

## Statistical interpretation of the local field inside dielectrics

Rubén G. Barrera

*Institute de Física, UNAM, Apdo. Postal 20-364 México 20, D.F*

P. A. Mello<sup>a)</sup>

*Departamento del Acelerador, Instituto Nacional de Investigaciones Nucleares, Mexico*

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We analyze and compare several derivations of the Clausius–Mossotti relation that appear in many textbooks. We then present a statistical-mechanical calculation of the local field for a classical system of harmonic oscillators interacting via the Coulomb potential. We derive the Clausius–Mossotti relation in order to analyze consistently the nature of the approximations used and their range of applicability.

### I. INTRODUCTION

The derivation of the Clausius–Mossotti relation through the concept of the local or the molecular field has been discussed in many textbooks (see, for example, Refs. 1–7). The molecular field  $E_m$  is defined as the average field at the site of a given molecule produced by the rest of the molecules in the system. The type of average that should be taken in each case has been very much discussed.<sup>8–12</sup> For example, in Refs. 1–3, the molecular field is obtained by treating the molecules contained within a small sphere centered at the given molecule, separately from those lying outside the sphere, the latter being treated in the continuum approximation. The average contribution  $E_{\text{near}}$  of the molecules within the small sphere vanishes when they are distributed at random or when they form a cubic lattice. The molecules outside the sphere give rise to two contributions: the polarization volume charge density  $-\nabla\cdot\mathbf{P}$  and the polarization surface charge density  $\mathbf{P}\cdot\hat{n}$  around the

sphere; here  $\mathbf{P}$  is the average dipole moment per unit volume and  $\hat{n}$  is a unit vector perpendicular to the surface of the sphere and directed inwards. Since the contribution of the volume charge density to the molecular field  $E_m$  is almost the same as its contribution to the macroscopic field  $\mathbf{E}$  (the latter includes the contribution of  $-\nabla\cdot\mathbf{P}$  from the volume of the sphere, which is very small), the difference between the two arises only from the contribution  $4\pi\mathbf{P}/3$  of the polarization surface charge density. The result is then  $E_m = E + 4\pi\mathbf{P}/3$ . In this analysis, the fact that one is calculating the field *on* a given molecule appears explicitly only in the case of the cubic lattice, where one is considering those molecules that lie on the various lattice sites that are different from the one occupied by the given molecule. But in the case of a random distribution, it is not stated explicitly where the assumption is made that one is sitting *on* a molecule. However, if we examine the calculation of  $E_{\text{near}}$ , it appears that no molecule is ever allowed to pass by the observation point: this is precisely what would happen

if we were on a molecule, and the probability for any other one to approach the one given were vanishingly small (vanishing correlation function at zero distance). It is probably at this point where the assumption is made.

Therefore, the same derivation could not be applied to the calculation of the macroscopic field  $\mathbf{E}$ , considered as the average field at an arbitrary point in space produced by all the other molecules, since, in this case, the probability that any molecule will approach that given point is finite; the contribution to  $\mathbf{E}$  of the nearby molecules is analyzed more carefully in Ref. 4, where it is shown to be given precisely by  $-4\pi\mathbf{P}/3$ , which then exactly cancels the surface contribution  $4\pi\mathbf{P}/3$  that was mentioned above.

In Ref. 4 the averaging process of the fields is done somewhat differently. It is stated that in order to calculate the field  $\mathbf{E}_m$  on a given molecule, one cannot regard the molecules close to the one in question within the continuum approximation, but rather as a discrete distribution. Therefore  $\mathbf{E}_m = \mathbf{E} + \mathbf{E}_{\text{near}} - \mathbf{E}_p$ , where  $\mathbf{E}_{\text{near}}$  is the actual contribution of the molecules contained in a sphere centered at the given molecule and  $\mathbf{E}_p$  is the average contribution from these same molecules treated in the continuum approximation and given in terms of the polarization field  $\mathbf{P}$ . Here  $\mathbf{E}$  is considered, apparently, as an average of the microscopic field  $\mathbf{e}$  over a small sphere. Then  $\mathbf{e}$  has contributions coming from charges outside the sphere and from those inside:  $\mathbf{e} = \mathbf{e}_{\text{out}} + \mathbf{e}_{\text{in}}$ . While the average of  $\mathbf{e}_{\text{out}}$  over the sphere contributes equally to  $\mathbf{E}$  and to  $\mathbf{E}_m$ , the contribution of  $\mathbf{e}_{\text{in}}$  is not same. Its contribution to  $\mathbf{E}$  is  $\mathbf{E}_p = -4\pi\mathbf{P}/3$ , whereas its contribution to  $\mathbf{E}_m$  is the  $\mathbf{E}_{\text{near}}$  discussed above and calculated from a discrete distribution as in Refs. 1-3. Again, it seems that a vanishing correlation function at zero distance is assumed tacitly in the calculation.

