Electrical response of heterogeneous systems of clustered inclusions

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An exact formalism to calculate the multipole moments, electric field, and the effective dielectric function of a heterogeneous system of clustered spherical particles is presented. The formalism is derived from a boundary-value problem corresponding to the typical low-frequency experimental configuration of a system placed between two parallel electrode plates. The formalism is then suited to cluster distributions, neglecting fluctuations. When the correlations among cluster pairs are short range and spherically symmetric, the results are remarkably simple: only the dipole moments of the other clusters and the images contribute to the local field acting on each cluster, and the effective dielectric function has the Clausius-Mossotti form, with cluster polarizabilities directly related to the cluster configurations. We study as an illustrative example systems containing particle chains along the direction of the applied field. We find that if the conductivity of the particles is much larger than that of the host material, the multipole moments and the effective dielectric function are greatly enhanced, whereas in the opposite case the effect of chaining is negligible.

I. INTRODUCTION

The electrical response of heterogeneous systems has been a subject of constant interest since the pionering works of Mossotti,[1] Clausius,[2] Maxwell,[3] Garnett,[4] and others.[5] Because of the complexity of the interactions among the inclusions, most theories consider systems of separate and dilute inclusions, although real systems often exhibit clustered inclusions. In fact, at high volume fractions, clustering invariably results from strong correlations among the particles. Since the particles in a cluster are quite close to each other, the resulting local field acting on each particle is very different from that for separate and dilute inclusions, and higher multipole moments may contribute considerably. Correspondingly, the induced multipole moments are quite different from those of separate dispersed particles. The effective dielectric function is then expected to be strongly affected by clustering. The unusually large far-infrared absorption of some heterogeneous systems has indeed been attributed to clustering effects.[6–9]

An analytic approach to this problem must relate the effective dielectric function of the system to the detailed configuration of the clustered inclusions. In this paper we present such a formalism, based upon a method that we have recently developed,[10] which treated all particles individually. As in that case, we consider the typical low-frequency experimental configuration of a system placed between two parallel electrode plates, and obtain the exact multipole moments and effective dielectric function. The idea here is to subdivide the particles in clusters. Within each cluster, we still treat the particles individually. However, the outside particles can be treated as clusters, reexpanding their potentials with respect to the cluster centers. Then, the number of interactions are greatly reduced. We obtain the exact multipole moments of the clusters, as well as those of the individual particles in each cluster, the exact field inside the system, and the effective dielectric function, all in terms of the positions and the configurations (structures and orientations) of the clusters, and the applied field. The derivation of these results is provided in Sec. II.

This formalism can be applied directly to crystals with complex unit cells. For disordered systems, we have considered pair distributions of clusters, neglecting fluctuations. We obtain the results for arbitrary pair distributions, including the multipole moments of all orders. We find that the interactions among the cluster multipole moments strongly depend on the pair distribution. In particular, for spherically symmetric pair distributions, we find that the multipole moments higher than dipoles, although nonvanishing in general, have no contribution and the average local field acting on each cluster is uniform. The effective dielectric function satisfies the Clausius-Mossotti's relation, with cluster polarizabilities determined explicitly in terms of the configuration of the clusters. These results are correct to all multipole orders, and do not depend on either the concentration or the specific form of the pair distribution, as long as it is spherically symmetric. On the other hand, if the pair distribution is not spherically symmetric, the contribution of higher multipole moments can be very significant. These results are obtained in Sec. III.

We have applied these results to linear chains of identical particles aligned with the applied field, a configuration which is often induced at high fields. Strong interactions among the particles within each cluster (chain) may occur, and their higher multipole moments may contribute significantly. Correspondingly, the effective dielectric function may largely deviate from the Maxwell-Garnett result. That occurs particularly when the particle conductivity is much larger than that of the host material: as the length of the chains increases, the absorption peak greatly increases over that of a system of

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separate particles at the same concentration. The absorption peak is also redshifted. On the other hand, if the particle conductivity is smaller than that of the host material, chaining has always a negligible effect. We report these results in Sec. IV.

II. FORMALISM

Consider a heterogeneous system containing clustered spherical particles, dispersed in a host medium with a complex dielectric function ϵ_m. The ith particle of the nth cluster, referred to as the nith particle, has a radius a_{ni} and a complex dielectric function ϵ_{ni}. We consider the typical low-frequency experimental configuration in which the system is placed between two parallel electrode plates at a distance d, subject to an alternating potential difference $V_0 e^{-j\omega t}$. We assume $\lambda \gg d > a_{ni}$, and hence ignore magnetic excitations.

Collecting particles in clusters, the potential inside any given nith particle is [cf. Eqs. (10) and (11) of Ref. 10]

$$U_{\rm in}(\mathbf{r}) = V_0/2 - \mathbf{E}_0\cdot\mathbf{r} + 4\pi\sum_{lm}\frac{q_{nilm}}{(2l+1)a_{ni}^{2l+1}}|\mathbf{r}-\mathbf{r}_{ni}|^l Y_{l,m}(\mathbf{r}-\mathbf{r}_{ni}) + 4\pi\sum_{i'lm}(1-\delta_i^{i'})\frac{q_{ni'lm}}{(2l+1)}\frac{Y_{l,m}(\mathbf{r}-\mathbf{r}_{ni'})}{|\mathbf{r}-\mathbf{r}_{ni'}|^{l+1}}$$
$$+4\pi\sum_{n'i'lmk}(1-\delta_n^{n'}\delta_k^0)(-1)^{(l+m+1)k}\frac{q_{n'i'lm}}{(2l+1)}\frac{Y_{l,m}(\mathbf{r}-\mathbf{r}_{n'i'k})}{|\mathbf{r}-\mathbf{r}_{n'i'k}|^{l+1}},\qquad |\mathbf{r}-\mathbf{r}_{ni}|\le a_{ni} \tag{1a}$$

