Analytic approach to the interfacial polarization of heterogeneous systems

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We have obtained an analytical solution of Maxwell's equations for a dielectric system of spherical particles in a medium. The system is placed between two parallel electrode plates, subject to a low-frequency alternating potential, and the solution is obtained from the corresponding boundary-value problem for the Green function. All the multipole moments and the electric field are expressed in terms of the applied potential at the electrodes and a matrix which depends on the system configuration. The effective dielectric function is then obtained as an average over the whole sample. For disordered systems, we solve exactly the case of two-particle distributions with short-range correlations and find that the form of the distribution plays a crucial role. In particular, we prove that for spherically symmetric two-particle distributions all multipole moments except dipoles are exactly zero, and the Maxwell-Garnett result, or, equivalently, the Clausius-Mossotti relation for spherical particles, is valid regardless of the particle concentration. Within the two-particle distribution, corrections to the Maxwell-Garnett result can only derive from nonsphericity in the distribution: in such a case, higher multipole moments are generally nonzero and may strongly affect the effective dielectric function. We provide the explicit expressions for all the multipole moments and the effective dielectric function, which can be computed straightforwardly for any given distribution. We show that an iterative unsymmetrical procedure proposed originally by Bruggeman is inconsistent with our results.

I. INTRODUCTION

The study of the electrical response in heterogeneous media has a long and distinguished history, originating with the works of Poisson, Mossotti,[1] Clausius,[2] Lorenz,[3] Lorentz,[4] Maxwell,[5] Garnett,[6] and Wagner.[7] All these works essentially reached equivalent conclusions, although they were based on somewhat different perspectives and hypotheses. A succinct but accurate review has been provided by Landauer.[8] These hypotheses, although quite plausible and ingenious, were made in the absence of an exact solution from first principles, which may have appeared prohibitively complex for a many-particle system. Subsequently, exact solutions have been obtained for regular arrays of spheres of uniform size, for example, by Doyle,[9] and McPhedran and co-workers.[10] A fully microscopic dipolar theory, within and beyond the so-called mean-field approximation, has been developed, for example, by Gómez *et al.*,[11] Persson and Liebsch,[12] and Barrera *et al.*[13] The role of higher multipole moments has also been discussed, for example, by Davis and Schwartz,[14] Felderhof and Jones,[15] and Claro and Brouers.[16]

In this paper we present an analytical approach and several rigorous results which derive from it. We consider a system of spherical particles surrounded by a host medium, with different dielectric functions. We place the system between two parallel electrode plates at a distance d, and apply to them an alternating potential, as in the common low-frequency experimental configuration. So, we have a perfectly well-defined boundary-value problem for Maxwell's equations. We solve it with the Green-function method, which generates the exact multipole moments of the particles and the exact electric field: these are expressed in terms of the applied field at the electrode plates and a matrix which depends on the system configuration. The exact electric field has contributions from the applied field, the field produced by all the particles, and the field produced by all the images of the particles. The external field, which is the superposition of the applied field in the absence of the sample and the field produced by the images, is in general nonuniform and depends on the properties and configuration of the system. Then we determine the effective dielectric function by averaging directly $\langle \epsilon \mathbf{E} \rangle$ over the whole sample. The effective dielectric function depends explicitly only on the induced dipole moments, which are in turn coupled to all the multipole moments of particles and images. This program is completed in Sec. II.

For disordered systems, the ensemble-averaged solution is determined in terms of m-particle distributions. We consider in this paper only two-particle distributions, which amounts to neglecting fluctuation effects. This is often referred to as the mean-field approximation. On the other hand, we do not make the dipole approximation: we include multipole moments of all orders for both the particles and their images. If the two-particle correlation has a short-range $R \ll d$, we prove first of all that (a) the higher multipole moments of the other particles outside the correlation range and of all the images give no contribution to the local field, while their dipole moments simply produce a uniform field. This result is caused by the distribution uniformity outside the correlation range, not by the decay over distance of the multipole contributions: it holds for a very short correlation range just as well. Therefore, in this situation, the external field is uniform in the bulk. Second, we prove that (b) the contributions of all the multipole moments of the other particles within the correlation range to the local field acting on a given particle depend crucially on the specific form of the two-particle distribution, being generally nonzero if the distribution is nonspherical. Both results (a) and (b) actually hold for particles of arbitrary shapes and orientations. For spherical particles, we provide the explicit expressions of all the multipole moments, electric field, and effective dielectric function, which can be computed immediately for any given distribution. The effective dielectric function differs from the Maxwell-Garnett result if the distribution is nonspherical: in such a case, the correction may be quite significant, and it is of first order in the particle volume fraction. These results are obtained in Sec. III.

A particular but important case is that of a spherically symmetric two-particle distribution. In such a case, the other particles within the correlation range give no contribution to the local field acting on a given particle. Therefore, each particle is subject to a uniform local field, whatever radial dependence the distribution may have, and whatever the particle shapes and orientations may be. If the particles are spherical, such a uniform local field can only induce dipole moments, while all the higher multipole moments vanish identically. Therefore, the Maxwell-Garnett result, or, equivalently, the Clausius-Mossotti relation for spherical particles, follows strictly, and is not limited to dilute systems or the dipole approximation. Correspondingly, within the mean-field approximation, modifications of the Maxwell-Garnett result which are only based on the particle concentration, without regard to the specific form of the two-particle distribution, are inconsistent with our results. A classical example[8] is an iterative unsymmetrical procedure proposed by Bruggeman.[17] These results are obtained in Sec. IV.

Using the approach presented in this paper, we have been able to solve the problem of clustered inclusions rigorously to all multipole orders.[18] This and the other results of our approach are summarized in the concluding section, Sec. V.

II. ANALYTIC APPROACH

Consider a heterogeneous system composed of spherical particles dispersed in a host medium described by a frequency-dependent complex dielectric function ϵ_m. The ith particle is centered at $\mathbf{r}_i$, has a radius a_i, and a frequency-dependent complex dielectric function ϵ_i. The system is placed between two electrode plates at $z = \pm d/2$. A sinusoidal potential of peak value V_0 is applied to the electrode plates. Assume that the transverse dimensions of the system are much greater than d, so that edge effects can be neglected. We consider low frequencies and small particles, $\lambda \gg d > a_i$, so that magnetic excitations can be ignored. Under such conditions, the time dependence can be factored out and the electric potential is expressed as

$$U(\mathbf{r},t) = U(\mathbf{r})e^{-j\omega t}. \tag{1}$$

It can be shown easily that in such a situation charges can only accumulate at the interfaces between the particles and the medium or between the medium and the electrodes. Therefore, $U(\mathbf{r})$ satisfies Laplace equation

$$\nabla^2 U(\mathbf{r}) = 0, \tag{2}$$

with boundary conditions

$$U(\mathbf{r})|_{z=-d/2} = V_0, \qquad U(\mathbf{r})|_{z=d/2} = 0, \tag{3a}$$

$$U_{\text{out}}(\mathbf{r})|_{s_i} = U_{\text{in}}(\mathbf{r})|_{s_i}, \tag{3b}$$

$$\epsilon_m \frac{\partial U_{\text{out}}(\mathbf{r})}{\partial n_i}\bigg|_{s_i} = \epsilon_i \frac{\partial U_{\text{in}}(\mathbf{r})}{\partial n_i}\bigg|_{s_i}. \tag{3c}$$

In Eqs. (3b) and (3c), s_i represents the surface of the ith particle, $\mathbf{n}_i$ its normal direction, and U_{out} and U_{in} refer to the potential outside and inside the particle, respectively.