The analysis of Ref. 5 is much less sophisticated than the ones of the previous references. The field at any given point inside a dielectric is considered as the sum of the field due to a spherical plug centered at the given point plus the field inside a spherical cavity that surrounds the plug. The latter is assumed to resemble the field felt by an individual molecule.

The treatment of Refs. 6 and 7 uses explicitly the fact that the dipole moment induced in atom  $A$  is determined by the field arising from all other sources but atom  $A$ . This field is not the same as the macroscopic field  $\mathbf{E}$  in the neighborhood of atom  $A$  since  $\mathbf{E}$  includes the contribution from the charges of atom  $A$  itself (this same statement can be found in Ref. 3, but as we discussed above, it is not clear at which point in the derivation is taken into account explicitly). Since the explicit calculation of the spatial average of the self-field gives  $-4\pi\mathbf{P}/3$ , the usual result is readily obtained.

Besides lacking a well-established methodology in order to deal with the averaging process, all the treatments mentioned above are static in nature since the dynamical properties of the system never appear and their result can hardly be considered a thermodynamical one.

The purpose of the present paper is to present a statistical-mechanical treatment of the macroscopic field  $\mathbf{E}$  and the molecular field  $\mathbf{E}_m$  in which the physical origin of their difference is clearly seen through a unified averaging process. We introduce, within a simple dynamical model, a true statistical-mechanical analysis of the problem, which is more rigorous than the usual derivations.

In Sec. II we introduce the model Hamiltonian of the

system and derive the expression for the molecular field  $\mathbf{E}_m$ , which is then compared with the corresponding expression for the macroscopic field  $\mathbf{E}$ . In Sec. III we derive the Clausius-Mossotti relation for a system of hard spheres and then we show its more general validity. We also analyze its range of applicability by considering the nature of the approximations used.

## II. CALCULATION OF THE MOLECULAR FIELD

Our model consists of a system of  $N$  atoms represented by a massive positive nucleus interacting with an electron through a harmonic oscillator force and interacting among themselves through the Coulomb potential. In order to study its response, the system is placed in an external electrostatic potential  $\phi_{\text{ext}}$ . The usual justification behind such a simplified atomic model relies in the fact that the quantum-mechanical linear response of an atom to an electromagnetic field can be written in a form that corresponds to the one of a set of classical oscillators with different "oscillator strengths."<sup>13</sup> For simplicity we shall assume only one oscillator (with natural frequency  $\omega_0$ ) per atom, so that our model will be represented by the following Hamiltonian:

$$H = \sum_{i=1}^N \Pi_i^2/2M + \sum_{i=1}^N \pi_i^2/2m + \frac{1}{2} \sum_{i=1}^N \sum_{\alpha=1}^3 m\omega_0^2 |\mathbf{r}_{i\alpha} - \mathbf{R}_{i\alpha}|^2 + \sum_{i<j} v(i,j) + e \sum_{i=1}^N [\phi_{\text{ext}}(\mathbf{R}_i) - \phi_{\text{ext}}(\mathbf{r}_i)], \quad (2.1)$$

where  $\mathbf{R}_i, \Pi_i$ , and  $M$  are the position, momentum, and mass of the  $i$ th nucleus and  $\mathbf{r}_i, \pi_i$ , and  $m$  are the corresponding quantities for the  $i$ th electron;  $N$  is the total number of atoms; the index  $\alpha$  represents the three Cartesian components,  $e$  is the absolute value of the electronic charge, and  $v(i,j)$  is the Coulomb interaction energy between atoms  $i$  and  $j$  given by

$$v(i,j) = e^2 \left( \frac{1}{|\mathbf{R}_i - \mathbf{R}_j|} - \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{1}{|\mathbf{R}_i - \mathbf{r}_j|} + \frac{1}{|\mathbf{r}_i - \mathbf{R}_j|} \right). \quad (2.2)$$

