics, University of Manchester Institute of Science and Technology, PO Box No 88, Sackville St, Manchester M60 1QD, UK

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**Abstract.** We give a microscopic derivation of a formula of Böttcher's type for the refractive index. In this a macroscopic cavity field replaces the Lorentz internal field and the polarizability is modified by many-body self-interactions. These combine both an Onsager type reaction field and a screened radiation reaction. The microscopic argument resolves apparent conflict between the two different macroscopic approaches to the internal field problem.

The real part of the reaction field is well approximated by a term involving only the pair-correlation function explicitly; but multiple scattering processes of all orders are summed and the whole hierarchy of correlations is concealed in an additional factor depending on the refractive index. This reaction field is a new result which accounts naturally for the choice of cavity size in the macroscopic theory.

The formula applies to a fluid of isotropically polarizable, nonpolar molecules. It will be more accurate than the Lorentz-Lorenz relation when the refractive index is close to unity. Additional multiple scattering terms not of the reaction type correct the formula and these make interpretation of experiments in terms of a simple Böttcher formula misleading for larger refractive indices. An analysis of experimental data for liquid argon seems to support these conclusions.

### 1. Introduction

The problem of the internal field inside a dielectric which is excited by an external field (oscillatory or not) has been a controversial one ever since the original work of Mossotti (1850), Clausius (1879), Lorentz (1880) and Lorenz (1880). Many-body theory solves the problem implicitly (Yvon 1937, Mazur and Mandel 1956, Bullough 1962, 1968, Bullough *et al* 1968, Bullough and Hynne 1968) by introducing the usual hierarchy of intermolecular correlation functions; but it does not free our understanding from sources of controversy because no very simple form of internal field factor emerges. For the same reason experimental results are not easily compared with the formulae of the theory. The purpose of this paper is to resolve an apparent conflict between two distinct and historically important 'macroscopic' approaches to the theory of the internal molecular field by showing that both are contained within the same microscopic theory. In this way we obtain a formula for the refractive index or dielectric constant which can be used to interpret experimental data as we shall show for liquid argon.

The two different approaches can be labelled succinctly as those of Lorentz (1909) on the one hand and of Onsager (1936) on the other. We shall consider a fluid of isotropically polarizable molecules with number density  $n$  and polarizability  $\alpha(\omega)$  at the frequency  $\omega$ . Lorentz's formula for the refractive index  $m(\omega)$  is the famous Lorentz-Lorenz relation

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

Modern methods (Darwin 1924, Born and Wolf 1959, Bullough 1968, to be referred to as I) justify this formula completely for a *continuous* distribution of molecules; but the continuous distribution means that from the microscopic point of view all intermolecular correlations are ignored (Rosenfeld 1951, I, Bullough 1969b).

However, Lorentz simply adopted a 'macroscopic' model of a dielectric in which each molecule is supposed to be exposed to a total field consisting of the macroscopic (Maxwell) field in the dielectric corrected by the presence of molecular dipoles. The more significant part of this correction is due to distant dipoles. The total field due to these was computed according to macroscopic dielectric theory as the field inside a spherical cavity of arbitrary radius centred on the reference molecule. The dipolar distribution outside the sphere carries with it an effective charge on the surface of the sphere and this surface charge corrects the field at the centre of the sphere from the Maxwell value  $\mathcal{E}$  to  $\frac{1}{3}(m^2+2)\mathcal{E}$ , that is, the field is enhanced by the 'Lorentz internal field factor'  $\frac{1}{3}(m^2+2)$ . Formula (1.1) then follows.

It is important to note that Lorentz's field is computed for the dipolar distribution which exists in the presence of the reference molecule. The spherical cavity is not a physical cavity and indeed Lorentz further corrected his field by a local field supposedly due to the actual local molecular distribution inside the sphere. By moderately sophisticated microscopic arguments Rosenfeld (1951) justified this approach by finding that (1.1) must be replaced by

$$\left(\frac{m^2(\omega)-1}{4\pi}\right)\left(\frac{3}{m^2(\omega)+2}\right) = \frac{n\alpha(\omega)}{1 - \frac{2}{3}ik_0^3\alpha(\omega) - n\alpha(\omega)J(\omega)} \quad (1.2)$$

where  $J(\omega)$  is an integral involving the two-body intermolecular correlation function  $g_2(r)$ , and  $k_0 \equiv \omega c^{-1}$ . We now know from the exact microscopic theory (eg Mazur and Mandel 1956, Bullough 1962, 1967 to be referred to as II), however, that  $J(\omega)$  is only the first term of an infinite series of terms involving  $g_3(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)$ ,  $g_4(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \mathbf{x}_4)$ , etc, that is, involving simultaneous correlation of three, four, and any number, of particles. Partial summation and rearrangement of this series enables us to change the apparent form of this generalization of the Lorentz-Lorenz formula (1.2). This is why Lorentz's approach is not necessarily the best macroscopic approach and it is this which is also the key to the development exhibited in this paper.

We should add at this point that the small purely imaginary term in the denominator of (1.2) is of great theoretical and practical interest; it describes the effect of radiation reaction on an individual radiating dipole; and though small ( $\sim 10^{-9}$  in  $\text{Re}(m)$  away from the resonances of  $\alpha(\omega)$ ) it makes a very significant contribution to the total optical scattering cross section of the many-particle system (Bullough *et al* 1968, to be referred to as III, Bullough and Hynne 1968, to be referred to as IV). This kind of radiation reaction field exhibited in (1.2) figures greatly in the theoretical analysis we give below.

Equation (1.1) on the other hand shows correctly that there is no scattering from the continuum.

An apparently quite different approach to a continuum model is that of Onsager (1936) who pointed out that in any such model of dielectric polarization the internal field acting on a single molecule should be split into two parts: a cavity field which is the field which would exist inside a real physical cavity surrounding the molecule in the absence of that molecule, and a second *reaction field* correcting the cavity field by the polarization of the medium induced by the molecular dipole which is actually present in the molecule inside the cavity.

Onsager was concerned with polar liquids where the distinction is essential because, as he showed, only the cavity field influences the orientation of the permanent dipole. The point of view is apparently applicable to any dipole inside the cavity, however, either permanent or induced. In the model introduced by Bell (1931) and Onsager (1936) and adopted by Böttcher (1942, 1952) one considers a molecule at the centre of a spherical cavity (radius  $a$ ) in a continuum of refractive index  $m$  and dielectric constant  $m^2$ . The molecular dipole moment  $\mathbf{p}$  inside the cavity induces a reaction field  $\mathbf{R} = f\mathbf{p}$  (say) at the site of the molecule and  $f$  is given by (Onsager 1936)

$$f = \frac{2}{a^3} \left( \frac{m^2 - 1}{2m^2 + 1} \right). \quad (1.3)$$

We shall refer to this field  $\mathbf{R}$  as the 'Onsager reaction field'. If the electric field in the medium at points distant from the cavity is uniform and denoted  $\mathcal{E}$ , it is  $3m^2(2m^2 + 1)^{-1}\mathcal{E}$  inside the empty cavity. When this is combined with the reaction field one obtains the relation

$$\left( \frac{m^2 - 1}{4\pi} \right) \left( \frac{2m^2 + 1}{3m^2} \right) = n \frac{\alpha}{1 - f\alpha}. \quad (1.4)$$

This form (1.4) with  $f$  given by (1.3) and  $a$  a constant has been introduced and extensively used by Böttcher (1952, and earlier works cited therein). We shall refer to it as the 'Böttcher formula' and the underlying model as the cavity model. In equation (1.4) the cavity field replaces the Lorentz internal field and the reaction field modifies the polarizability, which is replaced by an effective polarizability

$$\alpha^* = \alpha(1 - f\alpha)^{-1}. \quad (1.5)$$

This polarizability  $\alpha^*$  includes the effect of the interaction of the molecule with itself via the surrounding dielectric.

The two equations (1.1) and (1.4) have very different forms<sup>†</sup>. It is the main purpose of the paper to show that in a more general formulation of the theory there is nevertheless no actual conflict between the two expressions. However, this means extending both formulae, and (1.1) and (1.4) as they stand are certainly discrepant: we now show that a very different dependence on density in these two expressions at low densities is potentially important. We transform the Lorentz-Lorenz relation to the Böttcher form (1.4): the reaction term in the denominator of (1.5) for the Lorentz-Lorenz relation

<sup>†</sup> Although the right side of (1.2) is of the form of (1.5) the terms in the denominator are of a rather different character from that of the term  $f\alpha$  in (1.5). For only the radiation reaction term is a self-interaction of the type of  $f\alpha$  and this term is entirely imaginary.

takes the form

$$(f\alpha)_{LL} = \frac{2(m^2 - 1)^2}{(2m^2 + 1)(m^2 + 2)}. \tag{1.6}$$

This exhibits the most important difference between the two formulae (1.1) and (1.4): when the radius  $a$  of the cavity has a fixed value, as Böttcher (1942, p 947) assumes, the Onsager reaction field correction  $f\alpha$  in equation (1.3) is linear in  $n\alpha \simeq (m^2 - 1)/4\pi$  for small  $n\alpha$ , whereas the reaction field correction (1.6) of the Lorentz–Lorenz relation is quadratic in  $n\alpha$  for small  $n\alpha$ . If the reaction field is in fact linear, the experimentally determined Lorentz–Lorenz function must increase linearly as a function of  $n$  for small densities, go through a maximum, and decrease for larger densities (Onsager 1936, Böttcher 1952)—unless other corrections to the simple Lorentz model are large enough to blur this effect. Experiments (Michels and Botzen 1949) seem to indicate such a variation of the Lorentz–Lorenz function and the calculation of de Boer *et al* (1953) seems to confirm this for the corresponding Clausius–Mossotti relation.

In contrast to the Lorentz–Lorenz relation, the Böttcher formula contains a completely free parameter  $a$ . By a rather crude argument Böttcher (1942, footnote to p 947) concludes that  $a$  should be chosen as the (average) *molecular radius*. Evidently, the cavity model needs justification by microscopic arguments and these would then also provide an expression for the parameter of the model†. It is precisely these problems we solve in this paper; and we do this by *recasting* the microscopic theory into a form which generalizes the Böttcher formula (1.4) rather than the Lorentz–Lorenz relation (1.1). This reformulation follows in a very natural way from the ‘screened’ microscopic theory which has been reported (Hynne 1970, to be referred to as V). Therefore we now briefly describe some particular features of the theories III, IV and V which are essential to the understanding of the argument of this paper.