and in the host medium it is

$$U_{\rm out}(\mathbf{r}) = V_0/2 - \mathbf{E}_0\cdot\mathbf{r} + 4\pi\sum_{lm}\frac{q_{nilm}}{(2l+1)}\frac{Y_{l,m}(\mathbf{r}-\mathbf{r}_{ni})}{|\mathbf{r}-\mathbf{r}_{ni}|^{l+1}} + 4\pi\sum_{i'lm}(1-\delta_i^{i'})\frac{q_{ni'lm}}{(2l+1)}\frac{Y_{l,m}(\mathbf{r}-\mathbf{r}_{ni'})}{|\mathbf{r}-\mathbf{r}_{ni'}|^{l+1}}$$
$$+4\pi\sum_{n'i'lmk}(1-\delta_n^{n'}\delta_k^0)(-1)^{(l+m+1)k}\frac{q_{n'i'lm}}{(2l+1)}\frac{Y_{l,m}(\mathbf{r}-\mathbf{r}_{n'i'k})}{|\mathbf{r}-\mathbf{r}_{n'i'k}|^{l+1}},\quad a_{n'i'}\le|\mathbf{r}-\mathbf{r}_{n'i'}|\ \text{ for all } n', i', \tag{1b}$$

where

$$\mathbf{r}_{nik} = \{x_{ni}, y_{ni}, kd + (-1)^k z_{ni}\},\qquad k = 0, \pm1, \pm2, \ldots . \tag{1c}$$

Throughout this paper, the summations over i' only include particles within one cluster. In Eq. (1a), the four contributions are the applied potential, the potential produced by the nith particle itself, the potentials produced by all other particles of the nth cluster, and the potentials produced by all other clusters and all the images: the factors $(1-\delta_i^{i'})$ and $(1-\delta_n^{n'}\delta_k^0)$ are conveniently introduced to avoid double counting. Crossing the surface of the nith particle, only the potential produced by the nith particle itself changes form.

For each cluster n, we select a point $\mathbf{R}_n$ to be regarded as the cluster center. Then, we reexpand the potentials of the particles of the nth cluster with respect to $\mathbf{R}_n$. For any point $\mathbf{r}$ outside a minimum sphere of radius b_{n0}, centered at $\mathbf{R}_n$ and enclosing all the particles of the nth cluster, we have

$$4\pi\sum_{lm}\frac{q_{nilm}}{(2l+1)}\frac{Y_{l,m}(\mathbf{r}-\mathbf{r}_{ni})}{|\mathbf{r}-\mathbf{r}_{ni}|^{l+1}}$$
$$= 4\pi\sum_{lm}\frac{q'_{nilm}}{(2l+1)}\frac{Y_{l,m}(\mathbf{r}-\mathbf{R}_n)}{|\mathbf{r}-\mathbf{R}_n|^{l+1}},\quad |\mathbf{r}-\mathbf{R}_n|>b_{n0}, \tag{2}$$

where q'_{nilm} are the multipole moments of the nith particle with respect to $\mathbf{R}_n$. As shown in Eq. (A7) of the Appendix, the two sets of multipole moments are connected as

$$q'_{nilm} = \sum_{l'm'} T(n)_{ilm}^{i'l'm'} q_{ni'l'm'}, \tag{3a}$$

by the transformation matrix

$$T(n)_{ilm}^{i'l'm'} = \delta_i^{i'} t_{l,m}^{l',m'}(\mathbf{r}_{ni}-\mathbf{R}_n), \tag{3b}$$

where $t_{l,m}^{l',m'}(\mathbf{r}_{ni}-\mathbf{R}_n)$ is given in Eq. (A6) of the Appendix. The transformation matrix is block diagonal, each square block corresponding to a given particle. Furthermore, $T(n)_{ilm}^{i'l'm'} = 0$ for $|m-m'| > l-l'$, and $T(n)_{ilm}^{i'lm} = \delta_i^{i'}$: hence, a given multipole moment depends only on those of equal or lower order when the expansion point is changed, and the lowest nonvanishing moments are independent of the expansion point.

We now assume that clusters do not overlap: specifically, the minimum sphere of each cluster excludes all the particles belonging to other clusters. We reexpand in Eqs. (1a) and (1b) the potentials produced by the particles of all the clusters other than the nth cluster, and by all the images, with respect to their corresponding cluster centers. Using Eq. (A5) of the Appendix, with $\mathbf{r}' = \mathbf{r}_{n'i'k}$ and $\mathbf{r}'' = \mathbf{R}_{n'k}$, we obtain

$$\sum_{lm}(-1)^{(l+m+1)k}\frac{q_{n'i'lm}}{(2l+1)}\frac{Y_{l,m}(\mathbf{r}-\mathbf{r}_{n'i'k})}{|\mathbf{r}-\mathbf{r}_{n'i'k}|^{l+1}}$$

$$=\sum_{l'm'}(-1)^{(l'+m'+1)k}\frac{q'_{n'i'l'm'}}{(2l'+1)}\frac{Y_{l',m'}(\mathbf{r}-\mathbf{R}_{n'k})}{|\mathbf{r}-\mathbf{R}_{n'k}|^{l'+1}},\tag{4a}$$

$b_{n'0}\le|\mathbf{r}-\mathbf{R}_{n'}|,$

where we have used

$$t_{l,m}^{l',m'}(\mathbf{r}_{n'i'k}-\mathbf{R}_{n'k})=(-1)^{(l+m+l'+m')k}\times t_{l,m}^{l',m'}(\mathbf{r}_{n'i'}-\mathbf{R}_{n'}).\tag{4b}$$

Substituting Eq. (4a) into Eqs. (1a) and (1b), the potential inside the nith particle becomes

$$U_{\text{in}}(\mathbf{r})=V_0/2-\mathbf{E}_0\cdot\mathbf{r}+4\pi\sum_{lm}\frac{q_{nilm}}{(2l+1)a_{ni}^{2l+1}}|\mathbf{r}-\mathbf{r}_{ni}|^{l}Y_{l,m}(\mathbf{r}-\mathbf{r}_{ni})+4\pi\sum_{i'lm}(1-\delta_i^{i'})\frac{q_{ni'lm}}{(2l+1)}\frac{Y_{l,m}(\mathbf{r}-\mathbf{r}_{ni'})}{|\mathbf{r}-\mathbf{r}_{ni'}|^{l+1}}$$
$$+4\pi\sum_{n'lmk}(1-\delta_n^{n'}\delta_k^0)(-1)^{(l+m+1)k}\frac{Q_{n'lm}}{(2l+1)}\frac{Y_{l,m}(\mathbf{r}-\mathbf{R}_{n'k})}{|\mathbf{r}-\mathbf{R}_{n'k}|^{l+1}},\qquad |\mathbf{r}-\mathbf{r}_{ni}|\le a_{ni}\tag{5a}$$