The thermodynamical properties of the system appear through the polarization field, defined as

$$\mathbf{P}(\mathbf{R}) = \langle e \sum_{i=1}^N (\mathbf{R}_i - \mathbf{r}_i) \delta(\mathbf{R} - \mathbf{R}_i) \rangle, \quad (2.3)$$

where  $\delta$  is the Dirac delta function and  $\langle \dots \rangle$  stands for a thermodynamical average, i.e.,

$$\langle A \rangle = \int A \exp(-\beta H) d\Gamma / \int \exp(-\beta H) d\Gamma, \quad (2.4)$$

where

$$d\Gamma = d^3\Pi_1 \dots d^3\Pi_N d^3\pi_1 \dots d^3\pi_N d^3\mathbf{R}_1 \dots d^3\mathbf{R}_N d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N$$

is the volume element in phase space;  $\beta = (k_B T)^{-1}$ , where  $k_B$  is the Boltzmann constant and  $T$  the absolute temperature. The polarization field  $\mathbf{P}(\mathbf{R})$  as given by Eq. (2.3) is the thermal average of the dipole moments corresponding to the atomic charge distributions and we have chosen the "position of the  $i$ th dipole" at  $\mathbf{R}_i$ . The dependence of the result on this choice is expected to be weak, if the extension of the atoms is small compared with the mean interatomic distance.

We now calculate the polarization field using Eq. (2.3).

We seek an expression for  $\mathbf{R}_i - \mathbf{r}_i$ . Differentiating both sides of Eq. (2.1) with respect to  $r_{i\alpha}$  we have

$$\frac{\partial H}{\partial r_{i\alpha}} = m\omega_0^2(r_{i\alpha} - R_{i\alpha}) + e[E_{\text{mol},\alpha}(\mathbf{r}_i) + E_{\text{ext},\alpha}(\mathbf{r}_i)], \quad (2.5)$$

where  $\mathbf{E}_{\text{ext}} = -\nabla\phi_{\text{ext}}$  is the external electrostatic field and

$$\mathbf{e}_{\text{mol},\alpha}(\mathbf{r}_i) = \sum_{j \neq i} \mathbf{e}_{\text{mol},\alpha}^{(j)}(\mathbf{r}_i) = -\frac{\partial}{\partial x_{i\alpha}} \sum_{j \neq i} \left( \frac{1}{|\mathbf{r}_i - \mathbf{R}_j|} - \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right) \quad (2.6)$$

is the field felt by the  $i$ th electron placed at  $\mathbf{r}_i$ , produced by all the other atoms. If we multiply Eq. (2.5) by  $\delta(\mathbf{R} - \mathbf{R}_i)$  and average, the left-hand side gives zero. Indeed, for  $\mathbf{R}_i$  fixed, let us integrate over  $r_{i\alpha}$  first:

$$\int \frac{\partial H}{\partial r_{i\alpha}} e^{-\beta H} dr_{i\alpha} = -\frac{1}{\beta} \int \frac{\partial e^{-\beta H}}{\partial r_{i\alpha}} dr_{i\alpha} = -\frac{1}{\beta} [e^{-\beta H}]_{r_{i\alpha}=-\infty}^{r_{i\alpha}=\infty}. \quad (2.7)$$

Since the atoms are bound by a harmonic oscillator, if we take  $\mathbf{r}_i$  far away with  $\mathbf{R}_i$  fixed,  $H \rightarrow +\infty$  and the above term vanishes. Substituting the first term on the right-hand side of Eq. (2.5) in Eq. (2.3) we then have

$$\mathbf{P}(\mathbf{R}) = \alpha \langle \sum_i [E_{\text{ext}}(\mathbf{r}_i) + \mathbf{e}_{\text{mol}}(\mathbf{r}_i)] \delta(\mathbf{R} - \mathbf{R}_i) \rangle, \quad (2.8a)$$

where

$$\alpha \equiv e^2/m\omega_0^2. \quad (2.8b)$$

This equation *proves* that the polarization is proportional to the average field felt by each atom due to the other atoms and the external sources. That is,

$$\mathbf{P}(\mathbf{R}) = \alpha N \rho(\mathbf{R}) \mathbf{E}_m(\mathbf{R}_1 = \mathbf{R}), \quad (2.9)$$

where

$$\mathbf{E}_m(\mathbf{R}_1 = \mathbf{R}) = [1/\rho(\mathbf{R})] \langle [E_{\text{ext}}(\mathbf{r}_1) + \mathbf{e}_{\text{mol}}(\mathbf{r}_1)] \delta(\mathbf{R} - \mathbf{R}_1) \rangle \quad (2.10)$$

is the molecular field and  $\rho(\mathbf{R})$  is the probability of finding a nucleus at  $\mathbf{R}_1$ . In Eq. (2.10) we have made use of the fact that the Hamiltonian is invariant under a relabeling of the atoms.