Microscopic theories (Yvon 1937, Hoek 1939, Mazur and Mandel 1956, Bullough 1962, 1965, and the references I, II, III, IV) usually result in the expression (1.2) with  $J(\omega)$  a power series in  $n\alpha(\omega)$  involving all orders of intermolecular correlation and thus describing all orders of multiple scattering. The papers III and IV in particular report (in brief) the solution to the whole multiple scattering problem. One result there‡ is an expression for  $(m^2(\omega) - 1)/4\pi$  as a power series in  $n\alpha(\omega)$  in which the contribution to the Lorentz internal field factor is absorbed in a series of integrals which are initially conditionally convergent. This is accomplished by first extending the domains of integration to include the singularities of the integrands; then the divergent integrals are interpreted in a generalized function sense. A typical divergent integral that appears in the theory by this procedure has the form

$$\int_V \mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) f(\mathbf{x}') d\mathbf{x}' \tag{1.7}$$

in which  $f(\mathbf{x}')$  is some function continuous at  $\mathbf{x}$ . The integration is taken over the macroscopic region  $V$  containing  $\mathbf{x}$ . The tensor  $\mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega)$  is a ‘photon propagator’ defined by

$$\mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) \equiv (\nabla\nabla + k_0^2 \mathbf{U}) \left( \frac{\exp(ik_0 r)}{r} \right) \quad k_0 \equiv \omega c^{-1}; r = |\mathbf{x} - \mathbf{x}'| \tag{1.8}$$

† This problem has also been attacked by Linder and Hoernschemeyer (1967). We comment on their paper in the long footnote to p 1288.

‡ cf equation (11) and the definitions (9) and (10) of III.

where  $\mathbf{U}$  is the unit tensor. By this construction the integral (1.7) is then to be interpreted as

$$\lim_{v \rightarrow 0} \int_{V-v} \mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) f(\mathbf{x}') d\mathbf{x}' + \lim_{v \rightarrow 0} \int_v \mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) f(\mathbf{x}') d\mathbf{x}'. \tag{1.9}$$

The first term is the original conditionally convergent integral in which the exclusion of a 'vanishingly small sphere'  $v$  centred on  $\mathbf{x}$  ensures the convergence. (Below we shall usually omit the limit symbols in front of the integrals.) The second integral is then defined as  $-\frac{4}{3}\pi\mathbf{U}f(\mathbf{x})$ , and we see that this corresponds to a generalized function interpretation of this otherwise divergent integral: for if the integral of  $\mathbf{F}$  exists it must be isotropic and its trace is the integral of

$$\nabla^2|\mathbf{x} - \mathbf{x}'|^{-1} = -4\pi\delta(\mathbf{x} - \mathbf{x}')$$

(cf III, and again Bullough 1970a, 1970b). This interpretation can be carried systematically and without ambiguity through the theory. Evidently it is simply a series of such terms which becomes the Lorentz field factor  $\frac{1}{3}(m^2 + 2)$  in an expression like (1.1)†.

A second convenience of the theory of great importance for the present derivation is to carry radiation reaction through it as one-particle self-correlation. This means the interpretation

$$\int \mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega)\delta(\mathbf{x} - \mathbf{x}') d\mathbf{x}' \equiv \frac{2}{3}ik_0^3\mathbf{U} \tag{1.10}$$

which is merely the finite part of this otherwise undefined integral. This interpretation is consistent with radiation reaction as it is exhibited in (1.2).

In the papers III and IV the long range of the intermolecular interaction (1.8) which includes the radiation field forced us to consider macroscopic systems of only finite extent. The difficulty this introduces was there isolated in the form of a special class of terms we call surface terms: these appear at three-body and all higher orders of intermolecular correlation. These surface terms can, however, be summed and concealed in the 'screened' photon propagator (V)

$$\tilde{\mathbf{F}}(\mathbf{x}, \mathbf{x}'; \omega) = (\nabla\nabla + m^2(\omega)k_0^2\mathbf{U}) \left( \frac{\exp(im(\omega)k_0r)}{m^2(\omega)r} \right). \tag{1.11}$$

This form obviously 'screens' scattering processes described in terms of (1.8) so that they may be said to be taking place in the medium of refractive index  $m$  rather than *in vacuo*.

To obtain the closed form (1.11) it is necessary to introduce an approximation, the bulk approximation described in V. This has the effect of eliminating surface effects and making the theory translationally invariant‡. We shall call this approximate theory the 'screened theory'. The theory described in III and IV employs the unscreened (free field) interaction  $\mathbf{F}$  of (1.8). We call this form of the theory the 'unscreened theory'.

† Compare the footnote on p 1285.

‡ These surface effects depend explicitly on the surface geometry of the macroscopic system. Associated with them are terms which we call 'surface terms' and which do not depend on that geometry (they arise at lower rather than upper limits of integrals: lower limits involve points inside the material). In this paper we use 'surface terms' in a narrow sense as 'surface terms' associated with the screening processes converting (1.8) to (1.11). There are terms classified as surface terms in III and IV which do not contribute to the screening process (cf V).

The screened theory is developed from the unscreened theory in two stages. The first stage can be conceived simply as a *rearrangement* of the terms of the unscreened theory by formulating the results of the unscreened theory in terms of a photon propagator  $\mathcal{F}(\mathbf{x}, \mathbf{x}'; \omega)$  which can be defined as a series of 'unscreened' terms. Thus the formulation in terms of  $\mathcal{F}$  is *entirely* equivalent to the unscreened theory and we shall therefore call it the 'exact screened theory' and  $\mathcal{F}(\mathbf{x}, \mathbf{x}'; \omega)$  the 'exact screened propagator' in § 3 where frequent reference is made to it. From the intermediate stage the 'screened theory' is reached by applying what we have called the bulk approximation: this involves in particular the replacement of  $\mathcal{F}(\mathbf{x}, \mathbf{x}'; \omega)$  (which is a series) by  $\bar{\mathbf{F}}(\mathbf{x}, \mathbf{x}'; \omega)$ , which is given as a closed form by equation (1.11). Although this replacement makes the 'screened theory' particularly easy to understand, the existence of the exact screened theory is very important for the development of this paper because it enables us to resolve certain ambiguities which appear in the screened theory entirely because of the bulk approximation. Apart from such ambiguities comparisons show that the bulk approximation is, as one would expect, a good approximation but this question still needs further investigation.

The screened theory yields an expression for  $(m^2(\omega) - 1)/4\pi$  which is analogous to that obtained in III and IV. But because  $\bar{\mathbf{F}}$  replaces  $\mathbf{F}$  we find a 'screened Lorentz term'  $-(4\pi/3m^2)\mathbf{U}$  replacing the  $-(4\pi/3)\mathbf{U}$  from (1.9) and a 'screened self-interaction term' containing a screened radiation reaction  $\frac{2}{3}im(\omega)k_0^3\mathbf{U}$ , again from a self-correlation, replacing (1.10). An important point is that an additional real valued reaction field accompanies this screened radiation reaction. The derivation in this article of the generalization of the Böttcher formula (1.4) is based on the summation of precisely these two types of contributions. Thus the central part of our argument is the summation of a double series. This is carried out in a formal way in the following section (§ 2) and the argument is completed in § 3 which is entirely devoted to the screened self-interaction. In § 4 the generalized Böttcher formula reached in § 3 is considered in the light of available experimental data. We summarize the results and conclusions of the paper in § 5.

The main result of the paper is the generalized Böttcher formula (3.12) (with associated definitions in (3.9*b*) and (2.9*b, c*)). It appears in simplified form in (4.1). The complex reaction field is exhibited in approximate form in (3.15).

## 2. Derivation of the fundamental formula

An obvious starting point for any semiclassical refractive index theory is the equation

$$\mathbf{P}^{\text{in}}(\mathbf{x}, \omega) = \rho(\mathbf{x})\alpha(\omega) \left( \mathbf{E}(\mathbf{x}, \omega) + \int_V \mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) \cdot \mathbf{P}^{\text{in}}(\mathbf{x}'; \omega) d\mathbf{x}' \right). \quad (2.1)$$

$\mathbf{P}^{\text{in}}(\mathbf{x}, \omega)$  is the instantaneous dipole density for a system of isotropically polarizable molecules of polarizability  $\alpha(\omega)$  occupying an arbitrary configuration of sites  $\mathbf{x}_j^{\text{in}}$ . The (instantaneous) particle density is

$$\rho(\mathbf{x}) = \sum_j \delta(\mathbf{x} - \mathbf{x}_j^{\text{in}}) \quad (2.2)$$

and its ensemble average will be denoted by  $n$ ; the system is supposed macroscopically homogeneous within a region  $V$  and  $n$  is independent of  $\mathbf{x}$  inside  $V$ . Equation (2.1) states that the total field polarizing the  $j$ th molecule at  $\mathbf{x}_j^{\text{in}}$  is the sum of the external

field  $E$  and the field due to all the molecules induced by the dipole density  $P^{in}(x', \omega)$ . This field includes the self-field of molecule  $j$  by the prescription (1.10). The equation (2.1) has been deduced as an approximate consequence of a second quantized theory as was reported in III.

Equation (2.1) readily yields the generalized Lorentz–Lorenz relation for which it is well adapted: the argument is sketched in III. But the same equation (2.1) can be recast as a screened integral equation and the generalized Böttcher formula can be derived from this as we show in § 3. This indicates the strict equivalence of the two theories and as a further check we indicate in § 3 (in the note below (3.10)) how the arguments for the Böttcher formula used there can themselves be used to obtain the Lorentz–Lorenz formula from a version of (2.1).

Rather than attempting to move from one integral equation to another at this stage however it is convenient to start instead from one of the simpler results of the screened theory: this is the result for the refractive index expressed in terms of the screened photon propagator  $\bar{F}$  and was reported in V. The result is

$$\frac{m^2(\omega) - 1}{4\pi} = \sum_{p=1}^{\infty} (n\alpha(\omega))^p \chi_p(m, \omega) \tag{2.3a}$$

in which  $\chi_1(m, \omega) \equiv 1$  and, for  $p \geq 2$

$$\chi_p(m, \omega) \equiv \mathbf{u} \mathbf{u} : \int d\mathbf{x}_2 \int d\mathbf{x}_3 \dots \int d\mathbf{x}_p \bar{F}_{12} \cdot \bar{F}_{23} \dots \bar{F}_{p-1p} \exp\{im(\omega)\mathbf{k}_0 \cdot (\mathbf{x}_p - \mathbf{x}_1)\} Y_{123\dots p} \tag{2.3b}$$

In equation (2.3b) all integrations are taken over all space. The wavevector  $\mathbf{k}_0$  has the length  $k_0 = \omega c^{-1}$  and is orthogonal to the polarization unit vector  $\mathbf{u}$  but otherwise  $\mathbf{k}_0$  and  $\mathbf{u}$  have arbitrary directions. Here we use indices to denote position variables:  $\bar{F}_{12} \equiv \bar{F}(\mathbf{x}_1, \mathbf{x}_2; \omega)$ , for example, and the function  $Y_{123\dots p} = n^{-p} \mathcal{Y}_{123\dots p}$  depends on  $\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_p$  whilst  $\mathcal{Y}_{123\dots p}$  is the ensemble average of the configurational dependent function  $\mathcal{Y}_{123\dots p}^{in}$ , which is given by the recurrence relation

$$\begin{aligned} \mathcal{Y}_1^{in} &\equiv \rho_1 \equiv \rho(\mathbf{x}_1) \\ \mathcal{Y}_{123\dots p}^{in} &= \mathcal{Y}_{123\dots p-1}^{in} \rho_p - \sum_{q=1}^{p-1} \mathcal{Y}_{12\dots q}^{in} \mathcal{Y}_{q-1\dots p} \end{aligned} \tag{2.4}$$

These results reported in V are actually derived from (2.1). The precise details of the argument are given in the Appendix to the present paper. We show there that (2.1) transforms to the entirely equivalent integral equation exhibited in (3.6). This contains the screened photon propagator  $\mathcal{F}$  and is the key equation of the whole theory. We show in the Appendix also how both equation (2.3) and the associated recurrence relation (2.4) follow from the integral equation (3.6) in the bulk approximation. The complete argument from (2.1) to each and every result of this paper is therefore available on reference to the arguments developed in the Appendix.