while in the host medium, outside the minimum spheres of other clusters, it is

$$U_{\text{out}}(\mathbf{r})=V_0/2-\mathbf{E}_0\cdot\mathbf{r}+4\pi\sum_{lm}\frac{q_{nilm}}{(2l+1)}\frac{Y_{l,m}(\mathbf{r}-\mathbf{r}_{ni})}{|\mathbf{r}-\mathbf{r}_{ni}|^{l+1}}+4\pi\sum_{i'lm}(1-\delta_i^{i'})\frac{q_{ni'lm}}{(2l+1)}\frac{Y_{l,m}(\mathbf{r}-\mathbf{r}_{ni'})}{|\mathbf{r}-\mathbf{r}_{ni'}|^{l+1}}$$
$$+4\pi\sum_{n'i'lmk}(1-\delta_n^{n'}\delta_k^0)(-1)^{(l+m+1)k}\frac{Q_{n'lm}}{(2l+1)}\frac{Y_{l,m}(\mathbf{r}-\mathbf{R}_{n'k})}{|\mathbf{r}-\mathbf{R}_{n'k}|^{l+1}},$$
$$a_{ni'}\le|\mathbf{r}-\mathbf{r}_{ni'}|\text{ for all }i'\text{ and }b_{n'0}\le|\mathbf{r}-\mathbf{R}_{n'}|\text{ for all }n'\neq n.\tag{5b}$$

Here, $Q_{nlm}=\sum_i q'_{nilm}$ are the multipole moments of the nth cluster with respect to its center.

Inside the minimum sphere of the nth cluster but outside the minimum spheres of the neighboring clusters, the potentials produced by all other clusters and all the images can be expanded around $\mathbf{R}_n$ using Eq. (A2): we obtain

$$U_{\text{in}}(\mathbf{r})=(V_0/2-\mathbf{E}_0\cdot\mathbf{R}_n)-\mathbf{E}_0\cdot(\mathbf{r}-\mathbf{R}_n)++4\pi\sum_{lm}\frac{q_{nilm}}{(2l+1)a_{ni}^{2l+1}}|\mathbf{r}-\mathbf{r}_{ni}|^{l}Y_{l,m}(\mathbf{r}-\mathbf{r}_{ni})$$
$$+4\pi\sum_{i'lm}(1-\delta_i^{i'})\frac{q_{ni'lm}}{(2l+1)}\frac{Y_{l,m}(\mathbf{r}-\mathbf{r}_{ni'})}{|\mathbf{r}-\mathbf{r}_{ni'}|^{l+1}}$$
$$+4\pi\sum_{lm}\left[\sum_{n'l'm'}C_{l,m}^{l',m'}(\mathbf{R}_{n'}-\mathbf{R}_n)Q_{n'l'm'}\right]|\mathbf{r}-\mathbf{R}_n|^{l}Y_{l,m}(\mathbf{r}-\mathbf{R}_n),\quad |\mathbf{r}-\mathbf{r}_{ni}|\le a_{ni}\tag{6a}$$

and

$$U_{\text{out}}(\mathbf{r})=(V_0/2-\mathbf{E}_0\cdot\mathbf{R}_n)-\mathbf{E}_0\cdot(\mathbf{r}-\mathbf{R}_n)+4\pi\sum_{lm}\frac{q_{nilm}}{(2l+1)}\frac{Y_{l,m}(\mathbf{r}-\mathbf{r}_{ni})}{|\mathbf{r}-\mathbf{r}_{ni}|^{l+1}}+4\pi\sum_{i'lm}(1-\delta_i^{i'})\frac{q_{ni'lm}}{(2l+1)}\frac{Y_{l,m}(\mathbf{r}-\mathbf{r}_{ni'})}{|\mathbf{r}-\mathbf{r}_{ni'}|^{l+1}}$$
$$+4\pi\sum_{lm}\left[\sum_{n'l'm'}C_{l,m}^{l',m'}(\mathbf{R}_{n'}-\mathbf{R}_n)Q_{n'l'm'}\right]|\mathbf{r}-\mathbf{R}_n|^{l}Y_{l,m}(\mathbf{r}-\mathbf{R}_n),$$
$$a_{ni'}\le|\mathbf{r}-\mathbf{r}_{ni'}|\text{ for all }i',\quad |\mathbf{r}-\mathbf{R}_n|\le b_{n0},\text{ and }b_{n'0}\le|\mathbf{r}-\mathbf{R}_{n'}|\text{ for all }n'\neq n.\tag{6b}$$

Here we define

$$C_{l,m}^{l',m'}(\mathbf{R}_{n'}-\mathbf{R}_n)=\sum_k(-1)^{(l'+m'+1)k}(1-\delta_n^{n'}\delta_k^0)A_{l,m}^{l',m'}(\mathbf{R}_{n'k}-\mathbf{R}_n),\tag{6c}$$

which is similar to Eq. (14) of Ref. 10, but refers to clusters. In the region of the nith particle, outside all the other particles of the nth cluster, we can further use Eq. (A2) to expand the terms in the second summation of Eqs. (6a) and (6b), and Eq. (A11) to expand the terms in the third summation, around $\mathbf{r}_{ni}$. We obtain

$$U_{\rm in}(\mathbf{r}) = (V_0/2 - \mathbf{E}_0 \cdot \mathbf{r}_{ni}) - \mathbf{E}_0 \cdot (\mathbf{r} - \mathbf{r}_{ni}) + 4\pi \sum_{lm} \frac{q_{nilm}}{(2l+1)a_{ni}^{2l+1}} |\mathbf{r} - \mathbf{r}_{ni}|^l Y_{l,m}(\mathbf{r} - \mathbf{r}_{ni})$$
$$+4\pi \sum_{lm} \left[\sum_{i'l'm'} (1 - \delta_i^{i'}) A_{l,m}^{l',m'}(\mathbf{r}_{ni'} - \mathbf{r}_{ni}) q_{ni'l'm'} \right] |\mathbf{r} - \mathbf{r}_{ni}|^l Y_{l,m}(\mathbf{r} - \mathbf{r}_{ni}) +$$
$$+4\pi \sum_{lm} \left\{ \sum_{l''m''} t_{l'',m''}^{l,m}(\mathbf{r}_{ni} - \mathbf{R}_n)^* \sum_{n'l'm'} [C_{l'',m''}^{l',m'}(\mathbf{R}_{n'} - \mathbf{R}_n) Q_{n'l'm'}] \right\} |\mathbf{r} - \mathbf{r}_{ni}|^l Y_{l,m}(\mathbf{r} - \mathbf{r}_{ni}),$$
$$|\mathbf{r} - \mathbf{r}_{ni}| \le a_{ni} \quad \text{(7a)}$$