Now, if the total field

$$\mathbf{E}_T(\mathbf{r}_1) = \mathbf{E}_{\text{ext}}(\mathbf{r}_1) + \mathbf{e}_{\text{mol}}(\mathbf{r}_1) \quad (2.11)$$

on an electron does *not* vary appreciably within a length  $u_1 = |\mathbf{r}_1 - \mathbf{R}_1|$  of atomic dimensions, that is,

$$|\nabla[\mathbf{E}_T(\mathbf{r}_1) \cdot \mathbf{u}_1]|/|\mathbf{E}_T(\mathbf{r}_1)| \ll 1, \quad (2.12)$$

then  $\mathbf{E}_T(\mathbf{r}_1) \approx \mathbf{E}_T(\mathbf{R}_1)$  and *no* net force is felt on an atom. This means that gradients in the density will not arise and the thermal averages can be thus taken in the absence of the external field and will be denoted by  $\langle \dots \rangle_0$ .

Therefore Eq. (2.10) for the molecular field can be written as

$$\mathbf{E}_m(\mathbf{R}) = \mathbf{E}_{\text{ext}}(\mathbf{R}) + [1/\rho(\mathbf{R})] \langle \mathbf{e}_{\text{mol}}(\mathbf{R}_1) \delta(\mathbf{R} - \mathbf{R}_1) \rangle_0 \quad (2.13)$$

or

$$\mathbf{E}_m(\mathbf{R}) - \mathbf{E}_{\text{ext}}(\mathbf{R}) = [1/\rho(\mathbf{R})] \sum_{j \neq 1} \langle \mathbf{e}_{\text{mol}}^{(j)}(\mathbf{R}_1) \delta(\mathbf{R} - \mathbf{R}_1) \rangle_0 \quad (2.14)$$

$$= [(N-1)/\rho(\mathbf{R})] \langle \mathbf{e}_{\text{mol}}^{(2)}(\mathbf{R}_1) \delta(\mathbf{R} - \mathbf{R}_1) \rangle_0, \quad (2.15)$$

where we have used the fact that each term  $j$  in Eq. (2.14) contributes equally to the sum. Since  $\mathbf{u}_j \equiv \mathbf{r}_j - \mathbf{R}_j$  is always of the order of atomic dimensions, we can make a multipole expansion of the field and, to lowest order in  $\mathbf{u}_j$ , we obtain

$$\mathbf{e}_{\text{mol}}^{(2)}(\mathbf{R}_1) \approx e \nabla_{\mathbf{R}_1} [\mathbf{u}_2 \cdot \nabla_{\mathbf{R}_2} (1/|\mathbf{R}_1 - \mathbf{R}_2|)] \equiv e \vec{\mathbf{T}}(\mathbf{R}_1 - \mathbf{R}_2) \cdot (\mathbf{r}_2 - \mathbf{R}_2), \quad (2.16)$$

where we have defined

$$\vec{\mathbf{T}}(\mathbf{R}_1 - \mathbf{R}_2) \equiv \nabla_{\mathbf{R}_1} \nabla_{\mathbf{R}_2} (1/|\mathbf{R}_1 - \mathbf{R}_2|). \quad (2.17)$$

We now substitute Eq. (2.16) into Eq. (2.15) and integrate over  $\mathbf{r}_1$  and over atoms 3, ...,  $N$  yielding

$$\begin{aligned} \mathbf{E}_m(\mathbf{R}_1) - \mathbf{E}_{\text{ext}}(\mathbf{R}_1) &= \frac{(N-1)e}{\rho(\mathbf{R})} \int \int \vec{\mathbf{T}}(\mathbf{R}_1 - \mathbf{R}_2) \cdot (\mathbf{r}_2 - \mathbf{R}_2) \\ &\quad \times \delta(\mathbf{R} - \mathbf{R}_1) \rho(\mathbf{R}_1, \mathbf{R}_2, \mathbf{r}_2) d^3\mathbf{R}_1 d^3\mathbf{R}_2 d^3\mathbf{r}_2 \\ &= e \frac{N-1}{\rho(\mathbf{R})} \int \int \vec{\mathbf{T}}(\mathbf{R} - \mathbf{R}_2) \cdot (\mathbf{r}_2 - \mathbf{R}_2) \\ &\quad \times \rho(\mathbf{R}_1 = \mathbf{R}, \mathbf{R}_2, \mathbf{r}_2) d^3\mathbf{R}_2 d^3\mathbf{r}_2, \end{aligned} \quad (2.18)$$