The result (2.3) depends on  $\bar{F}$  rather than  $\mathcal{F}$ : it is to that extent conceptually the more simple. We therefore now return to it and will develop it.

The expression (2.3) is actually a very complicated implicit equation for  $m$  given  $\alpha$ ,  $n$ , and the temperature. Because we lack knowledge about the  $p$  body correlation functions, especially for larger  $p$  and in dense fluids, a general solution to equation (2.3) is unattainable. However, there are important contributions to each term  $\chi_p(m, \omega)$  of



(2.3) which are (formally) independent of the correlation functions. These are the terms with products of powers of the screened Lorentz term and powers of the screened self-interaction. The screened Lorentz terms are concealed in the integrals (2.3*b*) as the contributions from the 'small spheres' given as we described in § 1 by

$$\lim_{v \rightarrow 0} \int_v \bar{\mathbf{F}}(\mathbf{x}, \mathbf{x}'; \omega) d\mathbf{x}' = \frac{-4\pi}{3m^2(\omega)} \mathbf{U}. \tag{2.5}$$

As in (1.9) the integration in (2.5) is taken over a vanishingly small sphere centred on  $\mathbf{x}$ . Every integral of the multiple integral (2.3*b*) is then defined as the sum of the contribution from the small sphere, defined by (2.5), and the conditionally convergent integral now taken over *all space* outside the small spherical region. We stress that the 'small spheres' appear for strictly mathematical reasons in a mathematically rigorous argument with initially convergent integrals and we nowhere introduce (or need to introduce) any physical cavity.

The screened self-interaction† is formally given by the analogue of (1.10)

$$\mathbf{r}(\omega) \equiv \int \bar{\mathbf{F}}(\mathbf{x}, \mathbf{x}'; \omega) \delta(\mathbf{x} - \mathbf{x}') d\mathbf{x}'. \tag{2.6}$$

For the moment it can be thought of as simply the convergent part of the integral which is  $\frac{2}{3}im(\omega)k_0^3\mathbf{U}$ . However the integral requires a very careful analysis for its proper interpretation and we shall defer this until the next section. The problem is that we need to isolate a real valued reaction field in the self-interaction as well as the screened radiation reaction.

Our procedure now is to isolate those contributions to  $(m^2 - 1)/4\pi$  in (2.1) which do not depend explicitly on the correlation functions. We therefore write equation (2.1) as

$$\frac{m^2 - 1}{4\pi} = \frac{3m^2}{4\pi} L(t, w) + C(n\alpha) \tag{2.7}$$

in which  $L(t, w)$  is the double series

$$L(t, w) = \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} a_{ij} t^i w^j \tag{2.8}$$

containing all terms obtained by extracting either the Lorentz term or the self-interaction associated with each  $\bar{\mathbf{F}}$  tensor. The self-interaction is an isotropic tensor:  $\mathbf{r}(\omega) = r(\omega)\mathbf{U}$  and  $w \equiv \alpha(\omega)r(\omega)$ , whereas  $t \equiv \frac{4}{3}\pi m^{-2}(\omega)n\alpha(\omega)$ . The second term of equation (2.7) is the power series in  $n\alpha$  of the remaining terms from equation (2.1) all of which explicitly contain correlation functions

$$C(n\alpha) = C_2(n\alpha)^2 + \left\{ C_3 + \frac{1}{n}C'_3 + \left( \frac{16\pi}{3m^2} + 2\frac{w}{n\alpha} \right) C_2 \right\} (n\alpha)^3 + \dots \tag{2.9a}$$

$$C_2 = \mathbf{u}\mathbf{u} : \int_{-v} d\mathbf{x}' \bar{\mathbf{F}}(\mathbf{x}, \mathbf{x}'; \omega) \exp\{im\mathbf{k}_0 \cdot (\mathbf{x}' - \mathbf{x})\} (g_2(\mathbf{x}, \mathbf{x}') - 1) \tag{2.9b}$$

† Screening of the self-interaction has been considered in effect by Doniach (1963) in an interesting paper. Reference to the quantal basis of the present theory (eg ref. III) shows that a result only hazarded by Doniach is here proved—namely that (1.10) is 'screened' by a factor  $m(\omega)$ .

$$C_3 = \mathbf{uu} : \int_{-v} dx' \int_{-v} dx'' \bar{\mathbf{F}}(\mathbf{x}, \mathbf{x}'; \omega) \cdot \bar{\mathbf{F}}(\mathbf{x}', \mathbf{x}''; \omega) \exp\{im\mathbf{k}_0 \cdot (\mathbf{x}'' - \mathbf{x})\} \\ \times (g_3(\mathbf{x}, \mathbf{x}', \mathbf{x}'') - g_2(\mathbf{x}, \mathbf{x}') - g_2(\mathbf{x}', \mathbf{x}'') - g_2(\mathbf{x}'', \mathbf{x}) + 2) \tag{2.9c}$$

$$C'_3 = \mathbf{uu} : \int dx' \bar{\mathbf{F}}(\mathbf{x}, \mathbf{x}'; \omega) \cdot \bar{\mathbf{F}}(\mathbf{x}', \mathbf{x}; \omega) (g_2(\mathbf{x}, \mathbf{x}') - 1). \tag{2.9d}$$

The integrations with respect to  $\mathbf{x}'$  and  $\mathbf{x}''$  in (2.9b) and (2.9c) are taken over all space except for vanishingly small spheres centred on  $\mathbf{x}$  and  $\mathbf{x}'$  respectively. (These regions are symbolized  $-v$ .) The integral  $C'_3$  is actually strongly divergent at the lower limit  $\mathbf{x}' \simeq \mathbf{x}$ , but we must discuss this problem in the next section.

There are two kinds of self-correlations in the terms (2.3b). The one we sum here connects two successive indices, whereas the second kind connects nonsuccessive indices and therefore does not 'cover' an  $\bar{\mathbf{F}}$  tensor. It is necessary to integrate all the  $\delta$  functions out before the small spheres are taken out. In this way one avoids treating a self-correlation of the second kind as a self-correlation of the first kind by the limiting process in equation (2.5). With this prescription we can now sum the double power series (2.8) to all orders.

The term  $a_{ij}t^i w^j$  in (2.8) is of the order  $p = i + j$  in  $n\alpha$ . The complete contribution  $L_p(t, w)$  to the  $p$ th order comes from the term  $4\pi(3m^2)^{-1}(n\alpha)^p \chi_p(m, \omega)$  and we can write  $L(t, w)$  as the single sum

$$L(t, w) = \sum_{p=1}^{\infty} L_p(t, w) \tag{2.10}$$

with

$$L_p(t, w) = \sum_{i=0}^{p-1} a_{(p-j)} t^{p-j} w^j$$

in which  $L_1(t, w) = t$  because  $\chi_1(m, \omega) = 1$ . For  $p \geq 2$  we can find a recurrence relation for the terms  $L_p(t, w)$  by substituting the averaged right hand side of the recurrence relation (2.4) for  $\mathcal{Y}_{12\dots p}^{in}$  in the expression (2.3b) for  $\chi_p(m, \omega)$ . By equation (2.4)  $\mathcal{Y}_{12\dots p}$  can be expressed in terms of correlation functions. Only terms which contain no correlations other than self-correlations of the first kind contribute to  $L_p(t, w)$ . In the averaged first term of (2.4) the first and last points are correlated so this term can only contribute the pure self-interaction term, and we see that this appears with coefficient  $a_{1(p-1)} = 1$ , so the contribution from the first term of (2.4) is  $tw^{p-1}$ . The averaged second term of (2.4) produces a sum of terms each of which contains a Lorentz factor  $(-4\pi/3m^2)$  coming from the  $\bar{\mathbf{F}}_{q(q+1)}$  tensor in  $\chi_p(m, \omega)$  that connects the two  $\mathcal{Y}$  functions. Because the two remaining parts of the multiple integral are both covered by  $\mathcal{Y}$  functions, the complete multiple integral in each term of the sum can be expressed as a product of two lower order  $L_q(t, w)$  functions, and we obtain the following recurrence relation for the terms  $L_p(t, w)$ :

$$L_p(t, w) = tw^{p-1} + \sum_{q=1}^{p-1} L_q(t, w)L_{p-q}(t, w) \tag{2.11}$$

in which, by definition, the sum gives nothing for  $p = 1$ . When the right side of (2.11)

is substituted for  $L_p(t, w)$  in the series (2.10) for  $L(t, w)$  we immediately obtain the following relation for  $L(t, w)$ :

$$L(t, w) = \frac{t}{1-w} + (L(t, w))^2 \tag{2.12}$$

from which  $L(t, w)$  can be obtained in closed form. By equation (2.12) we see that  $L(t, w)$  has the very suggestive property

$$L(t, w) = L\left(\frac{t}{1-w}, 0\right). \tag{2.13}$$

Since  $L(t, 0)$  is the sum of all pure Lorentz terms, equation (2.13) shows that the effect of including the self-interactions is that the polarizability  $\alpha(\omega)$  is replaced by

$$\tilde{\gamma}(\omega) \equiv \frac{\alpha(\omega)}{1-r(\omega)\alpha(\omega)}. \tag{2.14}$$

This is an effective polarizability of the many-body system and it is a very natural generalization of the complex polarizability which appears implicitly in (1.2):

$$\gamma(\omega) \equiv \frac{\alpha(\omega)}{1-\frac{2}{3}ik_0^3\alpha(\omega)}. \tag{2.15}$$

We now complete the derivation of the fundamental dispersion formula by substituting  $L(t, w)$  given by equation (2.7) into the identity

$$L(t, w)(1-L(t, w)) = \frac{t}{1-w} \tag{2.16}$$

obtained from equation (2.12): in this way we find

$$\left(\frac{m^2(\omega)-1}{4\pi}\right)\left(\frac{2m^2(\omega)+1}{3m^2(\omega)}\right) = n\frac{\alpha(\omega)}{1-r(\omega)\alpha(\omega)} + \frac{m^2(\omega)+2}{3m^2(\omega)}C(n\alpha) + \frac{4\pi}{3m^2(\omega)}C^2(n\alpha). \tag{2.17}$$

This is the generalization of equation (1.4) and the fundamental formula from which we shall obtain explicit expressions below. It is so far a formal result because the expression (2.6) is a formal one. In the following section we shall actually analyse the screened self-interaction  $r(\omega)$  and see how to interpret the result (2.17) as a physically meaningful relation.