The potential $U(\mathbf{r})$ can now be written as a superposition

$$U(\mathbf{r}) = U^0(\mathbf{r}) + U^1(\mathbf{r}). \tag{4}$$

In Eq. (4), the first term represents the applied potential

$$U^0(\mathbf{r}) = V_0/2 - \mathbf{E}_0 \cdot \mathbf{r} = V_0/2 - \mathbf{E}_0 \cdot \mathbf{r}_i - \mathbf{E}_0 \cdot (\mathbf{r} - \mathbf{r}_i), \tag{5}$$

and $\mathbf{E}_0 = \mathbf{e}_z V_0/d$ is defined as the applied electric field. The second term of Eq. (4) represents the potential produced by all the particles and the charges induced by them at the electrode plates, satisfying

$$\nabla^2 U^1(\mathbf{r}) = 0, \qquad U^1(\mathbf{r})|_{z=\pm d/2} = 0. \tag{6}$$

The Green function for Dirichlet boundary conditions at the electrode plates is

$$G(\mathbf{r},\mathbf{r}') = \sum_k \frac{(-1)^k}{|\mathbf{r} - \mathbf{r}'_k|}, \tag{7a}$$

where

$$\mathbf{r}'_k = \{x', y', kd + (-1)^k z'\}, \quad k = 0, \pm 1, \pm 2, \dots . \tag{7b}$$

In Eq. (7a), the term corresponding to $\mathbf{r}'_0 \equiv \mathbf{r}'$ represents the potential of a unit charge at $\mathbf{r}'$, while all the other terms with $k \neq 0$ represent the potentials produced by the images of that unit charge. Since charges accumulate only at interfaces, we have

$$U^1(\mathbf{r}) = \sum_{ik} (-1)^k \int_{s_i} \frac{\sigma_i(\mathbf{r}')ds'}{|\mathbf{r} - \mathbf{r}'_k|}, \tag{8}$$

where $\sigma_i(\mathbf{r}')$ is the total surface charge density of the ith particle, while the surface integral at the electrode plates vanishes because of the boundary conditions of Eq. (6).

We may now expand

$$\frac{1}{|\mathbf{r}-\mathbf{r}'_k|} = \frac{1}{|(\mathbf{r}-\mathbf{r}_{ik})-(\mathbf{r}'_k-\mathbf{r}_{ik})|} = 4\pi\sum_{lm}\frac{1}{(2l+1)}\frac{r_<^l}{r_>^{l+1}}Y^*_{l,m}(\mathbf{r}'_k-\mathbf{r}_{ik})Y_{l,m}(\mathbf{r}-\mathbf{r}_{ik})$$
$$= 4\pi\sum_{lm}\frac{(-1)^{(l+m)k}}{(2l+1)}\frac{r_<^l}{r_>^{l+1}}Y^*_{l,m}(\mathbf{r}'-\mathbf{r}_i)Y_{l,m}(\mathbf{r}-\mathbf{r}_{ik}), \quad (9)$$

where $\mathbf{r}_{ik}$ are defined as in Eq. (7b) but for the particle centers, $|\mathbf{r}'_k-\mathbf{r}_{ik}| = |\mathbf{r}'-\mathbf{r}_i| = a_i$, $Y_{l,m}(\mathbf{r}'_k-\mathbf{r}_{ik}) = (-1)^{(l+m)k}Y_{l,m}(\mathbf{r}'-\mathbf{r}_i)$, and $r_<$ $(r_>)$ denotes the smaller (larger) between a_i and $|\mathbf{r}-\mathbf{r}_{ik}|$. Substituting Eq. (9) into Eq. (8), and combining with Eq. (5), we obtain the total potential as

$$U_{\text{in}}(\mathbf{r}) = (V_0/2-\mathbf{E}_0\cdot\mathbf{r}_i) - \mathbf{E}_0\cdot(\mathbf{r}-\mathbf{r}_i) + 4\pi\sum_{lm}\frac{q_{ilm}}{(2l+1)a_i^{2l+1}}|\mathbf{r}-\mathbf{r}_i|^l Y_{l,m}(\mathbf{r}-\mathbf{r}_i)$$
$$+4\pi\sum_{i'l'm'k}(-1)^{(l'+m'+1)k}(1-\delta_i^{i'}\delta_k^0)\frac{q_{i'l'm'}}{(2l'+1)}\frac{Y_{l',m'}(\mathbf{r}-\mathbf{r}_{i'k})}{|\mathbf{r}-\mathbf{r}_{i'k}|^{l'+1}}, \quad |\mathbf{r}-\mathbf{r}_i| \le a_i \quad (10)$$

and

$$U_{\text{out}}(\mathbf{r}) = (V_0/2-\mathbf{E}_0\cdot\mathbf{r}_i) - \mathbf{E}_0\cdot(\mathbf{r}-\mathbf{r}_i) + 4\pi\sum_{lm}\frac{q_{ilm}}{(2l+1)}\frac{Y_{l,m}(\mathbf{r}-\mathbf{r}_i)}{|\mathbf{r}-\mathbf{r}_i|^{l+1}}$$
$$+4\pi\sum_{i'l'm'k}(-1)^{(l'+m'+1)k}(1-\delta_i^{i'}\delta_k^0)\frac{q_{i'l'm'}}{(2l'+1)}\frac{Y_{l',m'}(\mathbf{r}-\mathbf{r}_{i'k})}{|\mathbf{r}-\mathbf{r}_{i'k}|^{l'+1}}, \quad a_i \le |\mathbf{r}-\mathbf{r}_i| \le |\mathbf{r}_{i'}-\mathbf{r}_i| - a_{i'},\ i' \ne i. \quad (11)$$

In Eqs. (10) and (11), q_{ilm}'s are the multipole moments of the ith particle with respect to the particle center, and the factor $(1-\delta_i^{i'}\delta_k^0)$ is introduced to avoid double counting of the ith particle. The three contributions in Eqs. (10) and (11) are easily identified as the applied potential, the potential produced by the ith particle, and the potential of the other particles ($k=0$) and all the images ($k \ne 0$). Equations (10) and (11) show that the field produced by the images depends on the properties of the system, hence the external field, which is the applied field plus the field produced by all the images, is generally neither uniform nor experimentally controlled. That is typically the case if the system is a thin film, in which d is comparable to a_i, or, if d is comparable to a scale in which the system is inhomogeneous. Notice that the expressions (10) and (11) for the potentials are valid for particles of arbitrary shapes and orientations, except for the potential produced by the ith particle itself, which would require a modification.

The potential given in Eqs. (10) and (11) satisfies the Laplace equation and boundary conditions (3a) and (3b); Eq. (3c) will be used later to determine the multipole moments for spherical particles. But first we express all terms in Eqs. (10) and (11) as functions of $\mathbf{r}-\mathbf{r}_i$. For any $\mathbf{r}_{i'k} \ne \mathbf{r}_i$, we can expand

$$\frac{Y_{l',m'}(\mathbf{r}-\mathbf{r}_{i'k})}{(2l'+1)|\mathbf{r}-\mathbf{r}_{i'k}|^{l'+1}} = \sum_{lm}A_{lm}^{l'm'}(\mathbf{r}_{i'k}-\mathbf{r}_i)|\mathbf{r}-\mathbf{r}_i|^l Y_{l,m}(\mathbf{r}-\mathbf{r}_i),$$
$$|\mathbf{r}-\mathbf{r}_i| < |\mathbf{r}_{i'k}-\mathbf{r}_i|, \quad (12)$$

since the left-hand side satisfies the Laplace equation in this region. The expansion coefficients are obtained in Appendix A [cf. Eq. (A5)]:

$$A_{lm}^{l'm'}(\mathbf{r}_{i'k}-\mathbf{r}_i) = \frac{Y^*_{l+l',m-m'}(\mathbf{r}_{i'k}-\mathbf{r}_i)}{|\mathbf{r}_{i'k}-\mathbf{r}_i|^{l+l'+1}}$$
$$\times(-1)^{l'+m'}\left[\frac{4\pi(l+l'+m-m')!(l+l'-m+m')!}{(2l+1)(2l'+1)(2l+2l'+1)(l+m)!(l-m)!(l'+m')!(l'-m')!}\right]^{1/2}. \quad (13)$$