where  $\rho(\mathbf{R}_1, \mathbf{R}_2, \mathbf{r}_2)$  is the joint probability of finding an electron at  $\mathbf{r}_2$  and nuclei at  $\mathbf{R}_1$  and  $\mathbf{R}_2$ . We can write this joint probability

$$\rho(\mathbf{R}_1, \mathbf{R}_2, \mathbf{r}_2) \equiv \rho(\mathbf{R}_1 | \mathbf{R}_2, \mathbf{r}_2) \rho(\mathbf{R}_2, \mathbf{r}_2) \quad (2.19)$$

in terms of the conditional probability  $\rho(\mathbf{R}_1 | \mathbf{R}_2, \mathbf{r}_2)$  that nucleus 1 be at  $\mathbf{R}_1$ , with the condition that atom 2 be at  $\mathbf{R}_2, \mathbf{r}_2$ .

The problem simplifies greatly if we assume that the position of nucleus 1 is not very sensitive to the position of the electron in atom 2, so that

$$\rho(\mathbf{R}_1, \mathbf{R}_2, \mathbf{r}_2) \approx \rho(\mathbf{R}_1 | \mathbf{R}_2) \rho(\mathbf{R}_2, \mathbf{r}_2). \quad (2.20)$$

With this approximation, Eq. (2.18) can be written finally as

$$\begin{aligned} \mathbf{E}_m(\mathbf{R}) - \mathbf{E}_{\text{ext}}(\mathbf{R}) &= e \frac{N-1}{\rho(\mathbf{R})} \int d^3\mathbf{R}_2 \vec{\mathbf{T}}(\mathbf{R} - \mathbf{R}_2) \rho(\mathbf{R} | \mathbf{R}_2) \\ &\quad \cdot \int d^3\mathbf{r}_2 (\mathbf{r}_2 - \mathbf{R}_2) \rho(\mathbf{R}_2, \mathbf{r}_2) \\ &= -\frac{N-1}{N} \int \vec{\mathbf{T}}(\mathbf{R} - \mathbf{R}_2) \cdot \mathbf{P}(\mathbf{R}_2) c(\mathbf{R}, \mathbf{R}_2) d^3\mathbf{R}_2, \end{aligned} \quad (2.21)$$

where we have introduced the two-particle correlation function

$$c(\mathbf{R}_1, \mathbf{R}_2) \equiv \rho(\mathbf{R}_1 | \mathbf{R}_2) / \rho(\mathbf{R}_1), \quad (2.22)$$

and using Eq. (2.3) we have identified

$$\mathbf{P}(\mathbf{R}_2) = -Ne \int d^3\mathbf{r}_2 (\mathbf{r}_2 - \mathbf{R}_2) \rho(\mathbf{R}_2, \mathbf{r}_2). \quad (2.23)$$

We notice that the peculiarity of the expressions for the molecular field is that the  $\mathbf{R}$  that appears in Eq. (2.18) and all subsequent equations always indicate the *position of a particle*. This fact appears explicitly through the two-particle correlation function in Eq. (2.21).

On the other hand, if we were considering the macroscopic field  $\mathbf{E}(\mathbf{R})$ , the argument  $\mathbf{R}$  would simply denote an *arbitrary* observation point within the medium. In this case Eq. (2.15) should be replaced by

$$\mathbf{E}(\mathbf{R}) - \mathbf{E}_{\text{ext}}(\mathbf{R}) = \sum_{j=1}^N \langle \mathbf{e}_{\text{mol}}^{(j)}(\mathbf{R}) \rangle = N \langle \mathbf{e}_{\text{mol}}^{(1)}(\mathbf{R}) \rangle, \quad (2.24)$$

where  $\mathbf{e}_{\text{mol}}^{(1)}(\mathbf{R})$  is the field at  $\mathbf{R}$  produced by atom 1 and can be approximated [as in Eq. (2.16)] by

$$\mathbf{e}_{\text{mol}}^{(1)}(\mathbf{R}) \approx e \vec{\mathbf{T}}(\mathbf{R} - \mathbf{R}_1) \cdot (\mathbf{r}_1 - \mathbf{R}_1). \quad (2.25)$$