### 3. The screened self-interaction

We now discuss the expression (2.6) for the screened self-interaction. As it stands of course the integral is certainly undefined. It may then appear that it is sufficient simply to make a convergent part interpretation in exact analogy with (1.10). In this case the screened self-interaction  $r(\omega)$  is just the screened radiation reaction  $\frac{2}{3}im(\omega)k_0^3\mathbf{U}$ . The problem is however that we need to extract a physically significant real valued reaction field term: as it stands the real part of (2.6) diverges.

By representing the  $\mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega)$  propagator by the Neumann solution of the integral equation which defines it (V, Bullough 1970b) one obtains the self-interaction (2.6) as a formal series of integrals containing only 'closed loops' of unscreened  $\mathbf{F}$  propagators (the reason for the usage 'close loops' is self-evident from the figure 1(c) of V). Such closed

loops describe (virtual) scattering processes in which photons emerge from a single particle, interact with the rest of the dielectric and return to the original particle. The first term of this series is the unscreened self-interaction given by (1.10). The divergent part of this integral is related to the electron self-energy as has been shown explicitly (Bullough 1969a, Bullough and Caudrey 1971): the convergent part gives the radiation reaction which appears in (1.2) and the convergent part interpretation exhibited in (1.10) has been used systematically without inconsistency in the unscreened theory (III).

But it can be seen now that the higher terms in the series expansion of the screened self-interaction  $r(\omega)$  are divergent†, and that these divergences are of a kind different from the electron self-energy. We can trace them back to a splitting of what were originally convergent terms into pairs or multiples of terms whose divergences are mutually compensating. This artificial procedure is forced upon us by the definition of the photon propagator  $\mathcal{F}(x, x'; \omega)$  in the exact screened theory described in § 1, a choice dictated by the wish to obtain the simple form  $\tilde{\mathbf{F}}(x, x'; \omega)$  in the bulk approximation. This choice of  $\mathcal{F}(x, x'; \omega)$  makes the screened self-interaction as defined by (2.6) with  $\mathcal{F}$  replacing  $\tilde{\mathbf{F}}$  inadequate: it still diverges and fails to include all the relevant self-interaction (closed loop) terms. But now it is plain that the inclusion of the remaining closed loop terms in the screened self-interaction is exactly what is needed to eliminate these divergences.

Once the bulk approximation has been used and  $\tilde{\mathbf{F}}$  introduced the matching of compensating divergences is no longer simple. We shall therefore appeal to the exact screened theory for the complete elimination of the divergences from the theory. However, because we shall ultimately work within the bulk approximation and use the results of § 2, it is instructive to see how the divergences can be eliminated from the lowest order divergent terms of equation (2.7). These are the self-interaction  $nx^2r(\omega)$  from  $3m^2(4\pi)^{-1}L(t, w)$  and the term  $C'_3$  given by (2.9d) from  $C(nx)$ . The argument at lowest order goes in detail as follows. By using the integral equation that defines  $\tilde{\mathbf{F}}(x, x'; \omega)$  (equation (11) of V, now taken in the bulk approximation) we can split the unscreened self-interaction (1.10) off (compare Bullough 1969a)

$$r(\omega) = \int \mathbf{F}(x, x'; \omega)\delta(x - x') dx' + \frac{m^2(\omega) - 1}{4\pi} \int \mathbf{F}(x, x'; \omega) \cdot \tilde{\mathbf{F}}(x', x; \omega) dx'. \tag{3.1}$$

To first order in  $nx$  we can write  $n\alpha \simeq (m^2 - 1)/4\pi$  and replace the first  $\tilde{\mathbf{F}}$  tensor in  $C'_3$  (equation (2.9d)) by  $\mathbf{F}$  to get

$$n^2\alpha^3 C'_3 \simeq n\alpha^2 \frac{m^2 - 1}{4\pi} \mathbf{u}\mathbf{u} : \int \mathbf{F}(x, x'; \omega) \cdot \tilde{\mathbf{F}}(x', x; \omega)(g_2(x, x') - 1) dx'. \tag{3.2}$$

This combines with the second term in  $nx^2r(\omega)$  taken from (3.1) to give the integral

$$n\alpha^2 \left( \frac{m^2 - 1}{4\pi} \mathbf{u}\mathbf{u} : \int \mathbf{F}(x, x'; \omega) \cdot \tilde{\mathbf{F}}(x', x; \omega) g_2(x, x') dx' \right). \tag{3.3}$$

This expression is convergent at the lower limit (ie at the point  $x$ ) because  $g_2(x, x')$  vanishes there.

We shall not pursue this matching of divergences further but instead now deal with another difficulty of equation (3.1): the second integral is also not convergent at its

† The next term in the series is  $(m^2 - 1)(4\pi)^{-1} \int \mathbf{F}(x, x'; \omega) \cdot \mathbf{F}(x', x; \omega) dx'$  in which the integrand diverges as  $r^{-4}$  in the neighbourhood of  $r \equiv |x - x'| = 0$ .

upper limit (ie for  $|\mathbf{x} - \mathbf{x}'| \rightarrow \infty$ ) where it at least oscillates finitely. This divergence can be systematically removed by a prescription of the bulk approximation. We can define the integral by Fourier transforming to  $\mathbf{k}$  space and neglecting the surface contribution. We split the tensors  $\mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega)$  and  $\tilde{\mathbf{F}}(\mathbf{x}, \mathbf{x}'; \omega)$  into their longitudinal and transverse parts: the longitudinal parts are the pure Coulomb field parts and the transverse parts are the contributions of the radiation field so that the splitting is achieved as follows (I):

$$\mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) = \nabla \nabla |\mathbf{x} - \mathbf{x}'|^{-1} + \mathbf{R}(\mathbf{x}, \mathbf{x}'; \omega) \tag{3.4a}$$

$$\tilde{\mathbf{F}}(\mathbf{x}, \mathbf{x}'; \omega) = m^{-2}(\omega) \nabla \nabla |\mathbf{x} - \mathbf{x}'|^{-1} + \tilde{\mathbf{R}}(\mathbf{x}, \mathbf{x}'; \omega) \tag{3.4b}$$

which expressions define the radiation field contributions  $\mathbf{R}$  and  $\tilde{\mathbf{R}}$ .

We can now evaluate the second integral of equation (3.1) as an integral in  $\mathbf{k}$  space by Parseval's theorem, and we find that the radiation field contributions alone give precisely  $\frac{2}{3}i(m(\omega) - 1)k_0^3 \mathbf{U}$ : this combines with the first term of (3.1) in the interpretation (1.10) to yield the screened radiation reaction  $\frac{2}{3}im(\omega)k_0^3 \mathbf{U}$ —just as we expect it from a convergent part interpretation of (2.6) (and indeed as it was actually presented in V). There are cross terms in the second term of (3.1) between longitudinal and transverse parts; but these necessarily vanish because such parts are orthogonal in  $\mathbf{k}$  space.

However, we have still to treat the pure Coulomb terms. In reference V such terms were omitted from the screened self-interactions with the understanding that they should really be taken together with the other divergent terms of the theory so that the divergences matched and mutually compensated. Here we take an opposite view and deliberately collect all these mutually compensating terms with their net finite parts into the screened self-interaction.

Thus we must now look carefully at the problem of finding a physically and mathematically satisfactory definition of a screened self-interaction in the exact screened theory. We shall use the instantaneous polarization kernel  $\Lambda^{\text{in}}(\mathbf{x}, \mathbf{x}'; \omega)$  and its ensemble average  $\Lambda(\mathbf{x}, \mathbf{x}'; \omega)$  introduced in V and defined in equation (A.3). As discussed in the Appendix  $\Lambda$  is related to the refractive index by the relation

$$\frac{m^2(\omega) - 1}{4\pi} = \mathbf{u}\mathbf{u} : \int_V \Lambda(\mathbf{x}, \mathbf{x}'; \omega) \exp\{im(\omega)\mathbf{k}_0 \cdot (\mathbf{x}' - \mathbf{x})\} d\mathbf{x}'. \tag{3.5}$$

In equation (3.5) the integration is taken over the finite macroscopic volume  $V$  of the system (conveniently a parallel-sided slab with  $\mathbf{k}_0$  normal to the parallel surfaces†). In the Appendix we show that  $\Lambda^{\text{in}}$  satisfies the nonlinear integral equation

$$\begin{aligned} \Lambda^{\text{in}}(\mathbf{x}, \mathbf{x}'; \omega) = & \Pi_0(\mathbf{x}, \mathbf{x}'; \omega) + \int_V d\mathbf{x}'' \int_V d\mathbf{x}''' \Lambda^{\text{in}}(\mathbf{x}, \mathbf{x}''; \omega) \cdot \mathcal{F}(\mathbf{x}'', \mathbf{x}'''; \omega) \\ & \cdot (\Pi_0(\mathbf{x}''', \mathbf{x}'; \omega) - \Lambda(\mathbf{x}''', \mathbf{x}'; \omega)). \end{aligned} \tag{3.6}$$

Here

$$\Pi_0(\mathbf{x}, \mathbf{x}'; \omega) = \rho(\mathbf{x})\alpha(\omega)\delta(\mathbf{x} - \mathbf{x}')\mathbf{U}$$

(see also III).

† This is strictly speaking, infinite in volume but it has a well defined surface: we take the slab as a cylinder of infinite radius and ignore contributions from the cylindrical surfaces at infinity.