and

$$U_{\rm out}(\mathbf{r}) = (V_0/2 - \mathbf{E}_0 \cdot \mathbf{r}_{ni}) - \mathbf{E}_0 \cdot (\mathbf{r} - \mathbf{r}_{ni}) + 4\pi \sum_{lm} \frac{q_{nilm}}{(2l+1)} \frac{Y_{l,m}(\mathbf{r} - \mathbf{r}_{ni})}{|\mathbf{r} - \mathbf{r}_{ni}|^{l+1}}$$
$$+4\pi \sum_{lm} \left[\sum_{i'l'm'} (1 - \delta_i^{i'}) A_{l,m}^{l',m'}(\mathbf{r}_{ni'} - \mathbf{r}_{ni}) q_{ni'l'm'} \right] |\mathbf{r} - \mathbf{r}_{ni}|^l Y_{l,m}(\mathbf{r} - \mathbf{r}_{ni})$$
$$+4\pi \sum_{lm} \left\{ \sum_{l''m''} t_{l'',m''}^{l,m}(\mathbf{r}_{ni} - \mathbf{R}_n)^* \sum_{n'l'm'} [C_{l'',m''}^{l',m'}(\mathbf{R}_{n'} - \mathbf{R}_n) Q_{n'l'm'}] \right\} |\mathbf{r} - \mathbf{r}_{ni}|^l Y_{l,m}(\mathbf{r} - \mathbf{r}_{ni}),$$
$$a_{ni'} \le |\mathbf{r} - \mathbf{r}_{ni'}| \text{ for all } i', |\mathbf{r} - \mathbf{R}_n| \le b_{n0}, \text{ and } b_{n'0} \le |\mathbf{r} - \mathbf{R}_{n'}| \text{ for all } n' \ne n. \quad \text{(7b)}$$

Substituting Eqs. (7a) and (7b) into the boundary condition on the surface of the nith particle

$$\left[\epsilon_{ni} \frac{\partial U_{\rm in}}{\partial |\mathbf{r} - \mathbf{r}_{ni}|} - \epsilon_m \frac{\partial U_{\rm out}}{\partial |\mathbf{r} - \mathbf{r}_{ni}|} \right]_{|\mathbf{r} - \mathbf{r}_{ni}| = a_{ni}} = 0, \quad \text{(8)}$$

we obtain

$$q_{nilm} = \beta_{ni1} \sqrt{\frac{3}{4\pi}} E_0 \delta_l^1 \delta_m^0 - (2l+1)\beta_{nil} \left[\sum_{i'l'm'} A_{l,m}^{l',m'}(\mathbf{r}_{ni'} - \mathbf{r}_{ni})(1 - \delta_i^{i'}) q_{ni'l'm'} \right.$$
$$\left. - \sum_{n'l'm'} Q_{n'l'm'} \sum_{l'',m''} t_{l'',m''}^{l,m}(\mathbf{r}_{ni} - \mathbf{R}_n)^* C_{l'',m''}^{l',m'}(\mathbf{R}_{n'} - \mathbf{R}_n) \right], \quad \text{(9a)}$$

where

$$\beta_{nil} = \frac{(\epsilon_{ni} - \epsilon_m) l a_{ni}^{2l+1}}{l\epsilon_{ni} + (l+1)\epsilon_m}. \quad \text{(9b)}$$

We now define the cluster configuration matrices

$$g(n)_{ilm}^{i'l'm'} = \delta_i^{i'} \delta_l^{l'} \delta_m^{m'} + (1 - \delta_i^{i'})(2l+1)\beta_{nil} A_{l,m}^{l',m'}(\mathbf{r}_{ni'} - \mathbf{r}_{ni}), \quad \text{(10)}$$

and rewrite Eq. (9a) as

$$\sum_{i'l'm'} g(n)_{ilm}^{i'l'm'} q_{ni'l'm'} = \beta_{ni1} \sqrt{\frac{3}{4\pi}} E_0 \delta_l^1 \delta_m^0 - (2l+1)\beta_{nil} \sum_{n'l'm'} Q_{n'l'm'} \sum_{l'',m''} t_{l'',m''}^{l,m}(\mathbf{r}_{ni} - \mathbf{R}_n)^* C_{l'',m''}^{l',m'}(\mathbf{R}_{n'} - \mathbf{R}_n). \quad \text{(11)}$$

Solving for q_{nilm} in Eq. (11), we obtain

$$q_{nilm} = \sqrt{\frac{3}{4\pi}} \gamma_{nilm} E_0 - 3 \sum_{l''m''} \lambda_{nilm}^{l''m''} \left[\sum_{n'l'm'} C_{l'',m''}^{l',m'}(\mathbf{R}_{n'} - \mathbf{R}_n) Q_{n'l'm'} \right], \quad \text{(12a)}$$

where

$$\gamma_{nilm} = \sum_{i'} [g(n)^{-1}]^{i'10}_{ilm} \beta_{ni'1}, \tag{12b}$$

and

$$\lambda^{l''m''}_{nilm} = \tfrac{1}{3} \sum_{i'l'm'} (2l'+1)[g(n)^{-1}]^{i'l'm'}_{ilm} \beta_{ni'l'} t^{l',m'}_{l'',m''}(\mathbf{r}_{ni'} - \mathbf{R}_n)^*. \tag{12c}$$