Substituting Eq. (2.25) into Eq. (2.24) we obtain

$$\begin{aligned} \mathbf{E}(\mathbf{R}) - \mathbf{E}_{\text{ext}}(\mathbf{R}) &= Ne \iint \vec{\mathbf{T}}(\mathbf{R} - \mathbf{R}_1) \cdot (\mathbf{r}_1 - \mathbf{R}_1) \rho(\mathbf{R}_1, \mathbf{r}_1) d^3 \mathbf{R}_1 d^3 \mathbf{r}_1 \quad (2.26a) \\ &= - \int \vec{\mathbf{T}}(\mathbf{R} - \mathbf{R}_1) \cdot \mathbf{P}(\mathbf{R}_1) d^3 \mathbf{R}_1 \quad (2.26b) \\ &= - \nabla_{\mathbf{R}} \int \frac{-\nabla_{\mathbf{R}_1} \cdot \mathbf{P}(\mathbf{R}_1)}{|\mathbf{R} - \mathbf{R}_1|} d^3 \mathbf{R}_1. \quad (2.26c) \end{aligned}$$

Thus the essential difference between Eqs. (2.26b) and (2.21) is the appearance of the two-particle correlation function in the latter. Equation (2.26c) is the familiar expression for the macroscopic field that appears in most textbooks and is obtained from Eq. (2.26b) by using the definition of  $\vec{\mathbf{T}}(\mathbf{R} - \mathbf{R}_1)$  (Eq. 2.17) and an integration by parts.

### III. CLAUSIUS-MOSSOTTI RELATION

In Sec. II we derived Eq. (2.21), which provides a relationship between the molecular field and the polarization field, once the correlation function  $c(\mathbf{R}_1, \mathbf{R}_2)$  is given.

In order to obtain a simple analytical relation we shall analyze, in this section, a very simple model for  $c(\mathbf{R}_1, \mathbf{R}_2)$ , by assuming that the atoms can be treated as hard spheres; the correlation function is taken then as

$$c(\mathbf{R}_1, \mathbf{R}_2) = \begin{cases} 0 & R < a \\ 1 & R > a, \end{cases} \quad (3.1)$$

where  $R = |\mathbf{R}_1 - \mathbf{R}_2|$  and  $a/2$  is the radius of the spheres. Then we have that the molecular field is given by Eq. (2.21), where the integral of  $\vec{\mathbf{T}} \cdot \mathbf{P}$  is taken over all space, with a small sphere around  $\mathbf{R}_2 = \mathbf{R}$  excluded; that is

$$\mathbf{E}_m(\mathbf{R}) = \mathbf{E}_{\text{ext}}(\mathbf{R}) - \int_{\infty - \text{sphere}} \vec{\mathbf{T}}(\mathbf{R} - \mathbf{R}_2) \cdot \mathbf{P}(\mathbf{R}_2) d^3 \mathbf{R}_2, \quad (3.2)$$

where we have also taken the large- $N$  limit. Using the definition of  $\vec{\mathbf{T}}(\mathbf{R} - \mathbf{R}_2)$  [Eq. (2.17)], we have

$$\begin{aligned} \mathbf{E}_m(\mathbf{R}) = \mathbf{E}_{\text{ext}}(\mathbf{R}) &- \int_{\infty - \text{sphere}} \nabla_{\mathbf{R}} (\nabla_{\mathbf{R}_2} \cdot 1/|\mathbf{R} - \mathbf{R}_2|) \cdot \mathbf{P}(\mathbf{R}_2) d^3 \mathbf{R}_2 \\ &= \mathbf{E}_{\text{ext}}(\mathbf{R}) + \int_{\infty - \text{sphere}} \nabla_{\mathbf{R}} \frac{\nabla_{\mathbf{R}_2} \cdot \mathbf{P}(\mathbf{R}_2)}{|\mathbf{R} - \mathbf{R}_2|} d^3 \mathbf{R}_2 \\ &- \int \nabla_{\mathbf{R}} \left( \nabla_{\mathbf{R}_2} \cdot \frac{\mathbf{P}(\mathbf{R}_2)}{|\mathbf{R} - \mathbf{R}_2|} \right) d^3 \mathbf{R}_2. \quad (3.4) \end{aligned}$$

In the second term on the right-hand side in Eq. (3.4) the integrand goes as  $|\mathbf{R} - \mathbf{R}_2|^{-2}$  near  $\mathbf{R}_2 = \mathbf{R}$ ; this factor is compensated by the quadratic radial dependence of the volume differential, thus giving a finite contribution when integrated over a small sphere around  $\mathbf{R}_2 = \mathbf{R}$ . This contribution is proportional to the volume of the sphere, which we have taken of atomic dimensions; the integral can thus be extended over all space and  $\nabla_{\mathbf{R}}$  taken outside the inte-

gral. Therefore the first two terms on the right-hand side in Eq. (3.4) correspond to the macroscopic field  $\mathbf{E}$  [see Eq. (2.26c)].