Substituting Eq. (12) into Eqs. (10) and (11), and defining

$$C_{lm}^{l'm'}(\mathbf{r}_{i'}-\mathbf{r}_i) = \sum_k(-1)^{(l'+m'+1)k}A_{lm}^{l'm'}(\mathbf{r}_{i'k}-\mathbf{r}_i)(1-\delta_i^{i'}\delta_k^0), \quad (14)$$

we obtain

$$U_{\text{in}}(\mathbf{r}) = (V_0/2-\mathbf{E}_0\cdot\mathbf{r}_i) - \mathbf{E}_0\cdot(\mathbf{r}-\mathbf{r}_i) + 4\pi\sum_{lm}\frac{q_{ilm}}{(2l+1)a_i^{2l+1}}|\mathbf{r}-\mathbf{r}_i|^l Y_{l,m}(\mathbf{r}-\mathbf{r}_i)$$
$$+4\pi\sum_{i'l'm'}q_{i'l'm'}\sum_{lm}C_{lm}^{l'm'}(\mathbf{r}_{i'}-\mathbf{r}_i)|\mathbf{r}-\mathbf{r}_i|^l Y_{l,m}(\mathbf{r}-\mathbf{r}_i), \quad |\mathbf{r}-\mathbf{r}_i| \le a_i \quad (15)$$

and

$$U_{\rm out}(\mathbf{r}) = (V_0/2 - \mathbf{E}_0\cdot\mathbf{r}_i) - \mathbf{E}_0\cdot(\mathbf{r}-\mathbf{r}_i) + 4\pi\sum_{lm}\frac{q_{ilm}}{(2l+1)}\frac{Y_{l,m}(\mathbf{r}-\mathbf{r}_i)}{|\mathbf{r}-\mathbf{r}_i|^{l+1}}$$
$$+4\pi\sum_{i'l'm'}q_{i'l'm'}\sum_{lm}C_{lm}^{l'm'}(\mathbf{r}_{i'}-\mathbf{r}_i)|\mathbf{r}-\mathbf{r}_i|^l Y_{l,m}(\mathbf{r}-\mathbf{r}_i),\quad a_i\le|\mathbf{r}-\mathbf{r}_i|\le|\mathbf{r}_{i'}-\mathbf{r}_i|-a_{i'},\ i'\ne i. \tag{16}$$

We remark explicitly that the last terms in Eqs. (15) and (16), representing the potential produced by the other particles and all the images, and the corresponding coupling coefficients $C_{lm}^{l'm'}(\mathbf{r}_{i'}-\mathbf{r}_i)$ still apply to particles of arbitrary shapes and orientations.

For spherical particles, substituting Eqs. (15) and (16) into the boundary condition (3c), we obtain

$$\sum_{lm}\frac{l\epsilon_i+(l+1)\epsilon_m}{(2l+1)a_i^{l+2}}q_{ilm}Y_{l,m}(\mathbf{r}-\mathbf{r}_i)$$
$$=(\epsilon_i-\epsilon_m)\left\{\frac{E_0}{\sqrt{12\pi}}Y_{1,0}(\mathbf{r}-\mathbf{r}_i)-\sum_{lm}\left[la_i^{l-1}\sum_{i'l'm'}C_{lm}^{l'm'}(\mathbf{r}_{i'}-\mathbf{r}_i)q_{i'l'm'}\right]Y_{l,m}(\mathbf{r}-\mathbf{r}_i)\right\}. \tag{17}$$

Comparing the coefficients of the corresponding spherical harmonics, we obtain

$$q_{ilm}=\sqrt{\frac{3}{4\pi}}\beta_{i1}E_0\delta_l^1\delta_m^0$$
$$-(2l+1)\beta_{il}\sum_{i'l'm'}C_{lm}^{l'm'}(\mathbf{r}_{i'}-\mathbf{r}_i)q_{i'l'm'}, \tag{18}$$

where

$$\beta_{il}=\frac{(\epsilon_i-\epsilon_m)la_i^{2l+1}}{l\epsilon_i+(l+1)\epsilon_m}. \tag{19}$$

Since $\beta_{i0}=0$, $q_{i00}=0$ as expected, and $l,l'\ge1$ is assumed henceforth.

Collecting q_{ilm}'s to the left-hand side of Eq. (18), we can write in matrix form

$$Gq=\sqrt{\frac{3}{4\pi}}hE_0, \tag{20a}$$

where q is a column matrix consisting of all q_{ilm}'s,

$$G_{ilm}^{i'l'm'}=\delta_i^{i'}\delta_l^{l'}\delta_m^{m'}+(2l+1)\beta_{il}C_{lm}^{l'm'}(\mathbf{r}_{i'}-\mathbf{r}_i) \tag{20b}$$

represents the system configuration matrix, and

$$h_{ilm}=\beta_{i1}\delta_l^1\delta_m^0. \tag{20c}$$

By matrix inversion, we finally obtain

$$q=\sqrt{\frac{3}{4\pi}}G^{-1}hE_0, \tag{21a}$$

or, explicitly,

$$q_{ilm}=\sqrt{\frac{3}{4\pi}}\sum_{i'}(G^{-1})_{ilm}^{i'10}\beta_{i'1}E_0. \tag{21b}$$

Thus, all multipole moments are expressed explicitly in terms of the applied field and the system configuration matrix.

Since we have determined the electric field exactly everywhere, we can obtain the effective dielectric function by averaging directly $\mathbf{D}=\epsilon\mathbf{E}$ over the whole sample, as

$$\langle\epsilon\mathbf{E}\rangle=\left(\frac{1}{V}\right)\int_V\epsilon\mathbf{E}(\mathbf{r})d^3\mathbf{r}$$
$$=\epsilon_m\mathbf{E}_0+\frac{1}{V}\sum_i(\epsilon_i-\epsilon_m)\left(\frac{4\pi a_i^3}{3}\right)\langle\mathbf{E}\rangle_i, \tag{22a}$$

where $\langle\mathbf{E}\rangle_i$ is the average electric field inside the ith particle. We used

$$\langle\mathbf{E}\rangle=\frac{1}{V}\int\int dx\,dy\int_{-d/2}^{d/2}\mathbf{E}(\mathbf{r})dz=\mathbf{E}_0, \tag{22b}$$

which follows from the boundary condition (3a), if we assume $x\to-x$ and $y\to-y$ symmetries, hence $\langle E_x\rangle=\langle E_y\rangle=0$.

In order to evaluate $\langle\mathbf{E}\rangle_i$, we use the following result [see, for example, Eq. (4.19), p. 141 of Jackson[19]]: the contribution to the average field in a sphere of radius r from the sources outside the sphere equals the field produced by those sources at the center of the sphere. Taking r slightly smaller than a_i and using Eq. (15) (notice that only the $l=1$ terms count and only the z component is needed), we obtain

$$\langle E_z\rangle_i=E_0-\sqrt{\frac{4\pi}{3}}\frac{q_{i10}}{a_i^3}$$
$$-\sqrt{12\pi}\sum_{i'l'm'}C_{10}^{l'm'}(\mathbf{r}_{i'}-\mathbf{r}_i)q_{i'l'm'}. \tag{23}$$

From Eq. (18), we have

$$\sum_{i'l'm'}C_{10}^{l'm'}(\mathbf{r}_{i'}-\mathbf{r}_i)q_{i'l'm'}=\sqrt{\frac{1}{12\pi}}E_0-\frac{q_{i10}}{3\beta_{i1}}. \tag{24}$$

Substituting Eq. (24) into Eq. (23), we obtain

$$\langle E_z\rangle_i=\sqrt{12\pi}\frac{\epsilon_m q_{i10}}{(\epsilon_i-\epsilon_m)a_i^3}. \tag{25}$$