By taking the average value on both sides of equation (3.6) and using equation (3.5) we obtain

$$\begin{aligned} \frac{m^2(\omega) - 1}{4\pi} &= n\alpha(\omega) + \alpha(\omega)\mathbf{uu} : \int_V d\mathbf{x}' \int_V d\mathbf{x}'' \langle \Lambda^{\text{in}}(\mathbf{x}, \mathbf{x}'; \omega) \cdot \mathcal{F}(\mathbf{x}', \mathbf{x}''; \omega) \rho(\mathbf{x}'') \rangle_{\text{av}} \\ &\quad \times \exp\{im(\omega)\mathbf{k}_0 \cdot (\mathbf{x}'' - \mathbf{x})\} - \mathbf{uu} : \int_V d\mathbf{x}' \int_V d\mathbf{x}'' \int_V d\mathbf{x}''' \Lambda(\mathbf{x}, \mathbf{x}'; \omega) \\ &\quad \cdot \mathcal{F}(\mathbf{x}', \mathbf{x}''; \omega) \cdot \Lambda(\mathbf{x}'', \mathbf{x}'''; \omega) \exp\{im(\omega)\mathbf{k}_0 \cdot (\mathbf{x}''' - \mathbf{x})\}. \end{aligned} \tag{3.7}$$

We want to isolate the ‘pure’ self-interaction terms†: these are those in which the chain of **F** tensors begins and ends at the same point **x**. This requires that the integrands have a  $\delta$  function connecting the first and last point. Such terms are only contained in the second term of equation (3.7). Equation (3.6) shows that  $\Lambda^{\text{in}}(\mathbf{x}, \mathbf{x}'; \omega)$  has  $\rho(\mathbf{x})$  as a factor which together with  $\rho(\mathbf{x}'')$  produces a  $\delta$  function

$$\rho(\mathbf{x})\rho(\mathbf{x}'') = \rho(\mathbf{x})\delta(\mathbf{x} - \mathbf{x}'') + \sum_i \sum_{j \neq i} \delta(\mathbf{x} - \mathbf{x}_i)\delta(\mathbf{x}'' - \mathbf{x}_j).$$

We want to define an effective polarizability  $\beta(\omega)$  and a screened self-interaction  $s(\omega) \equiv \mathbf{uu} : \mathbf{s}(\omega)$  which are related by an equation like (2.14):

$$\beta(\omega) \simeq \frac{\alpha(\omega)}{1 - s(\omega)\alpha(\omega)} = \alpha(\omega) + \alpha^2(\omega) \frac{s(\omega)}{1 - s(\omega)\alpha(\omega)}. \tag{3.8}$$

We first define  $\beta(\omega)$ :

$$\frac{\beta(\omega) - \alpha(\omega)}{\alpha^2(\omega)} \equiv (n\alpha(\omega))^{-1} \mathbf{uu} : \int_V d\mathbf{x}' \Lambda(\mathbf{x}_1, \mathbf{x}'; \omega) \cdot \mathcal{F}(\mathbf{x}', \mathbf{x}_1; \omega) \tag{3.9a}$$

$$\begin{aligned} &= \mathbf{uu} : \left\{ \int \mathbf{F}(\mathbf{x}_1, \mathbf{x}'; \omega) \delta(\mathbf{x}_1 - \mathbf{x}') d\mathbf{x}' \right. \\ &\quad \left. + \sum_{p=2}^{\infty} (n\alpha(\omega))^{p-1} \int_V d\mathbf{x}_2 \dots \int_V d\mathbf{x}_p \mathbf{F}_{12} \cdot \mathbf{F}_{23} \dots \mathbf{F}_{p1} G_{123\dots p} \right\} \end{aligned} \tag{3.9b}$$

$$\begin{aligned} &= \mathbf{uu} : \left\{ \int \mathbf{F}(\mathbf{x}_1, \mathbf{x}'; \omega) \delta(\mathbf{x}_1 - \mathbf{x}') d\mathbf{x}' \right. \\ &\quad \left. + n^{-1} \int_V d\mathbf{x}' \int_V d\mathbf{x}'' \langle \rho(\mathbf{x}_1) \mathbf{F}(\mathbf{x}_1, \mathbf{x}'; \omega) \cdot \Lambda^{\text{in}}(\mathbf{x}', \mathbf{x}''; \omega) \rangle_{\text{av}} \cdot \mathcal{F}(\mathbf{x}'', \mathbf{x}_1; \omega) \right\}. \end{aligned} \tag{3.9c}$$

Here  $G_{123\dots p} = n^{-p} \mathcal{G}_{123\dots p} = n^{-p} \langle \rho(\mathbf{x}_1) \rho(\mathbf{x}_2) \dots \rho(\mathbf{x}_p) \rangle_{\text{av}}$  is the generalized correlation function (III) which includes all self-correlations. The expansion (3.9b) is derived in the Appendix. The last form (3.9c) is obtained by using equations (A.4) and (A.5) and will be used later as a basis for approximations.

To obtain a definition of  $s(\omega)$  we notice that by (3.8) the series (3.9b) is to represent  $s(\omega)(1 - s(\omega)\alpha(\omega))^{-1}$ . The higher powers of  $s(\omega)$  in the expansion of this quantity are naturally associated with the multiple closed loop terms that arise in (3.9b) from the

† Evidently there are scattering processes which involve a number of self-interactions mingled with a number of interparticle processes.

contributions to each function  $G_{123\dots p}$  which have  $\delta$  functions of the form  $\delta(\mathbf{x}_1 - \mathbf{x}_q)$  as factors. (Here, 'closed loop' means a loop that begins and ends at point one:  $G_{123\dots p}$  also contains self-correlations  $\delta(\mathbf{x}_q - \mathbf{x}_r)$  with  $q \neq 1 \neq r$ .) It is therefore natural to define  $s(\omega)$  as the series obtained from (3.9b) by omitting all such contributions and given explicitly by (3.9b) when the functions  $G_{123\dots p}$  are replaced by

$$G_{1;23\dots p} \equiv n^{-p} \left\langle \sum_i \delta(\mathbf{x}_1 - \mathbf{x}_i^{in}) \sum_{j \neq i} \delta(\mathbf{x}_2 - \mathbf{x}_j^{in}) \sum_{k \neq i} \delta(\mathbf{x}_3 - \mathbf{x}_k^{in}) \cdots \sum_{l \neq i} \delta(\mathbf{x}_p - \mathbf{x}_l^{in}) \right\rangle_{av} .$$

This definition of  $s(\omega)$  is physically very natural although (3.8) is then only valid in the approximation which ignores all correlations between points of different closed loops, in the expansion (3.9b) for  $\beta(\omega)$ . However, this really means that  $\beta(\omega)$  is more fundamental in the theory than  $s(\omega)$ . We may contrast this definition of  $s(\omega)$  with (2.6) for  $r(\omega)$  with  $\mathbf{F}$  replaced by  $\mathcal{F}$ . This expression can be obtained from (3.9b) by entirely omitting index one in each  $G_{123\dots p}$  as we show in the Appendix. It is this complete neglect of correlations involving particle one that causes the difficulties with  $r(\omega)$ .

We must now show how to incorporate the properly defined self-interaction  $s(\omega)$  in the results of § 2. We therefore now transform equation (3.7) to the form (2.17). We have already isolated a term  $n\beta(\omega)$  containing the effective polarizability given by (3.9) from the first two terms of (3.7). We now apply the bulk approximation in parts to the last term of equation (3.7): we replace the tensor  $\mathcal{F}(\mathbf{x}', \mathbf{x}''; \omega)$  that connects the two  $\Lambda$  tensors, by  $\bar{\mathbf{F}}(\mathbf{x}', \mathbf{x}''; \omega)$ . We extract the screened Lorentz term (2.5) associated with this  $\bar{\mathbf{F}}$  tensor, and evaluate the integral that multiplies this Lorentz factor in the bulk approximation. By using equation (3.5) and the isotropy of  $\Lambda$  in the bulk approximation we find that this term contributes exactly  $(4\pi/3m^2(\omega))\{(m^2(\omega) - 1)/4\pi\}^2$ . If this term is now moved to the left hand side of equation (3.7) we obtain

$$\left( \frac{m^2(\omega) - 1}{4\pi} \right) \left( \frac{2m^2(\omega) + 1}{3m^2(\omega)} \right) = n\beta(\omega) + D(m, \omega) \tag{3.10}$$

in which  $D(m, \omega)$  denotes the terms that remain from the right hand side of equation (3.7) when the pure self-interaction and the screened Lorentz contribution are removed as discussed above†.

The very simple transformation of (3.7) to (3.10) corresponds exactly to the derivation of equation (2.17) by series summation from (2.3), but now we have obtained a form in which  $s(\omega)$  replaces  $r(\omega)$  in the effective polarizability, which contains no other pure self-interaction terms, and which is free from divergences. From this result, and from the very similar structure of  $s(\omega)$  and  $r(\omega)$  (in the exact screened theory) we infer (by generalization) the following prescription for the elimination of the divergences from equation (2.17): replace every  $r(\omega)$  by  $s(\omega)$  and omit all terms which contain a closed loop of  $\bar{\mathbf{F}}$  tensors.

We consider the question of finding bulk type approximations to the screened self-interaction below. We first derive an explicit expansion of equation (2.17). By using

† To the integral equation (3.6) for  $\Lambda^{in}$  in the screened theory there corresponds the integral equation (A.4) which appears in the Appendix. The argument there shows that (A.4) is essentially the fundamental semi-classical equation (2.1) from which we start. By arguments exactly parallel to those leading from (3.6) to (3.10) applied now to (A.4) we get a term  $\frac{1}{2}n\alpha(m^2 - 1)$  on the right side and by transferring this term to the left side we obtain a generalized Lorentz-Lorenz relation.

equation (2.7) to eliminate the factor  $(m^2 + 2)/3m^2$  of  $C(n\alpha)$ , the right side of (2.17) takes the form

$$n\tilde{\gamma} + \left\{ 1 - 2L \left( \frac{4\pi n\tilde{\gamma}}{3m^2}, 0 \right) \right\} C(n\alpha) - \left( \frac{4\pi}{3m^2} \right) C^2(n\alpha) \tag{3.11}$$

where we have also used the property (2.13) of  $L(t, w)$ . We then observe that the only self-interaction term in  $C(n\alpha)$  (equation (2.9a)) up to the third order in  $n\alpha$  can be taken together with the second order term to give  $C_2(n\alpha)^2(1 + 2w)$ , which is the beginning of the expansion of  $C_2(n\tilde{\gamma})^2$  in powers of  $w$ . Thus, up to the third order in  $n\alpha$  (at least), all self-interactions can be absorbed in the effective polarizability  $\tilde{\gamma}$ . By using the prescription adopted above for the elimination of the divergences we now obtain an expansion of equation (2.17). This is

$$\left( \frac{m^2(\omega) - 1}{4\pi} \right) \left( \frac{2m^2(\omega) + 1}{3m^2(\omega)} \right) = n\beta(\omega) + C_2(n\beta(\omega))^2 + \left( C_3 + \frac{8\pi}{3m^2(\omega)} C_2 \right) (n\beta(\omega))^3 + \dots \tag{3.12}$$

This equation is an explicit form for the dispersion formula which generalizes the Böttcher formula (1.4). It is a new result, and perhaps the main result of this paper.

In the remaining part of this section we first briefly discuss the exact screened self-interaction  $s(\omega)$  we have now obtained. Then we find a useful approximation to it. The self-interaction  $s(\omega)$  is given implicitly by (3.9b) and is actually given explicitly by the right side once all multiple closed loop terms† are neglected. It contains the radiation reaction of the isolated molecule, and in addition it has contributions representing all those virtual processes in which light emitted from a particular molecule interacts in all possible ways with the remaining molecules of the many-body system and is finally absorbed back by the emitting molecule. These processes are naturally represented by the single closed loop terms of equation (3.9b)‡, and we show below that these combine with the one-particle radiation reaction in (3.9b) to produce both the screened radiation reaction (already reported as such in V) and a real valued reaction field precisely of Onsager’s type. It is also interesting to note that the screened self-interaction can describe the ground state of a molecular fluid very much as the unscreened self-interaction describes the ground state energy of a single molecule of the system (Bullough 1969a), and the expression for the screened self-interaction we have used here should be compared to the very similar ones appearing in the theory of the binding energy described in that paper.