Multiplying Eq. (12a) by the transformation matrix $T(n)$ and summing over i, we obtain

$$Q_{nlm} = \sqrt{\frac{3}{4\pi}} \Gamma_{nlm} E_0 - 3 \sum_{n'l'm'} \left[\sum_{l''m''} \Lambda^{l''m''}_{nlm} C^{l',m'}_{l'',m''}(\mathbf{R}_{n'} - \mathbf{R}_n) \right] Q_{n'l'm'}, \tag{13}$$

where

$$\Gamma_{nlm} = \sum_{ii'l'm'} T(n)^{i'l'm'}_{ilm} \gamma_{ni'l'm'} = \sum_{ii'l'm'} t^{l',m'}_{l,m}(\mathbf{r}_{ni} - \mathbf{R}_n)[g(n)^{-1}]^{i'10}_{il'm'} \beta_{ni'1}, \tag{14}$$

and

$$\begin{aligned}\Lambda^{l''m''}_{nlm} &= \sum_{ii'l'm'} T(n)^{i'l'm'}_{ilm} \lambda_{ni'l'm'} \\ &= \tfrac{1}{3} \sum_{ii'l'm'} \sum_{l'''m'''} (2l'''+1) t^{l',m'}_{l,m}(\mathbf{r}_{ni} - \mathbf{R}_n)[g(n)^{-1}]^{i'l'''m'''}_{il'm'} \beta_{ni'l'''} t^{l''',m'''}_{l'',m''}(\mathbf{r}_{ni'} - \mathbf{R}_n)^*. \end{aligned} \tag{15}$$

Both Γ_{nlm} and $\Lambda^{l''m''}_{nlm}$ are completely determined by the configuration of the nth cluster. From Eq. (13), we notice that $\sqrt{3/4\pi}\Gamma_{nlm}$ is the (lm)-multipole moment induced on the nth cluster by a uniform field of unit strength; in particular,

$$\Gamma_{n10} = \sum_{ii'} [g(n)^{-1}]^{i'10}_{i10} \beta_{ni'1} \tag{16}$$

is the polarizability of the nth cluster. To find the physical meaning of $\Lambda^{l''m''}_{nlm}$, we formally take

$$\sum_{n'l'm'} C^{l',m'}_{l'',m''}(\mathbf{R}_{n'} - \mathbf{R}_n) Q_{n'l'm'} = -\frac{1}{\sqrt{12\pi}} \delta^L_{l''} \delta^M_{m''}. \tag{17}$$

Then, the last summation in Eq. (6a), which represents the potentials produced by the other clusters and all the images, reduces to a single component

$$-\sqrt{\frac{4\pi}{3}} |\mathbf{r} - \mathbf{R}_n|^L Y_{L,M}(\mathbf{r} - \mathbf{R}_n). \tag{18}$$

Correspondingly, the last term in Eq. (13) reduces to $\sqrt{3/4\pi}\Lambda^{LM}_{nlm}$. Hence, $\sqrt{3/4\pi}\Lambda^{LM}_{nlm}$ is the (lm)-multipole moment induced on the nth cluster by the single component potential given in Eq. (18). When $L = 1, M = 0$, the potential in Eq. (18) becomes that of a uniform field of unit strength, and indeed we can verify that $\Lambda^{10}_{nlm} = \Gamma_{nlm}$. Similarly, γ_{nilm} and λ^{LM}_{nilm} represent the corresponding multipole moments induced on the nith particle with respect to the particle center. We also have $\lambda^{10}_{nilm} = \gamma_{nilm}$.

We now define the system configuration matrix

$$G^{n'l'm'}_{nlm} = \delta^{n'}_n \delta^{l'}_l \delta^{m'}_m + 3 \sum_{l''m''} \Lambda^{l''m''}_{nlm} C^{l',m'}_{l'',m''}(\mathbf{R}_{n'} - \mathbf{R}_n). \tag{19}$$

Then, Eq. (13) can be written as

$$GQ = \sqrt{\frac{3}{4\pi}} \Gamma E_0. \tag{20}$$

Solving for Q in Eq. (20), we obtain the cluster multipole moments

$$Q = \sqrt{\frac{3}{4\pi}} G^{-1} \Gamma E_0. \tag{21}$$

Notice that Eqs. (19)–(21) are quite similar to the corresponding equations in Ref. 10, where the particles are treated individually. The only difference is that the clusters have internal structures and their electrical properties are characterized by Γ_{nlm} and $\Lambda^{l''m''}_{nlm}$, whereas spherical particles have no internal structures and their properties are characterized simply by β_{nil}. In fact, if each cluster contains only one particle, taking $\mathbf{R}_n = \mathbf{r}_{ni}$, both $T(n)$ and $g(n)$ matrices reduce to unit matrices, and we have $\Gamma_{nlm} = \beta_{n1}\delta^1_l \delta^0_m$ and $\Lambda^{l''m''}_{nlm} = (1/3)(2l+1)\beta_{nl}\delta^{l''}_l \delta^{m''}_m$. Then, all these equations indeed reduce to those obtained in Ref. 10.

Substituting Eq. (21) into Eq. (12a), we obtain explicitly the multipole moments of the individual particles with respect to their centers:

$$q_{nilm} = \sqrt{\frac{3}{4\pi}} \left[\gamma_{nilm} - 3 \sum_{l'''m'''} \lambda^{l'''m'''}_{nilm} \sum_{n'l'm'} C^{l',m'}_{l''',m'''}(\mathbf{R}_{n'} - \mathbf{R}_n) \sum_{n''l''m''} (G^{-1})^{l''m''}_{n'l'm'} \Gamma_{n''l''m''} \right] E_0. \tag{22}$$

The tensor components of the effective dielectric function of the system are given by

$$\frac{\epsilon_{ezz}}{\epsilon_m} = 1 + \frac{4\pi}{V}\sqrt{\frac{4\pi}{3}}\sum_{ni}\frac{q_{ni10}}{E_0} = 1 + \frac{4\pi}{V}\sqrt{\frac{4\pi}{3}}\sum_{n}\frac{Q_{n10}}{E_0} = 1 + \frac{4\pi}{V}\sum_{nn'l'm'}(G^{-1})_{n10}^{n'l'm'}\Gamma_{n'l'm'}, \tag{23a}$$

$$\frac{\epsilon_{exz}}{\epsilon_m} = \frac{4\pi}{V}\sqrt{\frac{2\pi}{3}}\sum_{n}\frac{Q_{n1-1}-Q_{n11}}{E_0} = \frac{4\pi}{V}\frac{1}{\sqrt{2}}\sum_{nn'l'm'}[(G^{-1})_{n1-1}^{n'l'm'} - (G^{-1})_{n11}^{n'l'm'}]\Gamma_{n'l'm'}, \tag{23b}$$

$$\frac{\epsilon_{eyz}}{\epsilon_m} = \frac{4\pi}{V}\sqrt{\frac{2\pi}{3}}\sum_{n}\frac{Q_{n11}+Q_{n1-1}}{jE_0} = \frac{4\pi}{V}\frac{1}{j\sqrt{2}}\sum_{nn'l'm'}[(G^{-1})_{n11}^{n'l'm'} + (G^{-1})_{n1-1}^{n'l'm'}]\Gamma_{n'l'm'}. \tag{23c}$$

All the other tensor components have formally the same expressions, having rotated appropriately the system, i.e., the G matrix. Therefore, by reexpanding about the cluster centers we have reduced the work necessary to invert an extremely large matrix, involving all the particle multipole moments, to the simpler task of inverting the $g(n)$ and G matrices. For systems containing only one or a few species of identical clusters, the calculations are then tremendously simplified.