Defining the effective dielectric function as $\langle \mathbf{D} \rangle = \epsilon_e \langle \mathbf{E} \rangle$, the left-hand side of Eq. (22a) is simply $\epsilon_e \mathbf{E}_0$. Substituting Eq. (25) into Eq. (22a), we then obtain

$$\frac{\epsilon_e}{\epsilon_m} = 1 + \frac{4\pi}{V}\sqrt{\frac{4\pi}{3}}\sum_i \frac{q_{i10}}{E_0} = 1 + \frac{4\pi}{V}\sum_{ii'}(G^{-1})_{i10}^{i'10}\beta_{i'1}. \tag{26}$$

This result for the effective dielectric function is exact, in general, having made no assumptions on the system configuration. So, it applies also to cases in which the external field is not uniform, such as thin films or inhomogeneous systems on a scale comparable to d. In such cases, the system is not equivalent to an infinite one: the images play a crucial role and must be treated exactly.[20] No *a priori* assumption can be made on the external field, which is nonuniform and unknown: it depends in a complicated manner on the system itself, through the images. Therefore, the external field cannot be considered as the perturbing agent in which the system is immersed: it must be treated as part of the system response. In such cases, it is essential to solve the physical boundary-value problem, considering the applied field as the perturbing agent.

Also notice that only the particle dipole moments entering directly in the first expression in Eq. (26) for ϵ_e is an exact consequence of having averaged $\mathbf{D}$ and $\mathbf{E}$ over the whole sample. Different results may apply with other definitions, such as averaging $\mathbf{D}$ and $\mathbf{E}$ over small volumes (yet containing many particles), as in Eq. (6.74), p. 229 of Jackson.[19] One may then obtain a nonlocal relation between $\mathbf{D}$ and $\mathbf{E}$, possibly involving derivatives of higher multipole moments, as in Eq. (6.92), p. 232 of Jackson.[19] There is no contradiction between Jackson's result and ours, as they apply to different definitions: our result for ϵ_e in Eq. (26) is exact, having defined ϵ_e as a property of the sample as a whole.

Finally, we remark that the first expression in Eq. (26) can also be proved in general for particles of arbitrary shapes and orientations, while the second expression is valid only for spherical particles. The second expression shows explicitly the coupling of the particle dipole moments to all multipole moments of all the particles and all the images as provided by the system configuration matrix.

III. APPLICATION TO DISTRIBUTIONS WITH SHORT-RANGE CORRELATIONS

If all the particle positions are known, as in crystal structures, for example, we can determine precisely the system configuration matrix, and calculate the multipole moments and the effective dielectric function to any desired order. For disordered systems, the exact ensemble-averaged solution is determined in principle if the N-particle distribution is given. This is practically impossible for large systems, and only approximate solutions can be determined, corresponding to lower-order distributions. From now on, we shall consider only macroscopically homogeneous systems, hence uniform single-particle distributions, and include only up to two-particle distributions, which amounts to neglecting fluctuation effects. We consider a system of identical particles, with radius a and dielectric function ϵ_p, while a more general result for many-species systems is provided in Appendix B.

We rewrite Eq. (20a) as

$$\sum_{l'm'} q_{l'm'} \sum_{i'} G_{ilm}^{i'l'm'} = \sqrt{\frac{3}{4\pi}}\alpha a^3 E_0 \delta_l^1 \delta_m^0 + \sum_{i'l'm'} G_{ilm}^{i'l'm'}[q_{l'm'} - q_{i'l'm'}], \tag{27a}$$

where

$$\alpha = (\epsilon_p - \epsilon_m)/(\epsilon_p + 2\epsilon_m), \tag{27b}$$

and $q_{lm} = \langle q_{ilm} \rangle$ are the average multipole moments. After ensemble averaging, the last term in Eq. (27) represents the contribution due to fluctuations. It gives nonzero corrections only when three-particle or higher-order distributions are considered; hence these corrections are at least of second order in volume fraction and will be neglected here. That is the only basic approximation of this and the following section.

The two-particle distribution can be written generally as

$$n(\mathbf{r} - \mathbf{r}_i) = \delta(\mathbf{r} - \mathbf{r}_i) + n^0 + f(\mathbf{r} - \mathbf{r}_i), \tag{28a}$$

where $n^0 = (N-1)/V \simeq N/V$ is the average particle number density, and $f(\mathbf{r} - \mathbf{r}_i)$ describes the deviation from a uniform distribution due to correlations. We consider correlations with a short range $R \ll d$. Therefore, the function $f(\mathbf{r} - \mathbf{r}_i)$ must satisfy the following conditions: first,

$$f(\mathbf{r} - \mathbf{r}_i) = -n^0 \quad \text{for } |\mathbf{r} - \mathbf{r}_i| \le 2a, \tag{28b}$$

since inside that region there is only one particle; second,

$$f(\mathbf{r} - \mathbf{r}_i) = 0 \quad \text{for } |\mathbf{r} - \mathbf{r}_i| > R, \tag{28c}$$

since outside the correlation range the distribution becomes uniform; third, conservation of the total number of particles requires

$$\int_{|r - r_i| \le R} f(\mathbf{r} - \mathbf{r}_i) d^3\mathbf{r} = 0. \tag{28d}$$

Using Eq. (28a), we can replace the summation over i' in Eq. (27) by integration. Since each term in $C_{lm}^{l'm'}(\mathbf{r}_{i'} - \mathbf{r}_i)$ contains a factor $e^{j(m'-m)\phi_{i'i}}$, where $\phi_{i'i}$ is the azimuthal angle of the vector $\mathbf{r}_{i'} - \mathbf{r}_i$, integration over $\phi_{i'i}$ yields zero for $m' \neq m$, since the particle distribution has azimuthal symmetry. Thus, the equations for multipole moments with different m are decoupled. For $m \neq 0$ moments, we have a set of homogeneous linear equations with nonzero determinant: hence each $m \neq 0$ multipole moment must vanish.

For $m' = m = 0$, we obtain in Appendix A [cf. Eq. (A17)] the average for the coupling coefficients

$$\sum_{i'} C_{l0}^{l'0}(\mathbf{r}_{i'} - \mathbf{r}_i) = f_l^{l'} + \left(\frac{8\pi}{9}\right) n^0 \delta_l^1 \delta_1^{l'} - \left(\frac{4\pi}{3}\right) n^0 \delta_l^1 \delta_1^{l'}, \tag{29}$$

where

$$f_l^{l'} = \int_{|\mathbf{r}-\mathbf{r}_i| \le R} f(\mathbf{r} - \mathbf{r}_i) A_{l0}^{l'0}(\mathbf{r} - \mathbf{r}_i) d^3\mathbf{r}. \tag{30}$$

This term represents the contribution of the neighboring particles within the correlation range. In general, all the multipole moments of these particles contribute to the local field acting on the ith particle, depending on the specific form of $f(\mathbf{r} - \mathbf{r}_i)$. The second term in Eq. (29) represents the contribution of the other particles outside the correlation range, while the third term represents the contribution of all the images. The factor $\delta_l^1 \delta_1^{l'}$ indicates [cf. Eqs. (15) and (16)] that the higher multipole moments of those particles and all the images do not contribute to the local field, while their dipole moments produce only a uniform field. As we mentioned already, the coupling coefficients are independent of the particle shapes and orientations, and so then are these results.