On the other hand, when we evaluate the last integral on the right-hand side of Eq. (3.4), the exclusion of a small sphere around  $\mathbf{R}_2 = \mathbf{R}$  is essential, because the integrand goes as  $|\mathbf{R} - \mathbf{R}_2|^{-3}$ . We thus have

$$\begin{aligned} &- \int_{\infty - \text{sphere}} \nabla_{\mathbf{R}} \left( \nabla_{\mathbf{R}_2} \cdot \frac{\mathbf{P}(\mathbf{R}_2)}{|\mathbf{R} - \mathbf{R}_2|} \right) d^3 \mathbf{R}_2 \\ &= \oint_{|\mathbf{R} - \mathbf{R}_2| = a} \nabla_{\mathbf{R}} \frac{\mathbf{P}(\mathbf{R}_2) \cdot d\mathbf{S}_2}{|\mathbf{R} - \mathbf{R}_2|} \\ &= - \oint_{|\mathbf{R} - \mathbf{R}_2| = a} \frac{\mathbf{R} - \mathbf{R}_2}{|\mathbf{R} - \mathbf{R}_2|^3} \cdot \mathbf{P}(\mathbf{R}_2) \cdot d\mathbf{S}_2, \quad (3.5) \end{aligned}$$

where the volume integral was written, after an integration by parts, as an integral over the surface of the sphere of radius  $a$ . The contribution from the surface at infinity vanishes and  $d\mathbf{S}_2$  points outward from the sphere.

We now assume that  $\mathbf{P}(\mathbf{R})$  varies slowly in a length of the order of atomic dimensions, so that it can be taken out of the integral. Taking the  $z$  axis in the direction of  $\mathbf{P}$ , it can be seen that the last integral in Eq. (3.5) has only a  $z$  component, which can be written as

$$P \int \frac{z}{r^3} \cos \theta r^2 d\Omega = P \int \cos^2 \theta d\Omega = \frac{4\pi P}{3}, \quad (3.6)$$

where  $r = |\mathbf{R}_2 - \mathbf{R}|$  and  $d\Omega$  is the solid angle differential. Notice that this integral is independent of the radius of the sphere. Substituting Eq. (3.6) into Eq. (3.4), and using Eq. (2.26c) along with the arguments mentioned above, we can write finally

$$\mathbf{E}_m(\mathbf{R}) = \mathbf{E}(\mathbf{R}) + (4\pi/3) \mathbf{P}(\mathbf{R}). \quad (3.7a)$$

The term  $(4\pi/3) \mathbf{P}$  is known in the literature as the Lorentz correction to the molecular field; here we have derived relation (3.7a) as a particular case of the general expression, Eq. (2.21), when we assume a hard-sphere model for the pair-correlation function. From Eq. (3.7a) one can obtain<sup>1-7</sup> the well-known Clausius-Mossotti relation

$$\alpha = \frac{3}{4\pi N \rho} \frac{\epsilon - 1}{\epsilon + 2} \quad (3.7b)$$

between the microscopic polarizability  $\alpha$  and the dielectric constant  $\epsilon$ .

Nevertheless we shall now show that the Clausius-Mossotti relation has a more general validity than the one implied by the derivation given above.

Multiplying both sides of Eq. (2.21) by  $N\alpha\rho(\mathbf{R})$ , and using Eq. (2.9), we obtain

$$\begin{aligned} \mathbf{P}(\mathbf{R}) = N\alpha\rho(\mathbf{R}) \left( \mathbf{E}_{\text{ext}}(\mathbf{R}) \right. \\ \left. - \int \vec{\mathbf{T}}(\mathbf{R} - \mathbf{R}_2) \cdot \mathbf{P}(\mathbf{R}_2) c(\mathbf{R}_1, \mathbf{R}_2) d^3 \mathbf{R}_2 \right), \quad (3.8) \end{aligned}$$

an integral equation for the polarization field. Here we have taken the large- $N$  limit.