III. APPLICATION TO CLUSTER DISTRIBUTIONS

Equations (21), (22), and (23) are generally applicable to systems in which the positions of the clusters and their particles are known: for example, unit cells containing several particles in a crystal lattice. For disordered systems, ensemble averages should be taken. Each cluster in the system can be specified by its position (the cluster center $\mathbf{R}_n$), structure, and orientation. The orientation of the nth cluster can be determined by a set of Euler angles (ψ_n, θ_n, ϕ_n).[11] We assume that the orientation distribution about the azimuthal angle ψ_n is completely random. We divide the clusters into groups such that the clusters in the s group have the same structure, the same $\theta_n = \theta_s$ and $\phi_n = \phi_s$, but arbitrary ψ_n and position $\mathbf{R}_n$. We first replace in Eq. (20) the multipole moments of clusters by the average multipole moments $Q_{s'l'm'} = \langle Q_{n'l'm'}\rangle_{n'\in s'}$ in the corresponding group. This amounts to neglect of the fluctuations of cluster positions and azimuthal angles of orientation. Since the azimuthal angles of the cluster orientations are completely random, $Q_{s'l'm'} = 0$, for $m' \neq 0$. Hence, a typical equation corresponding to a multipole moment of an s-group cluster, Q_{sl0}, becomes

$$Q_{sl0} + 3\sum_{s'l'}\left[\sum_{l''}\Lambda_{sl0}^{l''0}\sum_{n'\in s'}C_{l'',0}^{l',0}(\mathbf{R}_{n'}-\mathbf{R}_s)\right]Q_{s'l'0} = \sqrt{\frac{3}{4\pi}}\Gamma_{sl0}E_0, \tag{24}$$

where $\Lambda_{sl0}^{l''0} = \langle\Lambda_{nl0}^{l''0}\rangle_{n\in s}$, $\Gamma_{sl0} = \langle\Gamma_{nl0}\rangle_{n\in s}$, and we have used $\Lambda_{sl0}^{l''m''} = 0$ for $m'' \neq 0$. Since $C_{l'',0}^{l',0}(\mathbf{R}_{n'} - \mathbf{R}_n)$ depends only on the positions of two clusters, the pair distribution is sufficient to carry out the summation over $n' \in s'$ in Eq. (24). The cluster pair distributions can generally be written as

$$N_s^{s'}(\mathbf{R}-\mathbf{R}_s) = \delta_s^{s'}\delta(\mathbf{R}-\mathbf{R}_s) + F_s^{s'}(\mathbf{R}-\mathbf{R}_s). \tag{25}$$

Here the function $F_s^{s'}(\mathbf{R}-\mathbf{R}_s)$ describes the probability of finding a cluster of s group at $\mathbf{R}$, given the presence of a cluster of s group at $\mathbf{R}_s$. We assume that all correlations have a short range $R_0 \ll d$. Then, $F_s^{s'}(\mathbf{R}-\mathbf{R}_s)$ satisfy the following conditions: firstly, they vanish inside the minimum sphere of the s' group center cluster, and become $N^{s'}$, the average number density of the s' group, outside R_0; secondly, the integration of each $F_s^{s'}(\mathbf{R}-\mathbf{R}_s)$ over a sphere of radius R_0 yields $(4\pi/3)N^{s'}R_0^3$, because of conservation of the total number of clusters for each group; thirdly, $F_s^{s'}(\mathbf{R}-\mathbf{R}_s)$ have azimuthal symmetry. Using the cluster pair distribution (25), we obtain

$$\sum_{n'\in s'}C_{l'',0}^{l',0}(\mathbf{R}_{n'}-\mathbf{R}_s) = \int N_s^{s'}(\mathbf{R}-\mathbf{R}_s)C_{l'',0}^{l',0}(\mathbf{R}-\mathbf{R}_s)d^3\mathbf{R} = F_{sl}^{s'l'} + \left(\frac{8\pi}{9}\right)N^{s'}\delta_l^1\delta_1^{l'} - \left(\frac{4\pi}{3}\right)N^{s'}\delta_l^1\delta_1^{l'}, \tag{26}$$

where the last step has been carried out in Ref. 10 [cf. Eq. (29) and Appendix A therein], and

$$F_{sl}^{s'l'} = \int_{|\mathbf{R}-\mathbf{R}_s|\leq R_0} F_s^{s'}(\mathbf{R}-\mathbf{R}_s)A_{l,0}^{l',0}(\mathbf{R}-\mathbf{R}_s)d^3\mathbf{R}. \tag{27}$$

In the last line of Eq. (26), the first term corresponds to the field produced by the clusters within the correlation range, the second term corresponds to the field produced by the clusters outside the correlation range, and the third term corresponds to the field produced by all the images. The factor $\delta_l^1\delta_1^{l'}$ in the second and third term indicates that the higher multipoles of the clusters outside the correlation range, and of all the images, do not contribute to the local field acting on the central cluster, while their dipoles contribute a uniform field. We also see that only the higher multipoles of the clusters within the correlation range may contribute, and their contributions are exactly determined by their distributions, through $F_{sl}^{s'l'}$. These conclusions parallel those for spherical particles.[10]