From Eqs. (20b) and (29), we obtain

$$\sum_{i'} G_{il0}^{i'l'0} = \delta_l^{l'} - v\alpha \delta_l^1 \delta_1^{l'} + (2l+1)\beta_l f_l^{l'} = G_l^{l'}, \tag{31}$$

where $v = (4\pi a^3/3)n^0$ is the volume fraction occupied by the particles, and

$$\beta_l = [(\epsilon_p - \epsilon_m) l a^{2l+1}]/[l\epsilon_p + (l+1)\epsilon_m]. \tag{32}$$

Equation (31) defines $G_l^{l'}$, the system configuration matrix with reduced dimensions. Now, Eq. (27) becomes

$$\sum_{l'} G_l^{l'} q_{l'0} = \sqrt{\frac{3}{4\pi}} \alpha a^3 E_0 \delta_l^1, \tag{33}$$

hence

$$q_{l0} = \sqrt{\frac{3}{4\pi}} \alpha a^3 (G^{-1})_l^1 E_0. \tag{34}$$

From Eq. (26) we obtain the effective dielectric function

$$\frac{\epsilon_e}{\epsilon_m} = 1 + 4\pi \sqrt{\frac{4\pi}{3}} \frac{n^0 q_{10}}{E_0} = 1 + 3v\alpha (G^{-1})_1^1. \tag{35}$$

In general, the higher multipole moments of the other particles within the correlation range contribute to the local field acting on each particle and make it nonuniform, which in turn generates higher multipoles even for spherical particles. Since the dipole moment of each particle is coupled to the higher multipoles of the other particles within the correlation range, the effective dielectric function is affected by the higher multipoles of those particles, and it deviates from the Maxwell-Garnett formula. These corrections depend specifically on the nonspherical part of the two-particle distribution, and are of first order in the volume fraction. We found them quite significant in some cases.[18]

We notice at this point that for a macroscopically homogeneous system, if we assume *a priori* a uniform external field rather than the parallel plate configuration, we can obtain equivalent results. Therefore, as it was reasonable to expect, the effective dielectric function is a bulk property for a macroscopically homogeneous system and does not depend on the configuration by which the system is excited.

IV. SOLUTION FOR SPHERICALLY SYMMETRIC TWO-PARTICLE DISTRIBUTIONS

A particular but important case occurs when $f(\mathbf{r} - \mathbf{r}_i)$ has complete spherical symmetry. Then, $f_l^{l'} = 0$ because of spherical harmonics orthogonality. This means that the other particles within the correlation range do not contribute at all to the local field acting on a given particle. Consequently, the local field becomes uniform, whatever the radial dependence of $f(\mathbf{r} - \mathbf{r}_i)$ may be. This applies to particles of arbitrary shapes and orientations. For spherical particles, Eq. (31) reduces to

$$G_l^{l'} = \delta_l^{l'} - v\alpha \delta_l^1 \delta_1^{l'}, \tag{36}$$

and we find immediately

$$(G^{-1})_l^{l'} = \delta_l^{l'} + \frac{v\alpha}{(1 - v\alpha)} \delta_l^1 \delta_1^{l'}. \tag{37}$$

Substituting Eq. (37) into Eq. (34), we obtain for the multipole moments

$$q_{l0} = \sqrt{\frac{3}{4\pi}} \frac{\alpha a^3 E_0}{(1 - v\alpha)} \delta_l^1. \tag{38}$$

We have thus proved that for any two-particle distribution with a short-range spherically symmetric correlation, only the dipole moments are nonzero.

Substituting Eq. (29), with $f_l^{l'} = 0$, and Eq. (38) into Eqs. (15) and (16), we then obtain for the electric field

$$\mathbf{E}_{\text{in}} = \mathbf{E}_0 + \frac{3v\alpha}{(1 - v\alpha)}\mathbf{E}_0 - \frac{2v\alpha}{(1 - v\alpha)}\mathbf{E}_0 - \frac{\alpha}{(1 - v\alpha)}\mathbf{E}_0, \qquad |\mathbf{r} - \mathbf{r}_i| \le a \tag{39}$$

and

$$\mathbf{E}_{\text{out}} = \mathbf{E}_0 + \frac{3v\alpha}{(1 - v\alpha)}\mathbf{E}_0 - \frac{2v\alpha}{(1 - v\alpha)}\mathbf{E}_0 + \frac{\alpha a^3[3\mathbf{n}_i(\mathbf{E}_0 \cdot \mathbf{n}_i) - \mathbf{E}_0]}{(1 - v\alpha)|\mathbf{r} - \mathbf{r}_i|^3}, \quad a \le |\mathbf{r} - \mathbf{r}_i| < a + \delta, \tag{40}$$

where $\mathbf{n}_i = (\mathbf{r}-\mathbf{r}_i)/|\mathbf{r}-\mathbf{r}_i|$. The contributions in Eqs. (39) and (40) are the applied field, the field produced by all the images, the field produced by the other particles, and the field produced by the ith particle itself. The external field, which is the applied field plus the field produced by the images, is indeed uniform, although it clearly depends on the properties of the system. Substituting Eq. (38), or Eq. (37), into Eq. (35), we obtain the effective dielectric function

$$\frac{\epsilon_e}{\epsilon_m} = \frac{(1+2v\alpha)}{(1-v\alpha)}, \tag{41}$$

which coincides with the Maxwell-Garnett formula. We have thus proved that it holds for any spherically symmetric two-particle distribution, regardless of the particle concentration.

Within the mean-field approximation, corrections to Maxwell-Garnett formula can only result from nonspherical distributions, in which the multipole moments of the neighboring particles contribute to the local field of a given particle. Those corrections arise directly from the coefficients $f_l^{l'}$, rather than the average particle concentration. Therefore, any theory within the mean-field approximation which predicts modifications of the Maxwell-Garnett formula simply based on the average particle concentration rather than the specific two-particle distribution is inconsistent with our results. An iterative unsymmetrical procedure introduced by Bruggeman[17] is a classical example, which has been widely used.[21–24] We therefore analyze this approach directly.

Bruggeman's iterative procedure consists in adding particles to the system step by step, increasing infinitesimally the volume fraction by dv'. It is assumed at each step that the medium with the particles already present in the system is equivalent to a homogeneous continuous medium with an effective dielectric function corresponding to the volume fraction v' at that step. The added particles are then surrounded by this "effective medium," and the Maxwell-Garnett formula is applied to the additional particles at each step, with the following replacements:

$$\epsilon_e \rightarrow \epsilon_e + d\epsilon_e, \quad \epsilon_m \rightarrow \epsilon_e, \quad v \rightarrow \frac{dv'}{(1-v')}. \tag{42}$$

The procedure is iterated until the volume fraction v' reaches its final value. By integration, one obtains

$$\left(\frac{\epsilon_e - \epsilon_p}{\epsilon_m - \epsilon_p}\right)\left(\frac{\epsilon_m}{\epsilon_e}\right)^{1/3} = 1 - v. \tag{43}$$

This approach is clearly within the mean-field approximation, as correctly pointed out by Davis and Schwartz.[14(a)] In fact, the mean-field Maxwell-Garnett formula is applied at each step, keeping only the first-order infinitesimal volume fraction of the added particles [that is v in Eq. (42), not to be confused with the final value of the volume fraction in Eq. (43), also denoted by v]. Therefore, fluctuation effects, which derive from higher-order infinitesimals in the volume fraction of added particles, cannot be introduced in any step. On the other hand, within the mean-field approximation, we have proved that, for a spherically symmetric two-particle distribution, the Maxwell-Garnett formula is exact for any volume fraction: the modification (43) is incompatible with that. For nonspherical distributions, the effective dielectric function is given by Eq. (35), and it depends on the specific form of the two-particle distribution: Eq. (43) makes no reference to the distribution, but only to the volume fraction. We have calculated practical examples of different distributions which yield vastly different results for the same volume fraction,[18] which is again incompatible with Eq. (43).