Equation (3.9b) exhibits the nature of the multiple scattering processes that build up the total reaction field. Although this description is important for our understanding, it is not very useful for a detailed comparison with macroscopic theories or with experiments. With the aim of revealing the nature of the screened self-interaction  $s(\omega)$  in ‘macroscopic’ form we therefore now develop a bulk type approximation to  $s(\omega)$ . The argument is based on equation (3.9c) which has a structure very similar to that of equation (3.1) for  $r(\omega)$ .

Equation (3.9c) contains the average value‡  $\langle \rho(\mathbf{x}_1) \Lambda^{\text{in}}(\mathbf{x}', \mathbf{x}''; \omega) \rangle_{\text{av}}$ . This describes the average ‘propagation of polarization’ from  $\mathbf{x}''$  to  $\mathbf{x}'$  under the condition that the point  $\mathbf{x}_1$  is certainly occupied by a molecule; and this in contradistinction to

† Equation (3.9b) appears to involve only ‘single closed loops’ like  $\mathbf{F}_{12} \cdot \mathbf{F}_{23} \dots \mathbf{F}_{p1}$ . However there are  $\delta$  functions in the  $G_{123\dots p}$  there which reduce this single closed loop to multiple closed loops like  $\mathbf{F}_{12} \cdot \mathbf{F}_{21} \cdot \mathbf{F}_{14} \cdot \mathbf{F}_{41} \cdot \mathbf{F}_{16} \dots \mathbf{F}_{p1}$  for example (which has 3 loops).

‡ We can place  $\mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega)$  under the average symbols or outside them: the average is taken on molecular sites and not on  $\mathbf{x}_1, \mathbf{x}'$ , or  $\mathbf{x}''$ ; but  $\Lambda^{\text{in}}$  depends on these sites.



$n\Lambda(\mathbf{x}', \mathbf{x}''; \omega) \equiv n\langle \Lambda^{\text{in}}(\mathbf{x}', \mathbf{x}''; \omega) \rangle_{\text{av}}$  which describes the same process but without any such condition on  $\mathbf{x}_1$ . In the bulk approximation in which  $\bar{\mathbf{F}}$  replaces  $\mathcal{F}$  in  $\Lambda(\mathbf{x}', \mathbf{x}''; \omega)$  this averaged polarization propagator is rather short range and can be further approximated to the strictly local form  $(m^2 - 1)(4\pi)^{-1} \mathbf{U} \delta(\mathbf{x}' - \mathbf{x}'')$  (compare (3.5)). In all cases where neither  $\mathbf{x}'$  nor  $\mathbf{x}''$  is close to  $\mathbf{x}_1$  the constraint on the average has little effect; but one significant consequence of the condition that  $\mathbf{x}_1$  is occupied is that it prevents molecules at  $\mathbf{x}'$  and  $\mathbf{x}''$  approaching arbitrarily closely to this point. We shall now introduce an approximation which incorporates this important property but otherwise neglects the condition. If we assume that  $\Lambda^{\text{in}}(\mathbf{x}', \mathbf{x}''; \omega)$  is itself strictly local, the remarks above finally suggest the approximation

$$\Lambda^{\text{in}}(\mathbf{x}', \mathbf{x}''; \omega) \simeq (m^2(\omega) - 1)(4\pi)^{-1} \mathbf{U} n^{-1} \rho(\mathbf{x}') \delta(\mathbf{x}' - \mathbf{x}''). \tag{3.13}$$

The factor  $n^{-1} \rho(\mathbf{x}')$  is included because  $\Lambda^{\text{in}}(\mathbf{x}', \mathbf{x}''; \omega)$  has  $\rho(\mathbf{x}')$  as a factor and the average value  $\Lambda(\mathbf{x}', \mathbf{x}''; \omega)$  is just the approximate local form quoted above. If we now use (3.13) in (3.9c) and adopt the prescription of the bulk approximation which replaces  $\mathcal{F}$  by  $\bar{\mathbf{F}}$  we have

$$\frac{s(\omega)}{1 - s(\omega)\alpha(\omega)} \simeq \mathbf{u} \mathbf{u} : \left\{ \int \mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) \delta(\mathbf{x} - \mathbf{x}') d\mathbf{x}' + n^{-2} \left( \frac{m^2(\omega) - 1}{4\pi} \right) \int_V \mathbf{F}(\mathbf{x}, \mathbf{x}'; \omega) \cdot \bar{\mathbf{F}}(\mathbf{x}', \mathbf{x}; \omega) \langle \rho(\mathbf{x}) \rho(\mathbf{x}') \rangle_{\text{av}} d\mathbf{x}' \right\}. \tag{3.14}$$

In order to obtain an expression for  $s(\omega)$  from equation (3.14) we must remove the  $\delta$  function from  $\langle \rho(\mathbf{x}) \rho(\mathbf{x}') \rangle_{\text{av}}$  and thus eliminate the multiple self-interaction terms in  $s(\omega)(1 - s(\omega)\alpha(\omega))^{-1}$ , that is eliminate the multiple closed loops in the expansion for this quantity, as discussed after equations (3.9). This simply means replacing this generalized correlation function by the ordinary pair-correlation function  $n^2 g_2(|\mathbf{x} - \mathbf{x}'|)$ . To evaluate the resulting second integral of (3.14) we then split the propagators into their longitudinal and transverse parts by equations (3.4a, b) as we did with equation (3.1). If the correlation length  $l$  is short compared to the wavelength of the light so that  $g_2(r) \simeq 1$  for  $r \gg l$ , the product of the transverse parts of the propagators must to a very good approximation give the same contribution as in equation (3.1). The cross terms between the longitudinal and transverse parts do not vanish identically as they did in equation (3.1), but for short correlation lengths their contribution must be small so we can ignore it. We therefore obtain the following important result:

$$\mathbf{s}(\omega) \simeq \frac{2}{3} i m(\omega) k_0^3 \mathbf{U} + \frac{m^2(\omega) - 1}{4\pi} \int \left( \nabla \nabla \frac{1}{r} \right) \cdot \left( m^{-2}(\omega) \nabla \nabla \frac{1}{r} \right) g_2(r) d\mathbf{r}. \tag{3.15}$$

This formula is evidently approximate; but it is particularly simple, and physically it seems very reasonable. The introduction of the pair correlation function  $g_2(r)$  into equation (3.1) is quite the simplest way of taking account of the missing correlation and so of guaranteeing the convergence of this equation at the point  $\mathbf{x}$  as the physical situation demands. It is also significant that (3.15) agrees closely with the simple result (3.3) of the 'divergence matching' where  $g_2(r)$  again ensures the convergence of the integral. However (3.3) is, of course, a lowest order result in which no distinction is made between  $(m^2 - 1)/4\pi$  and  $n\alpha$  or between  $\bar{\mathbf{F}}$  and  $\mathbf{F}$ .

We discuss the main result (3.12) with the simple form (3.15) for  $s(\omega)$  substituted in  $\beta(\omega)$  in the following § 4.

#### 4. Discussion of the generalized Böttcher formula

If we ignore the terms in equation (3.12) of order (in  $n\beta(\omega)$ ) higher than the first, we get an equation exactly of the Böttcher form (1.4); but now we have an *explicit* formula for the effective polarizability. Equation (3.12) truncated after the first term and with the simple approximation (3.15) (written as  $s(\omega) \simeq \frac{2}{3}im(\omega)k_0^3 + \zeta(m(\omega))$ ) for the screened self-interaction, has the form

$$\left(\frac{m^2(\omega)-1}{4\pi}\right)\left(\frac{2m^2(\omega)+1}{3m^2(\omega)}\right) = n \frac{\alpha(\omega)}{1 - \frac{2}{3}im(\omega)k_0^3\alpha(\omega) - \zeta(m(\omega))\alpha(\omega)}. \quad (4.1)$$

The purely imaginary term in the denominator is the screened radiation reaction of V, whilst

$$\zeta(m(\omega)) \equiv 2 \frac{m^2(\omega)-1}{m^2(\omega)} \int_0^\infty r^{-4} g_2(r) dr \quad (4.2)$$

is the coefficient of a real valued Onsager type reaction field corresponding to Böttcher's *f*. Notice how naturally the effective polarizability multiplying  $n$  in equation (4.1) generalizes both Böttcher's  $\alpha^*$  given by (1.5) and the complex polarizability  $\gamma(\omega)$  given by (2.15).

The weakest point in the macroscopic argument (Onsager 1936, Böttcher 1942) for the Böttcher formula is the choice of the cavity radius  $a$ . This problem is solved in a very natural way by the result (4.2), in which the pair-correlation function  $g_2(r)$  determines  $a$ . Indeed, if we choose the pair correlation function so that it imitates a 'macroscopic' cavity in a continuum by taking a unit step function for  $g_2(r)$  namely  $g_2(r) \simeq \theta(r-a)$ ,  $r > 0$  we obtain the expression

$$\zeta(m) \simeq \frac{2}{a^3} \left(\frac{m^2-1}{3m^2}\right) \quad (4.3)$$

which is almost, but not entirely, identical with the macroscopic Onsager reaction field (factor) given by (1.3)†. Equation (4.3) justifies (with qualifications discussed below) an interpretation of the cavity radius of the Böttcher macroscopic theory as an effective molecular diameter. Böttcher's assumption that  $a$  is constant has indeed a region of approximate validity: the integral in equation (4.2) has a nonzero limiting value for  $n \rightarrow 0$ , so the reaction field is really linear in  $n\alpha$  for small  $n\alpha$ .

To investigate (4.1) further we ignore the screened radiation reaction and introduce the approximate expression for the true one-particle polarizability  $\alpha(\omega)$  which is obtained by inverting this equation, namely

$$\alpha_s = \frac{1}{n} \left(\frac{m^2-1}{4\pi}\right) \left(\frac{2m^2+1}{3m^2}\right) \left(1 - 2\alpha \frac{m^2-1}{m^2} \int_0^\infty r^{-4} g_2(r) dr\right). \quad (4.4)$$

† After having written this article we discovered the paper by Linder and Hoernschemeyer (1967) on the 'Cavity concept in dielectric theory'. In this the reaction field is defined as the static equivalent of the sum in equation (3.9b), but with *all* self-correlations omitted. Linder and Hoernschemeyer find a power series in  $n\alpha$  for the cavity radius by forcing their reaction field into the macroscopic form (1.3); and they obtain  $a^{-3} = \int_0^\infty 3r^{-4} g_2(r) dr$  as a strictly lowest order result. In contrast, we obtain the (real) reaction field from the compact form (3.9c) directly in the form (4.2); and this takes the 'macroscopic form' (4.3) when (but only when)  $a^{-3}$  is defined as the integral. Evidently, our result (4.2) includes contributions of all orders from the series (3.9b). Moreover we obtain the reaction field in the generalized form (3.15) as a part of an actual derivation of the Böttcher formula. This derivation both produces the cavity field factor explicitly and also exhibits the several corrections which must be made to the simple Böttcher formula.