Substituting Eq. (26) into Eq. (24), we obtain

$$\sum_{s'l'} G_{sl}^{s'l'} Q_{s'l'0} = \sqrt{\frac{3}{4\pi}}\Gamma_{sl0}E_0, \tag{28a}$$

where

$$G_{sl}^{s'l'} = \delta_s^{s'}\delta_l^{l'} - \left(\frac{4\pi}{3}\right)\Gamma_{sl0}N^{s'}\delta_1^{l'} + 3\sum_{l''}\Lambda_{sl0}^{l''0}F_{sl''}^{s'l'} \tag{28b}$$

is the reduced system configuration matrix (we have used $\Lambda_{sl0}^{10} = \Gamma_{sl0}$). The cluster multipole moments are given by

$$Q_{sl0} = \sqrt{\frac{3}{4\pi}}\sum_{s'l'}(G^{-1})_{sl}^{s'l'}\Gamma_{s'l'0}E_0. \tag{29}$$

Now, the off-diagonal elements of the effective dielectric function vanish due to the azimuthal symmetry, and Eq. (23a) becomes

$$\begin{aligned}\frac{\epsilon_e}{\epsilon_m} &= 1 + 4\pi\sqrt{\frac{4\pi}{3}}\sum_s \frac{N^s Q_{s10}}{E_0} \\ &= 1 + 4\pi\sum_{ss'l'} N^s (G^{-1})_{s1}^{s'l'}\Gamma_{s'l'0},\end{aligned} \tag{30}$$

where we may omit the zz label from now on. When the cluster pair distributions are known, one can compute the coefficients $F_{sl}^{s'l'}$, and then obtain the multipole moments and effective dielectric function from Eqs. (29) and (30).

A particular but important situation occurs when all $F_s^{s'}(\mathbf{R} - \mathbf{R}_s)$ are spherically symmetric. Then, all $F_{sl}^{s'l'}$ vanish because of orthogonality of spherical harmonics, and Eq. (28b) reduces to

$$G_{sl}^{s'l'} = \delta_s^{s'}\delta_l^{l'} - \left(\frac{4\pi}{3}\right)\Gamma_{sl0}N^{s'}\delta_1^{l'}. \tag{31}$$

Hence, the clusters within the correlation range give no contribution. Now, Eq. (28a) becomes

$$Q_{sl0} - \left(\frac{4\pi}{3}\right)\Gamma_{sl0}\sum_{s'} N^{s'} Q_{s'10} = \sqrt{\frac{3}{4\pi}}\Gamma_{sl0}E_0. \tag{32}$$

In particular, the solution for $l = 1$ is

$$Q_{s10} = \sqrt{\frac{3}{4\pi}}\frac{\Gamma_{s10}E_0}{\left(1 - \frac{4\pi}{3}\sum_{s'} N^{s'}\Gamma_{s'10}\right)}. \tag{33}$$

Substituting Eq. (33) into Eq. (32), we then obtain all the cluster multipole moments

$$Q_{sl0} = \sqrt{\frac{3}{4\pi}}\frac{\Gamma_{sl0}E_0}{\left(1 - \frac{4\pi}{3}\sum_{s'} N^{s'}\Gamma_{s'10}\right)}. \tag{34}$$

Applying the same averaging procedure to Eq. (12a), and using Eq. (31), we also obtain the average multipole moments for the individual particles

$$q_{sil0} = \sqrt{\frac{3}{4\pi}}\frac{\gamma_{sil0}E_0}{\left(1 - \frac{4\pi}{3}\sum_{s'} N^{s'}\Gamma_{s'10}\right)}. \tag{35}$$

The average potentials can be obtained by applying the ensemble averaging procedure to the corresponding equations, and using the results (33) and (35). The field produced by the particles within a cluster is complicated in general, due to the complex structure of the cluster. We omit these detailed expressions, and write only the average local field acting on any cluster

$$\begin{aligned}\mathbf{E}_{\text{local}} = \mathbf{E}_0 &- 2\frac{\frac{4\pi}{3}\sum_{s'} N^{s'}\Gamma_{s'10}}{\left(1 - \frac{4\pi}{3}\sum_{s'} N^{s'}\Gamma_{s'10}\right)}\mathbf{E}_0 \\ &+ 3\frac{\frac{4\pi}{3}\sum_{s'} N^{s'}\Gamma_{s'10}}{\left(1 - \frac{4\pi}{3}\sum_{s'} N^{s'}\Gamma_{s'10}\right)}\mathbf{E}_0.\end{aligned} \tag{36}$$

In the right-hand side of Eq. (36), we have three contributions, from the applied field, the field produced by the other clusters, and the field produced by all the images. This result proves that for short-range spherically symmetric cluster correlations all other clusters and all the images simply provide a uniform field acting on any given cluster. Finally, substituting Eq. (33) into Eq. (30), we obtain the effective dielectric function

$$\frac{\epsilon_e}{\epsilon_m} = \frac{1 + \frac{8\pi}{3}\sum_s N^s\Gamma_{s10}}{\left(1 - \frac{4\pi}{3}\sum_s N^s\Gamma_{s10}\right)}. \tag{37}$$

This has the Clausius-Mossotti's form, with the average cluster polarizabilities Γ_{s10} determined from Eq. (16) for any given cluster structure and orientation. These results show that for spherically symmetric pair distributions, even though clusters generally have all higher multipole moments, these do not contribute to the local field and to the effective dielectric function.

We may further average Eqs. (34)–(37) over the remaining Euler angles of orientation (θ_s, ϕ_s). The averaged equations retain their form, but the groups are extended to clusters of the same structure and various orientations, and Γ_{sl0} become the averages of each species over space and orientations.