Aside from our results, Bruggeman's procedure is seriously flawed in this respect: it implies that in the final state of a fictitious procedure the particles added at different steps end up with different dipole moments, since the dielectric function of the effective medium varies from step to step. The particles added earlier to the system affect particles added later, but not vice versa. Such inconsistency stems from nonconservation of charge in Bruggeman's procedure. In this topology, the particles are always surrounded by the medium, which has strictly dielectric function ϵ_m, regardless of the particle concentration. The surface charge at a particle-medium interface, hence the multipole moments draw contributions from both the particle itself and the surrounding medium. In Bruggeman's procedure, when the medium with the particles already present is replaced by the effective medium, the charges belonging to those particles become the charges of this effective medium. Consequently, some charges, which in reality belong to other particles surrounding an added particle, will end up being counted incorrectly as charges belonging to the added particle as well. As the procedure continues, some of these charges will be counted again as charges of the new added particles in the subsequent steps. This unphysical extracharge artificially generates unequal multipole moments for the particles added at different steps.

We notice at this point that there is another effective medium result, also due to Bruggeman,[17] which is completely different:

$$v_1\frac{\epsilon_1 - \epsilon_e}{\epsilon_1 + 2\epsilon_e} + v_2\frac{\epsilon_2 - \epsilon_e}{\epsilon_2 + 2\epsilon_e} = 0, \tag{44}$$

where 1 and 2 label the two different materials. This refers to the so-called "aggregate" topology, and it is called by many authors the CPA result, since it is roughly analogous to the coherent potential approximation of alloy theory. Our approach, as well as Bruggeman's iterative unsymmetrical result (43), refer to the so-called "cermet" topology that we have just described. A complete discussion of both Bruggeman's results is provided, for example, by Landauer.[8] We also obtain Eq. (44), if we make the same CPA assumptions of particles of different species completely and symmetrically filling all space, each particle being in contact with an effective medium of dielectric function ϵ_e. However, these assumptions are truly disconnected from our approach, which holds rigorously for a different topology. Therefore, we draw no conclusions about Bruggeman's symmetric result (44).

V. CONCLUSIONS

In conclusion, the analytical solution of Maxwell equations as a boundary-value problem for a heterogeneous system, although laborious to complete,[25] pays off at the end. Coupling that with the formalism of two-particle distributions has provided unambiguous answers to the validity of the Maxwell-Garnett result, or, equivalently, the Clausius-Mossotti relation for spherical particles. We expect that this solution, and particularly the knowledge of the exact fields anywhere in the system, will be quite valuable in the study of complex systems and distributions. In the case of suspensions, for example, the distribution depends on the particle dynamics, which is governed by the exact microscopic field, and that in turn must be generated from the distribution self-consistently.

In this paper, we have obtained specifically the exact expressions of the fields and all multipole moments in terms of the applied field at the electrode plates and the system configuration. In particular, we have obtained explicitly the external field, which has a contribution from all the image multipoles. If the sample is a thin film of thickness d comparable to the particle dimensions, or if d is comparable to a scale in which the system is inhomogeneous, the external field is not uniform and the general formulas in Sec. II should be used. On the other hand, the external field becomes uniform in the bulk of a macroscopically homogeneous system with a short-range two-particle distribution. The field produced by the particles outside the correlation range also becomes uniform, whatever the particle shapes and orientations. The field produced by the other particles inside the correlation range is generally not uniform and depends crucially on the form of the two-particle distribution. If that is spherical, these particles do not contribute to the local field acting on the central particle. Consequently, all multipole moments higher than dipole vanish, and the Maxwell-Garnett result is rigorous within the mean-field approximation. If the distribution is not spherical, all multipole moments are generally coupled and there may be a large correction to the Maxwell-Garnett result. We have provided the explicit expressions in Sec. III. Such correction is of first order in the volume fraction, and may easily outweigh corrections due to fluctuations, beyond the mean-field approximation, which are at least of second order in the volume fraction. Our results seriously question an iterative procedure proposed by Bruggeman, as discussed in Sec. IV.

We have further developed this exact formalism for clustered inclusions and calculated an example of particle chaining. We find in some cases large deviations from the Maxwell-Garnett formula, due to strong multipolar effects, depending on the length of the particle chains. This example represents an extreme deviation from a spherical distribution and the corrections to the Maxwell-Garnett formula are indeed of the first order in the volume fraction. The complete results will be reported elsewhere.[18]

A paper by Claro and Rojas has appeared,[27] in which they have also reached independently one of our conclusions, namely that there are no multipolar corrections to the Maxwell-Garnett result within the mean-field approximation. Our proof is more complete: only for spherically symmetric pair distributions is there no correction to the Maxwell-Garnett result, and we provide the correction for nonspherical pair distributions.

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APPENDIX A

In this appendix we outline some of the mathematics required in the paper. Using recurrence formulas for spherical harmonics, we obtain the following identities:[25]

$$\frac{\partial^{l-m}}{\partial z^{l-m}}\left(\frac{\partial}{\partial x}\pm j\frac{\partial}{\partial y}\right)^m \frac{Y_{l',m'}(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^{l'+1}} = (-1)^l(\mp 1)^m\left[\frac{(2l'+1)(l'+l\pm m'+m)!(l'+l\mp m'-m)!}{(2l'+2l+1)(l'+m')!(l'-m')!}\right]^{1/2}\frac{Y_{l'+l,m'\pm m}(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^{l'+l+1}},\quad 0\le m\le l,\quad |m'|\le l' \tag{A1}$$

and

$$\frac{\partial^{l-m}}{\partial z^{l-m}}\left(\frac{\partial}{\partial x}\pm j\frac{\partial}{\partial y}\right)^m \left[Y_{l',m'}(\mathbf{r}-\mathbf{r}')|\mathbf{r}-\mathbf{r}'|^{l'}\right] = (\pm 1)^m\left[\frac{(2l'+1)(l'+m')!(l'-m')!}{(2l'-2l+1)(l'-l\pm m'+m)!(l'-l\mp m'-m)!}\right]^{1/2} Y_{l'-l,m'\pm m}(\mathbf{r}-\mathbf{r}')|\mathbf{r}-\mathbf{r}'|^{l'-l},\quad 0\le m\le l,\quad |m'|\le l'. \tag{A2}$$

Taking $l'=m'=0$, Eq. (A1) reduces to

$$\frac{Y_{l,\pm m}(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^{l+1}} = (-1)^l(\mp 1)^m\left[\frac{2l+1}{4\pi(l+m)!(l-m)!}\right]^{1/2}\frac{\partial^{l-m}}{\partial z^{l-m}}\left(\frac{\partial}{\partial x}\pm j\frac{\partial}{\partial y}\right)^m\frac{1}{|\mathbf{r}-\mathbf{r}'|},\quad 0\le m\le l. \tag{A3}$$

Now, consider the expansion

$$\frac{Y_{l',m'}(\mathbf{r}-\mathbf{r}')}{(2l'+1)|\mathbf{r}-\mathbf{r}'|^{l'+1}} = \sum_{l''m''} A^{l'm'}_{l''m''}(\mathbf{r}'-\mathbf{r}'')|\mathbf{r}-\mathbf{r}''|^{l''}Y_{l'',m''}(\mathbf{r}-\mathbf{r}''), \quad |\mathbf{r}-\mathbf{r}''| < |\mathbf{r}'-\mathbf{r}''| \tag{A4}$$

as in Eq. (12). Apply $\partial^{l-m}/\partial z^{l-m}(\partial/\partial x \pm j\partial/\partial y)^m$ $(0 \le m \le l)$, and use the identities (A1) and (A2); then take the limit $\mathbf{r} \longrightarrow \mathbf{r}''$. The only surviving term on the right-hand side has $l'' = l$, $m'' = -m$ for the uppercase, or $l'' = l$, $m'' = m$ for the lowercase. With a few additional manipulations, we obtain

$$A^{l'm'}_{lm}(\mathbf{r}'-\mathbf{r}'') = \frac{Y^*_{l+l',m-m'}(\mathbf{r}'-\mathbf{r}'')}{|\mathbf{r}'-\mathbf{r}''|^{l+l'+1}} \times(-1)^{l'+m'}\left[\frac{4\pi(l+l'+m-m')!(l+l'-m+m')!}{(2l+1)(2l'+1)(2l+2l'+1)(l+m)!(l-m)!(l'+m')!(l'-m')!}\right]^{1/2}, \quad |m| \le l, \quad |m'| \le l'. \tag{A5}$$

Equivalent expressions are well known in the literature: see, for instance, the appendixes in Refs. 10(b) and 26.