It is a complication that the pair-correlation function is still not usually available as a function of density and temperature. However, we have its initial value by using  $g_2(r) \rightarrow \exp(-\phi(r)/k_B T)$  for  $n \rightarrow 0$  where  $\phi(r)$  is the pair potential,  $k_B$  is Boltzmann's constant, and  $T$  is the absolute temperature. From this we find the initial slope of the reaction field correction as a function of the refractive index:

$$\left(\frac{d\zeta(m)\alpha}{dm}\right)_{m=1} = 4\alpha \int_0^\infty r^{-4} \exp\left(\frac{-\phi(r)}{k_B T}\right) dr. \quad (4.5)$$

To indicate the order of magnitude of this correction we may consider argon at 25 °C with a Lennard-Jones potential. We can then use the value for the integral calculated by de Boer *et al* (1953) and the value  $\alpha = 1.667 \times 10^{-24} \text{ cm}^3$  for the polarizability at the (vacuum) wavelength 5876 Å determined by Larsén (1934). We then find that the initial slope (4.5) is 8.01 %.

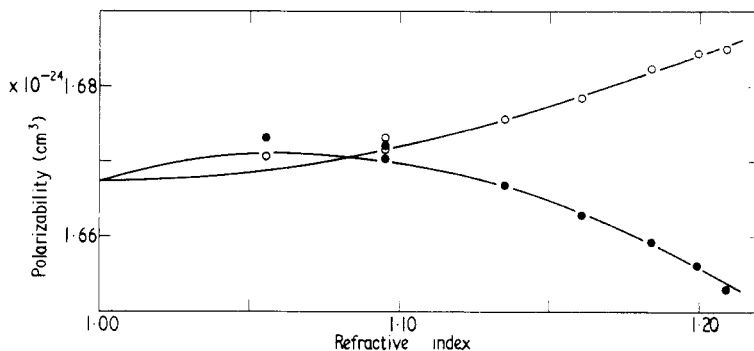
Equation (3.12) corrects the Böttcher formula (4.1) at lowest order by the term  $C_2(n\beta(\omega))^2$  and this term could give rise to a finite initial slope of  $\alpha_s$  against  $m$ . But  $C_2$  is small of the order  $O(k_0^2 l^2)$  when the correlation length  $l$  is small compared to the wavelength of the light, and the same is the case for the two-body term in  $J(\omega)$  in (1.2) in the unscreened theory. Thus except perhaps† close to the critical point we can neglect the term  $C_2$  in (3.12) and we then expect that to a good approximation  $\alpha_s$  will have zero initial slope. In contrast, the approximate polarizability  $\alpha_{LL}$  calculated from the Lorentz-Lorentz relation must then have the positive initial slope‡ given by equation (4.5). Because  $C_2 = O(k_0^2 l^2)$  the first numerically important correction to equation (4.1) comes from the term  $C_3(n\beta(\omega))^3$  at the third order in  $n\beta(\omega)$ . On the basis of a comparison of the corresponding term in the unscreened theory with the third order surface term, which we have found to be negative, we expect  $C_3$  to be positive. We therefore expect  $\alpha_s$  to have zero initial slope and upwards curvature as a function of  $n\alpha$  or as a function of  $m$ .

We compare these conclusions with experiments for argon, to which this theory should be very well applicable. We use the values of the Lorentz-Lorentz function at the wavelength 5876 Å given by Michels and Botzen (1949). These authors measured the refractive index at the constant temperature 25 °C as a function of density and used the density measurements of Michels *et al* (1949) performed at the same laboratory. Their results agree in the reliable region within approximately 0.3 % with those of Teague and Pings (1968) and with those of Sinnock and Smith (1969) even though these were obtained at much lower temperatures.

If we take the integral appearing in equation (4.4) to be independent of density and equal to its initial value we can find an approximate value for  $\alpha_s$  as a function of  $m$ . Figure 1 shows  $\alpha_s$  and  $\alpha_{LL}$  calculated this way from the data of Michels and Botzen (1949). In the region  $m \lesssim 1.05$  the uncertainty in the experimentally determined values of  $\alpha_s$  and  $\alpha_{LL}$  greatly exceeds the difference  $|\alpha_s - \alpha_{LL}|$  and these are omitted in figure 1 (compare Michels and Botzen 1949). For the true polarizability of the isolated particles we have adopted the value determined by Larsén who used a very accurate interferometric method. The experimental points for  $\alpha_s$  and  $\alpha_{LL}$  are shown as open and full

† Larsen *et al* (1965) have estimated the contribution of the (unscreened) two-body term under critical conditions and have found that even when  $k_0 l \simeq 1$  the real part is still negligible. (The imaginary part is also negligible compared to  $\text{Re}(m)$  but is not negligible compared to  $\text{Im}(m)$  when either  $k_0 l \simeq 1$  or  $k_0 l \ll 1$ .)

‡ Self-interactions accounting for this positive initial slope are included as a part of the correction to the Lorentz-Lorentz relation in the generalized form of equation (1.2).



**Figure 1.** Approximate polarizabilities  $\alpha_{LL}$  (full circles) and  $\alpha_S$  (open circles:  $g_2(r)$  approximated by  $\exp(-\phi(r)/k_B T)$ ) as functions of the refractive index for argon at 25°C and wavelength 5876 Å, calculated from the data of Michels and Botzen (1949) and Larsén (1934). For the curves: see the text.

circles respectively. The curves through the experimental points have the initial slopes and the spacing required by the theory but otherwise are just visually fitted to the experimental points. Notice that the experimental values of  $\alpha_S$  are very insensitive to the precise choice of  $\alpha$  within the limits determined by the experimental uncertainty of  $\alpha$ . Figure 1 shows that the experimental points can be fitted very naturally with curves satisfying the restraints of the theory, and we see that  $\alpha_S(m)$  does indeed show an upward curvature. Unfortunately, the inaccuracy of the experimental data in the region of small refractive indices prevents a quantitative determination of the initial slope of  $\alpha_S$  and  $\alpha_{LL}$ . Nevertheless the theory seems to be supported by this experiment to the extent that a comparison is immediately accessible.

We now discuss the validity of the cavity model and of the Böttcher formula for nonpolar fluids on the basis of our theory. The lowest order result (4.1) shows that there is indeed a molecular basis for the Böttcher formula when the radius of the cavity is taken to be an 'effective molecular diameter'. But the Böttcher formula can be expected to describe the situation well *only* in the low density region where pair interactions dominate. With increasing density the 'equivalent cavity radius' determined by  $g_2(r)$  changes because  $g_2(r)$  changes. This effect does not change the physical picture that underlies the cavity model. It only rationalizes a small dependence of the cavity radius on the density (and the temperature). But although many-body interactions of all orders are taken approximately into account in the lowest order term of the screened theory, strict many-body terms such as  $C_3(n\beta(\omega))^3$  (which are not of the reaction type) become important at higher densities. These corrections from the higher order terms of equation (3.12) constitute a far more serious obstacle to the interpretation of experiments solely in terms of the Böttcher formula. In contrast with the situation at low values of the refractive index, the measurements of the 'cavity radius' at higher refractive indices entirely lose their simple physical interpretation as an effective molecular diameter. Indeed, Böttcher's (1942, 1952) observation that equation (1.4) can be fitted to experiments when  $a$  is of the order of an average molecular *radius* (rather than diameter) can quite possibly be explained by the upwards curvature of  $\alpha_S$  as a function of  $m$  caused by the higher terms of equation (3.12). It should be noted, however, that the theory neither applies to solutions nor to anisotropically polarizable molecules—the cases studied by Böttcher. Nevertheless, the analysis of this paper gives good reasons

for believing that the restrictions on the validity of the simple Böttcher formula to the region of low refractive indices must also apply in these more general cases.

## 5. Summary of results and conclusions

We have recast the screened formulation of the refractive index theory, which has already been reported (V), into the new form (3.12) which generalizes the Böttcher formula (1.4). This result uses the effective polarizability  $\beta(\omega)$  defined in (3.9) which takes account of the interaction of a molecule with itself through interactions with the many-body system.

The self-interaction  $s(\omega)$  is given implicitly by equation (3.9b) as an expansion in terms of the unscreened photon propagator  $\mathbf{F}$ . Within a certain bulk type approximation it gives the physically very natural, new result (3.15). This screened self-interaction has two parts: the one part is the screened radiation reaction  $\frac{2}{3}im(\omega)k_0^3$ , which we have obtained previously (V) and the other part is (the coefficient of) a real valued Onsager type reaction field (4.2).

At lowest order given by equation (4.1) the result (3.12) partly justifies Böttcher's formula. The coefficient of  $n$  in (4.1) is an effective polarizability which generalizes Böttcher's  $\alpha^*$ . It can be regarded as the screened analogue of the complex polarizability  $\gamma(\omega)$  (equation (2.15)) which appears implicitly in (1.2) according to the simplest form of the unscreened theory. It is the natural interpretation of the formal quantity  $\tilde{\gamma}(\omega)$  given by (2.14) and (2.6), and it reduces to  $\gamma(\omega)$  for  $m(\omega) = 1$ . The real part of the reaction field of (4.1) is given by the simple and explicit expression (4.2) in which the 'cavity' is a 'molecular cavity' introduced naturally by an intermolecular correlation function. Equation (4.2) implies that the cavity radius to be used in the Onsager macroscopic reaction field can be interpreted as an effective molecular diameter in the region where the higher order contributions of (3.12) can be neglected. This follows from the form (4.3) which the real reaction field (4.2) takes when the correlation function is replaced by a unit step function—the obvious microscopic choice to imitate a macroscopic cavity in a continuum. However, we show that any simple one-molecule plus continuum interpretation of experiments gradually disappears as the refractive index increases much beyond unity and the 'cavity radius' obtained by fitting the Böttcher equation to experimental data for molecular fluids loses its meaning as a molecular diameter.

In the region of low refractive indices the dispersion relation (4.1) differs from the Lorentz–Lorentz relation in one important respect: the (real) reaction field (4.2) is *linear* in  $n\alpha$  (for small  $n\alpha$ ) whilst the Lorentz–Lorentz relation employs the *quadratic* reaction field (1.6). From this we conclude that equation (4.1) offers a better description of the physical situation than does the simple Lorentz–Lorentz relation when the refractive index is close to unity.

A number of approximations underlie our arguments. One is that the theory can be constructed in terms of the polarizability of a single isolated molecule although this approximation is likely to be good for molecular fluids like, for example, argon. The nature of the approximation is evident from the procedure initially adopted to decorrelate the quantum theory: in this all quantum mechanical excitation processes (Raman type processes and others) are eliminated except those in which single particles are first excited from their ground states and then are immediately de-excited back to these states. This is the content of the 'polarization diagram approximation' (PDA) of reference III. The integral equation derived there (displayed here as (A.8) in fact) underlies the semiclassical equation (2.1) and hence all of the present theory.