Since the thermal averages can be approximated by averages in the absence of the external field, then  $c(\mathbf{R}_1, \mathbf{R}_2) = c(|\mathbf{R}_1 - \mathbf{R}_2|)$  and  $N\rho(\mathbf{R}) = n_0$ ; thus we can solve Eq. (3.8) by taking its Fourier transform<sup>14</sup>

$$\mathcal{P}(\mathbf{k}) = n_0 \alpha \left[ \mathcal{E}_{\text{ext}}(\mathbf{k}) - \vec{\mathbf{Q}}(\mathbf{k}) \cdot \mathcal{P}(\mathbf{k}) \right], \quad (3.9)$$

where the Fourier transform is defined as

$$\mathbf{P}(\mathbf{R}) = \int \mathcal{P}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{R}} \frac{d^3\mathbf{k}}{(2\pi)^3} \quad (3.10)$$

and

$$\bar{\mathbf{Q}}(\mathbf{k}) \equiv \int \bar{\mathbf{T}}(\mathbf{R}) c(\mathbf{R}) e^{i\mathbf{k}\cdot\mathbf{R}} d^3\mathbf{R}. \quad (3.11)$$

In the case of an external electrostatic field,  $\nabla \times \mathbf{E}_{\text{ext}} = 0$ ; thus  $\mathbf{E}_{\text{ext}}$  has no transverse component and consequently  $\mathcal{P}(\mathbf{k})$  is purely longitudinal. Therefore without loss of generality we take  $\mathbf{k}$  along the  $z$  axis and write

$$\mathcal{P}_z(\mathbf{k}) = n_0 \alpha \frac{1}{1 + n_0 \alpha Q_{zz}(\mathbf{k})} \mathcal{E}_{\text{ext},z}(\mathbf{k}). \quad (3.12)$$

Using the explicit form of  $\bar{\mathbf{T}}(\mathbf{R})$  given in Eq. (2.17) we are able to calculate  $Q_{zz}(\mathbf{k})$  through simple integration and we find

$$Q_{zz}(\mathbf{k}) = 8\pi \int_0^\infty \frac{j_1(kx)}{kx} \frac{dc(x)}{dx} dx, \quad (3.13)$$

where  $j_1(kx)$  is the spherical Bessel function of order 1.

Since  $c(x)$  is normalized to unity at infinity, there is always a length  $a$  (usually of atomic dimensions) such that

$$c(a) \approx 1, \quad (3.14)$$

$$\left( \frac{dc(x)}{dx} \right)_{x=a} \approx 0. \quad (3.15)$$

Thus we can replace the upper limit in the integral in Eq. (3.13) by  $a$ . Furthermore, if the external field does not vary appreciably within such a length  $a$ , then we need to consider only those Fourier components of the field with  $ka \ll 1$ . Using the limit

$$\frac{j_1(ka)}{ka} \xrightarrow{ka \ll 1} \frac{1}{3} \quad (3.16)$$

and the fact that  $c(x)$  vanishes at the origin, we can approximate the integral in Eq. (3.13) by

$$Q_{zz}(\mathbf{k}) \approx \frac{8\pi}{3} \int_0^a dc(x) = \frac{8\pi}{3}, \quad (3.17)$$

a result that is independent of the functional form of  $c(x)$ . Substituting Eq. (3.17) into Eq. (3.12) and performing an inverse Fourier transformation we obtain

$$\mathbf{P}(\mathbf{R}) = n_0 \alpha \frac{1}{1 + (8\pi/3)n_0 a} \mathbf{E}_{\text{ext}}(\mathbf{R}), \quad (3.18)$$

an expression that can be easily seen to be equivalent to the Clausius-Mossotti formula given by Eq. (3.7). This means

that as long as the external field does not vary appreciably within a length of order  $a$ , the Clausius-Mossotti is a relation of very general validity.

Corrections to the Clausius-Mossotti formula will arise for systems under the influence of external fields varying rapidly in lengths of the order of atomic dimensions,<sup>14,15</sup> or from the breakdown of the dipole approximation. Although our model is a classical one, a quantum-mechanical calculation on a more realistic model will not change neither the structure of our results nor the validity of our conclusions.<sup>14</sup>

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\*Permanent address: Instituto de Física, UNAM, Apartado Postal 20-364, México 20, D. F.

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