In order to establish Eq. (29), we write

$$\sum_{i'} C^{l'0}_{l0}(\mathbf{r}_{i'}-\mathbf{r}_i) = \sum_{i'} A^{l'0}_{l0}(\mathbf{r}_{i'}-\mathbf{r}_i)(1-\delta^{i'}_i) + \sum_{i'} B^{l'0}_{l0}(\mathbf{r}_{i'}-\mathbf{r}_i), \tag{A6}$$

where

$$B^{l'0}_{l0}(\mathbf{r}_{i'}-\mathbf{r}_i) = \sum_{k\neq 0}(-1)^{(l'+1)k}A^{l'0}_{l0}(\mathbf{r}_{i'k}-\mathbf{r}_i). \tag{A7}$$

The first summation in Eq. (A6) represents the contribution of all the particles other than the ith one, while the second summation represents the contribution of all the images. We now use the distribution function defined in Eqs. (28), and obtain

$$\begin{aligned}\sum_{i'} C^{l'0}_{l0}(\mathbf{r}_{i'}-\mathbf{r}_i) &= n^0\int_{|\mathbf{r}-\mathbf{r}_i|\le R} A^{l'0}_{l0}(\mathbf{r}-\mathbf{r}_i)d^3\mathbf{r} + \int_{|\mathbf{r}-\mathbf{r}_i|\le R} f(\mathbf{r}-\mathbf{r}_i)A^{l'0}_{l0}(\mathbf{r}-\mathbf{r}_i)d^3\mathbf{r} \\ &\quad + n^0\int_{\substack{R\le|\mathbf{r}-\mathbf{r}_i|\\ -d/2\le z\le d/2}} A^{l'0}_{l0}(\mathbf{r}-\mathbf{r}_i)d^3\mathbf{r} + n^0\int_{-d/2\le z\le d/2} B^{l'0}_{l0}(\mathbf{r}-\mathbf{r}_i)d^3\mathbf{r} \\ &\quad + \int_{|\mathbf{r}-\mathbf{r}_i|\le R} f(\mathbf{r}-\mathbf{r}_i)B^{l'0}_{l0}(\mathbf{r}-\mathbf{r}_i)d^3\mathbf{r} + B^{l'0}_{l0}(0).\end{aligned} \tag{A8}$$

In Eq. (A8), the first integral vanishes due to orthogonality of spherical harmonics $(l, l' \ge 1)$. In the fifth integral, since the distances involved in $B^{l'0}_{l0}(\mathbf{r}-\mathbf{r}_i)$ are of the order of $d \gg R$, $B^{l'0}_{l0}(\mathbf{r}-\mathbf{r}_i)$ is essentially a constant for $|\mathbf{r}-\mathbf{r}_i| \le R$: then, according to Eq. (28d), this integral also vanishes. In the third and fourth integral, disregarding edge effects, the limits on the transverse dimensions can be taken to infinity and the ith particle may be assumed on the z axis. Disregarding the relatively few particles which are very close to the electrode plates, we may always assume $z_i + R < d/2$ and $z_i - R > -d/2$.

The third integral in Eq. (A8) can then be evaluated as

$$\begin{aligned} n^0\int_{\substack{R\le|\mathbf{r}-\mathbf{r}_i|\\ -d/2\le z\le d/2}} A^{l'0}_{l0}(\mathbf{r}-\mathbf{r}_i)d^3\mathbf{r} &= (-1)^{l'}\frac{2\pi n^0(l+l')!}{\sqrt{(2l+1)(2l'+1)}\,l!l'!} \\ &\quad\times\left[\int_{-1}^{0} P_{l+l'}(x)dx\int_R^{(-d/2-z_i)/x}\frac{d|\mathbf{r}-\mathbf{r}_i|}{|\mathbf{r}-\mathbf{r}_i|^{l+l'-1}}\right. \\ &\quad\left.+\int_0^1 P_{l+l'}(x)dx\int_R^{(d/2-z_i)/x}\frac{d|\mathbf{r}-\mathbf{r}_i|}{|\mathbf{r}-\mathbf{r}_i|^{l+l'-1}}\right],\end{aligned} \tag{A9}$$

where $P_l(x)$ are Legendre polynomials, and $x = \cos\theta_i$, θ_i being the polar angle of $\mathbf{r}-\mathbf{r}_i$. For $l = l' = 1$, that is

$$-\left(\frac{4\pi}{3}\right)n^0\int_0^1\left\{\ln\left[\frac{(d/2+z_i)(d/2-z_i)}{R^2}\right] - 2\ln x\right\}P_2(x)dx = \left(\frac{8\pi}{9}\right)n^0. \tag{A10}$$

For $l + l' > 2$, that is

$$(-1)^{l'}\frac{4\pi n^0(l+l')!}{\sqrt{(2l+1)(2l'+1)l!l'!}}\left\{\frac{1}{R^{l+l'-2}}\int_{-1}^{+1}P_{l+l'}(x)dx - \left[\frac{1}{(d/2+z_i)^{l+l'-2}}+\frac{1}{(d/2-z_i)^{l+l'-2}}\right]\int_0^1 x^{l+l'-2}P_{l+l'}(x)dx\right\}. \quad \text{(A11)}$$

The first integral in Eq. (A11) vanishes due to orthogonality of Legendre polynomials. Using Rodrigues's formula and integrating by parts $l+l'-2$ times, one can prove that the second integral in Eq. (A11) also vanishes. Denoting by $f_l^{l'}$ the second integral in Eq. (A8), we thus obtain

$$\sum_{i'} A_{l0}^{l'0}(\mathbf{r}_{i'}-\mathbf{r}_i)(1-\delta_i^{i'}) = f_l^{l'} + \left(\frac{8\pi}{9}\right)n^0\delta_l^1\delta_1^{l'}, \quad \text{(A12)}$$

which represents the contribution from all particles other than the one under consideration.

To evaluate the fourth integral in Eq. (A8), we first assume that the integration region is a cylinder of radius R_0, and eventually let R_0 approach infinity, maintaining the condition $\lim_{R_0\to\infty,\, k\to\pm\infty} R_0/(kd)=0$, since for any given transverse dimension of the system the images always extend to infinity. Using cylindrical coordinates and the identity (A3), we can write a typical term in the fourth integral in Eq. (A8) as

$$\begin{aligned} n^0\int_{-d/2\le z\le d/2} A_{l0}^{l'0}(\mathbf{r}_k-\mathbf{r}_i)d^3\mathbf{r} &= \frac{(-1)^l 2\pi n^0}{\sqrt{(2l+1)(2l'+1)l!l'!}}\int_{-d/2}^{d/2}dz\frac{\partial^{l+l'}}{\partial z_k^{l+l'}}\int_0^{R_0}\frac{\rho d\rho}{\sqrt{\rho^2+(z_k-z_i)^2}} \\ &= \frac{(-1)^l 2\pi n^0}{\sqrt{(2l+1)(2l'+1)l!l'!}}\int_{(k-1/2)d}^{(k+1/2)d}du\frac{\partial^{l+l'}}{\partial u^{l+l'}}\left[\sqrt{R_0^2+(u-z_i)^2}-|u-z_i|\right], \end{aligned} \quad \text{(A13)}$$