There is the additional move towards translational invariance which replaces the ‘exact’ unscreened theory (exact only within the PDA) with the ‘screened theory’ by the bulk approximation. The divergence problem this introduces is wholly solved in this paper but although the bulk approximation then seems physically sound, some work remains to establish the validity of this translationally invariant theory in detail.

Leaving aside its exact status, however, the screened theory (in bulk approximation) is valuable because of the conceptual understanding it provides. Conversely the formulae like (4.1) which can be derived from it agree so well with results of physically well motivated macroscopic approaches to the dielectric problem that we can infer from this the validity of the origins and structure of the screened theory.

Certainly by presenting the microscopic arguments in the terms of this paper we show how to remove any possibility of paradox in the two different approaches of Onsager and Lorentz to the problem of the internal field in a macroscopic dielectric.

**Appendix. Derivation of equation (2.3) from (2.1), of (3.6), and of (3.9b)**

The instantaneous polarization density  $\mathbf{P}^{\text{in}}(\mathbf{x}, \omega)$  is related to the external field  $\mathbf{E}(\mathbf{x}, \omega)$  by (2.1) namely, in concise notation

$$\mathbf{P}^{\text{in}} = \rho\alpha \left( \mathbf{E} + \int_V \mathbf{F} \cdot \mathbf{P}^{\text{in}} \right) \tag{A.1}$$

with  $\alpha$  the scalar polarizability,  $\mathbf{F}$  defined by (1.8), and  $\rho$  by (2.2). We first derive (3.6) from this equation.

We define an average electric field  $\mathcal{E}(\mathbf{x}, \omega)$  by

$$\mathcal{E} = \mathbf{E} + \int_V \mathbf{F} \cdot \mathbf{P} \tag{A.2}$$

$\mathbf{P}(\mathbf{x}, \omega)$  is the ensemble average of  $\mathbf{P}^{\text{in}}(\mathbf{x}, \omega)$  and the integral is defined as discussed near equation (1.9). Equations (A.1) and (A.2) allow us to eliminate  $\mathbf{E}$ . We then define  $\Lambda^{\text{in}}(\mathbf{x}, \mathbf{x}'; \omega)$  and  $\Lambda(\mathbf{x}, \mathbf{x}'; \omega)$  by

$$\mathbf{P}^{\text{in}} = \int_V \Lambda^{\text{in}} \cdot \mathcal{E} \quad \text{and} \quad \mathbf{P} = \int_V \Lambda \cdot \mathcal{E} \tag{A.3}$$

and find that with  $\Pi_0(\mathbf{x}, \mathbf{x}'; \omega) \equiv \rho(\mathbf{x})\alpha(\omega)\mathbf{U}\delta(\mathbf{x} - \mathbf{x}')$  (A.1) implies the equation

$$\Lambda^{\text{in}} = \Pi_0 + \int_V \int_V \Pi_0 \cdot \mathbf{F} \cdot (\Lambda^{\text{in}} - \Lambda) \tag{A.4}$$

We have exhibited an explicit solution of this linear equation (A.4) for  $\Lambda$  (this is equation (9) of V). Thus  $\Lambda^{\text{in}}$  is well defined, its ensemble average  $\Lambda$  is well defined, and we can introduce a propagator  $\mathcal{F}(\mathbf{x}, \mathbf{x}'; \omega)$  defined, and well defined, by

$$\mathcal{F} = \mathbf{F} + \int_V \int_V \mathbf{F} \cdot \Lambda \cdot \mathcal{F} \tag{A.5}$$

This ‘screens’ the free field propagator  $\mathbf{F}$  as  $\mathcal{F}$ . We multiply (A.4) from the right by  $\mathcal{F}$ .

integrate, and apply (A.5). We then get

$$\int_V \Lambda^{in} \cdot \mathcal{F} = \int_V \Pi_0 \cdot \left( \mathbf{F} + \int_V \int_V \mathbf{F} \cdot \Lambda^{in} \cdot \mathcal{F} \right). \tag{A.6}$$

We can now define a polarization propagator  $\Pi(\mathbf{x}, \mathbf{x}'; \omega)$  by

$$\Pi = \Pi_0 + \int_V \int_V \Lambda^{in} \cdot \mathcal{F} \cdot \Pi_0. \tag{A.7}$$

We multiply (A.6) from the right by  $\Pi_0$ , integrate, and add  $\Pi_0$ . We then find the equation in  $\Pi$

$$\Pi = \Pi_0 + \int_V \int_V \Pi_0 \cdot \mathbf{F} \cdot \Pi \tag{A.8}$$

which is identical to that of III. Alternatively we multiply (A.6) from the right by  $\Lambda$ , integrate, and eliminate the term in  $\int_V \int_V \Pi_0 \cdot \mathbf{F} \cdot \Lambda$  by means of (A.4). It follows that

$$\Pi = \Lambda^{in} + \int_V \int_V \Lambda^{in} \cdot \mathcal{F} \cdot \Lambda \tag{A.9}$$

since the right side of (A.9) satisfies (A.8). (We assume that the inhomogeneous, linear, but singular integral equation (A.8) has a unique solution.) By substituting (A.9) for  $\Pi$  into (A.7) we obtain the equation (3.6) which concisely is

$$\Lambda^{in} = \Pi_0 + \int_V \int_V \Lambda^{in} \cdot \mathcal{F} \cdot (\Pi_0 - \Lambda). \tag{A.10}$$

This is a nonlinear integral equation in  $\Lambda^{in}$  (since  $\Lambda$  is its ensemble average).

As noted already the solution of (A.4) for  $\Lambda$  is exhibited in V (equation (9)). A comparable result for the refractive index which is based directly on (2.1) is quoted in III (equation (8)). Direct comparison shows that the refractive index can be obtained from  $\Lambda(\mathbf{x}, \mathbf{x}'; \omega)$  by the relation (3.5) namely

$$\frac{m^2(\omega) - 1}{4\pi} = \mathbf{u} \mathbf{u} \cdot \int_V \Lambda(\mathbf{x}, \mathbf{x}'; \omega) \exp\{im(\omega)\mathbf{k}_0 \cdot (\mathbf{x}' - \mathbf{x})\} d\mathbf{x}'. \tag{A.11}$$

Note that the defining relation in (A.3) exhibits  $\Lambda(\mathbf{x}, \mathbf{x}'; \omega)$  as a linear response function for the average field  $\mathcal{E}$  (certainly not the external stimulating field  $\mathbf{E}$ ). If the response were local we expect  $\Lambda$  is related to a frequency dependent dielectric constant  $\epsilon(\omega)$  by  $\Lambda = (\epsilon(\omega) - 1)\mathbf{U}\delta(\mathbf{x} - \mathbf{x}')/4\pi$ . Since it is not local (nor even translationally invariant) it should also depend on wavevectors  $\mathbf{k}$ . The result (A.11) shows explicitly that significant  $\mathbf{k}$  must satisfy a dispersion relation: it is here that the important physical concept of the refractive index enters the theory.

Equation (A.10) has a solution for  $\Lambda^{in}$  as a power series in  $n\alpha$  if and only if the coefficients contains the  $\mathcal{Y}^{in}$  functions satisfying the recurrence relation (2.4). This power series is exhibited as equation (12) in V. From it we obtain (2.3) immediately by substituting the average value of  $\Lambda^{in}$  into equation (A.11) and taking the result in the bulk approximation: this approximation replaces (cf equation (1.11))  $\mathcal{F}$  by  $\bar{\mathbf{F}}$  and  $V$  by all space. This completes the derivations of both (2.3) and (2.4) from (2.1). Explicit expressions for the  $\mathcal{Y}$  functions, the averages of the  $\mathcal{Y}^{in}$  functions are given in V, but we have no need of these here.

Finally we derive the expansion of (3.9b). We define  $\mathcal{F}^{\text{in}}(\mathbf{x}, \mathbf{x}'; \omega)$  with average  $\overline{\mathcal{F}}(\mathbf{x}, \mathbf{x}'; \omega)$  by

$$\mathcal{F}^{\text{in}} = \mathbf{F} + \int_V \int_V \mathbf{F} \cdot \mathbf{\Lambda}^{\text{in}} \cdot \mathcal{F}. \quad (\text{A.12})$$

There is a simpler integral equation for  $\mathcal{F}^{\text{in}}$ : we multiply (A.6) from the left by  $\mathbf{F}$ , integrate, and add  $\mathbf{F}$ . We find

$$\mathcal{F}^{\text{in}} = \mathbf{F} + \int_V \int_V \mathbf{F} \cdot \mathbf{\Pi}_0 \cdot \mathcal{F}^{\text{in}}. \quad (\text{A.13})$$

This equation has the simple Neumann expansion

$$\mathcal{F}^{\text{in}} = \mathbf{F} + \int_V \int_V \mathbf{F} \cdot \mathbf{\Pi}_0 \cdot \mathbf{F} + \int_V \int_V \int_V \int_V \mathbf{F} \cdot \mathbf{\Pi}_0 \cdot \mathbf{F} \cdot \mathbf{\Pi}_0 \cdot \mathbf{F} + \dots \quad (\text{A.14})$$

But each  $\mathbf{\Pi}_0$  contains a factor  $\rho$  (and a  $\delta$  function) and the average value of a product of several  $\rho$  gives a generalized correlation function. So (A.14) reveals how simply the structure of  $\mathcal{F}$  is described in terms of these and immediately gives the result for  $\int \mathcal{F}(\mathbf{x}, \mathbf{x}'; \omega) \delta(\mathbf{x} - \mathbf{x}') d\mathbf{x}'$  quoted with reference to this Appendix in the discussion following (3.9).

However, (A.12) shows that the bracket in (A.6) is simply  $\mathcal{F}^{\text{in}}$  so by taking the average value of (A.6) we have

$$\int_V \mathbf{\Lambda}(\mathbf{x}, \mathbf{x}'; \omega) \cdot \mathcal{F}(\mathbf{x}', \mathbf{x}; \omega) d\mathbf{x}' = \int_V \alpha(\omega) \langle \rho(\mathbf{x}) \cdot \mathcal{F}^{\text{in}}(\mathbf{x}', \mathbf{x}; \omega) \rangle_{\text{av}} \delta(\mathbf{x} - \mathbf{x}') d\mathbf{x}'. \quad (\text{A.15})$$

This result proves the identity of (3.9a) and (3.9b) when the Neumann expansion (A.14) is substituted for  $\mathcal{F}^{\text{in}}$  and it also exhibits the role of correlations involving the self-interacting molecule (through the factor  $\rho(\mathbf{x})$  under the average sign), in the relation between the self-interactions  $\mathbf{s}(\omega)$  and  $\mathbf{r}(\omega)$  discussed after (3.9).

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