where $\mathbf{r}_k=\{x,\ y,\ kd+(-1)^k z\}$, and we have changed to the integration variable $u=z_k=kd+(-1)^k z$, $k\neq 0$. This integral vanishes for $l+l'>2$ when we let $R_0\longrightarrow\infty$. For $l=l'=1$, we have

$$n^0\int B_{10}^{10}(\mathbf{r}-\mathbf{r}_i)d^3\mathbf{r} = -\left(\frac{2\pi}{3}\right)n^0\sum_{k\neq 0}\int_{(k-1/2)d}^{(k+1/2)d}df, \quad \text{(A14)}$$

where $df=du\partial^2/\partial u^2[\sqrt{R_0^2+(u-z_i)^2}-|u-z_i|]$. Then, we obtain

$$\begin{aligned} n^0\int_{-d/2\le z\le d/2} B_{10}^{10}(\mathbf{r}-\mathbf{r}_i)d^3\mathbf{r} &= -\left(\frac{2\pi}{3}\right)n^0\lim_{k\to\infty}\left[\int_{d/2}^{kd}df+\int_{-kd}^{-d/2}df\right] \\ &= -\left(\frac{2\pi}{3}\right)n^0\left[2-\frac{d/2-z_i}{\sqrt{R_0^2+(d/2-z_i)^2}}-\frac{d/2+z_i}{\sqrt{R_0^2+(d/2+z_i)^2}}\right]\longrightarrow -\left(\frac{4\pi}{3}\right)n^0, \end{aligned} \quad \text{(A15)}$$

where the limit $R_0\longrightarrow\infty$ has been taken last. Hence we obtain

$$\sum_{i'} B_{l0}^{l'0}(\mathbf{r}_{i'}-\mathbf{r}_i) = -\left(\frac{4\pi}{3}\right)n^0\delta_l^1\delta_1^{l'}, \quad \text{(A16)}$$

which represents the contribution of all the images: in fact we may disregard $B_{l0}^{l'0}(0)$ in Eq. (A8), which is at most of the order of $1/d^3 \ll n^0$.

Substituting Eqs. (A12) and (A16) into Eq. (A8), we obtain the final result

$$\sum_{i'} C_{l0}^{l'0}(\mathbf{r}_{i'}-\mathbf{r}_i) = f_l^{l'} + \left(\frac{8\pi}{9}\right)n^0\delta_l^1\delta_1^{l'} - \left(\frac{4\pi}{3}\right)n^0\delta_l^1\delta_1^{l'}. \quad \text{(A17)}$$

APPENDIX B

The results for a single-species system can be easily generalized to a many-species system. The two-particle distribution between the s' and s species can be written as

$$n_s^{s'}(\mathbf{r}-\mathbf{r}_s) = \delta_s^{s'}\delta(\mathbf{r}-\mathbf{r}_s) + n^{s'} + f_s^{s'}(\mathbf{r}-\mathbf{r}_s), \quad \text{(B1)}$$

where $n^{s'}$ is the average number density of the s' species. We assume a short-range correlation among all the particles; hence all $f_s^{s'}(\mathbf{r}-\mathbf{r}_s)$ satisfy similar conditions to the single-species case. Then, Eq. (29) is simply replaced by

$$\sum_{i'l'} C_{l0}^{l'0}(\mathbf{r}_{i'}-\mathbf{r}_i)q_{i'l'0} = \sum_{s'l'}\left[f_{sl}^{s'l'} - \left(\frac{4\pi}{9}\right)\delta_l^1 n^{s'}\delta_1^{l'}\right]q_{s'l'0}, \quad \text{(B2)}$$

where q_{slm} are the average multipole moments of the s species, and

$$f_{sl}^{s'l'} = \int_{|\mathbf{r}-\mathbf{r}_s|\le R} f_s^{s'}(\mathbf{r}-\mathbf{r}_s)A_{l0}^{l'0}(\mathbf{r}-\mathbf{r}_s)d^3\mathbf{r}. \quad \text{(B3)}$$

Similarly, we generalize the system configuration matrix with reduced dimensions as

$$G_{sl}^{s'l'} = \delta_s^{s'}\delta_l^{l'} - \frac{4\pi}{3}\alpha_s a_s^3 n^{s'}\delta_l^1\delta_1^{l'} + (2l+1)\beta_{sl} f_{sl}^{s'l'}, \quad \text{(B4)}$$

where $\alpha_s = (\epsilon_s - \epsilon_m)/(\epsilon_s + 2\epsilon_m)$ and $\beta_{sl} = [(\epsilon_s - \epsilon_m)la_s^3]/[l\epsilon_s + (l+1)\epsilon_m]$, ϵ_s and a_s being the dielectric function and the radius of the s-species particles, respectively. Then, the equation for the multipole moments of the particles for a many-species system with short-range correlation can be written as [cf. Eq. (33)]

$$\sum_{s'l'} G_{sl}^{s'l'} q_{s'l'0} = \sqrt{\frac{3}{4\pi}}\alpha_s a_s^3 E_0\ \delta_l^1. \quad \text{(B5)}$$

Solving for the multipole moments in Eq. (B5), we obtain

$$q_{sl0} = \sqrt{\frac{3}{4\pi}}\sum_{s'}(G^{-1})_{sl}^{s'1}\alpha_{s'}a_{s'}^3 E_0. \quad \text{(B6)}$$

The corresponding effective dielectric function is

$$\begin{aligned}\frac{\epsilon_e}{\epsilon_m} &= 1 + 4\pi\sqrt{\frac{4\pi}{3}}\sum_s \frac{n^s q_{s10}}{E_0} \\ &= 1 + 4\pi\sum_{ss'} n^s (G^{-1})_{s1}^{s'1}\alpha_{s'1}a_{s'}^3. \quad \text{(B7)}\end{aligned}$$

In particular, if all $f_s^{s'}(\mathbf{r}-\mathbf{r}_s)$ are spherically symmetric, $f_{sl}^{s'l'} = 0$. Then, from Eqs. (B5) and (B6), it follows that

$$q_{sl0} = \sqrt{\frac{3}{4\pi}}\frac{\alpha_s a_s^3 E_0}{\left(1 - \sum_{s'} v^{s'}\alpha_{s'}\right)}\delta_l^1, \quad \text{(B8)}$$

where $v^s = (4\pi a_s^3/3)n^s$ is the volume fraction of the s-species particles. The field inside an s-species particle is

$$\mathbf{E}_{\text{in}} = \frac{1-\alpha_s}{\left(1 - \sum_{s'} v^{s'}\alpha_{s'}\right)}\mathbf{E}_0, \quad |\mathbf{r}-\mathbf{r}_s| < a_s, \quad \text{(B9)}$$

while immediately outside the particle, where no other particles are present, it is

$$\mathbf{E}_{\text{out}} = \frac{\mathbf{E}_0}{\left(1 - \sum_{s'} v^{s'}\alpha_{s'}\right)} + \frac{\alpha_s a_s^3[3\mathbf{n}_s(\mathbf{E}_0\cdot\mathbf{n}_s) - \mathbf{E}_0]}{\left(1 - \sum_{s'} v^{s'}\alpha_{s'}\right)|\mathbf{r}-\mathbf{r}_s|^3},$$
$$a_s < |\mathbf{r}-\mathbf{r}_s| < a_s + \delta. \quad \text{(B10)}$$

The effective dielectric function is

$$\frac{\epsilon_e}{\epsilon_m} = \frac{1 + 2\sum_s v^s\alpha_s}{\left(1 - \sum_s v^s\alpha_s\right)}, \quad \text{(B11)}$$

which represents Maxwell-Garnett formula for a many-species system. When $\epsilon_m = 1$, this result coincides with the Clausius-Mossotti relation for spherical particles. We have thus proved that it is rigorous to all multipole orders and for all possible volume fractions in the case of short-range spherically symmetric two-particle distributions for all species, in the mean-field approximation.

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