We notice that Eqs. (34), (36), and (37) are again quite similar to the corresponding results for spherical particles,[10] except that β_{s1} is replaced by Γ_{s10}. In fact, if each cluster consists of only one particle, and $\mathbf{R}_s$ is taken as $\mathbf{r}_{si}$, both $g(n)$ and $T(n)$ reduce to unit matrices, and $\Gamma_{sl0} = \alpha_s a_s^3 \delta_l^1$, where $\alpha_s = (\epsilon_s - \epsilon_m)/(\epsilon_s + 2\epsilon_m)$. Then, Eqs. (34), (36), and (37) reduce to

$$Q_{sl0} = \sqrt{\frac{3}{4\pi}} \frac{\alpha_s a_s^3 E_0}{\left(1 - \sum_{s'} v^{s'} \alpha_{s'}\right)} \delta_l^1, \tag{38}$$

$$\mathbf{E}_{\text{local}} = \mathbf{E}_0 - 2 \frac{\sum_{s'} v^{s'} \alpha_{s'}}{\left(1 - \sum_{s'} v^{s'} \alpha_{s'}\right)} \mathbf{E}_0 + 3 \frac{\sum_{s'} v^{s'} \alpha_{s'}}{\left(1 - \sum_{s'} v^{s'} \alpha_{s'}\right)} \mathbf{E}_0, \tag{39}$$

and

$$\frac{\epsilon_e}{\epsilon_m} = \frac{1 + 2\sum_s v^s \alpha_s}{1 - \sum_s v^s \alpha_s}, \tag{40}$$

where v^s is the volume fraction of the s-group particles. These results coincide with those obtained directly in Ref. 10 [cf. Eqs. (B8), (B10), and (B11)]. We emphasize that Eqs.(34)–(37) hold for any short-range spherically symmetric pair correlations between clusters, with no approximation other than having ignored fluctuations (and assumed azimuthal symmetry).

IV. CHAINING EFFECTS

As an example of clustering, we consider particle chains along the applied field. This has practical importance for systems with a liquid or a gas host, since particles tend to align with the applied electric field to minimize the energy. For the purpose of illustration, let us assume that all the particles are identical, with a radius a and a complex dielectric function ϵ_p, and all the chains have the same length. Then, from Eq. (16), we obtain the cluster polarizability for a chain containing s particles

$$\Gamma_{s1} = \alpha a^3 \sum_{i,i'=1}^{s} [g(s)^{-1}]_{i10}^{i'10}, \tag{41}$$

where $\alpha = (\epsilon_p - \epsilon_m)/(\epsilon_p + 2\epsilon_m)$, and $g_{ilm}^{ilm}(s)$ is the cluster configuration matrix of a chain containing s particles, oriented along the applied field. Assuming that these chains are uniformly distributed in space, we can use Eq. (37) and obtain

$$\epsilon_e(s) = \epsilon_m \frac{1 + 2v\alpha K(s)}{1 - v\alpha K(s)}, \tag{42}$$

where v is the total volume fraction occupied by the particles, and

$$K(s) = (1/s) \sum_{i,i'=1}^{s} [g(s)^{-1}]_{i10}^{i'10} \tag{43}$$

gives a measure of the degree of chaining: nonchaining corresponds to $s = 1$ and $K(1) = 1$, and Eq. (42) reduces to the Maxwell-Garnett result.

We have calculated numerically $\epsilon_e(s)$ for metallic particles in an insulating host, varying the chain length while keeping constant the particle total volume fraction at $v = 0.1$. We have assumed

$$\epsilon_i = 1 + j4\pi\sigma_i/\omega, \quad i = p, m. \tag{44}$$

For typical values $\sigma_p = 9 \times 10^{16}$ sec^{-1} (metallic particles) and $\sigma_m = 0$ (insulating host), we have included the contribution of multipole moments up to $l = 20$. We find that contributions from higher multipoles are considerable, while it turns out that all results are independent of the particle radius. The real and imaginary parts of the effective dielectric function are plotted in Figs. 1 and 2, respectively. Saturation occurs for longer chains. Figure 2 shows that the absorption peak greatly increases, while being redshifted, as the length of the chains increases. We have also computed the opposite case of insulating particle chains in a metallic host. We find that the effective dielectric function decreases as the length of chains increases, but by very little. These results are easily understood as follows. In the first case, as the length increases, the multipole moments of the particles in a chain cooperatively enhance each other, since the field produced by the particles is in the same direction as the applied field. However, the particles beyond a certain range eventually cease to interact with each other due to their rapidly decaying mutipole fields, hence the chaining effect saturates for longer chains. In the second case, the fields produced by the particles in a chain are opposite to the applied field and tend to reduce the multipole moments, which does not induce any cooperative effect.

This study can also be analyzed in an alternative way. Rather than considering a chain as a cluster, we may consider it as a group of particles resulting from an extremely nonspherical two-particle distribution. Then, Eq. (42) represents a correction to the Maxwell-Garnett result, of first order in the volume fraction, due to the nonspherical two-particle distribution. This shows unequivocally

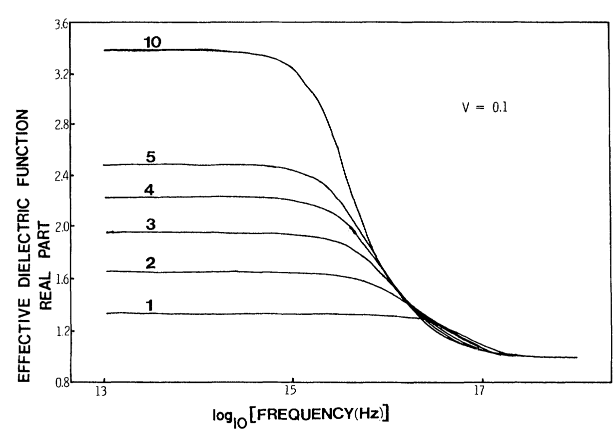

FIG. 1. Effective dielectric function (real part) at $v = 0.1$ vs the logarithm (base 10) of the frequency. The curves are labeled by $s = 1, \ldots, 10$, the number of particles in each chain.

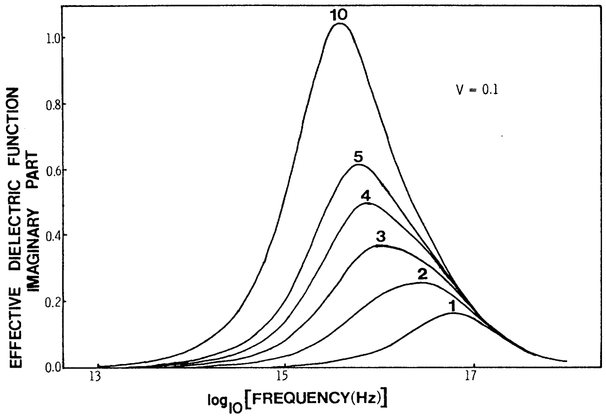

FIG. 2. Effective dielectric function (imaginary part) at $v = 0.1$.

that the effective dielectric function depends crucially on the two-particle distribution, greatly varying at the same volume fraction. The conclusions of Ref. 10 are thus confirmed.

We must point out that this numerical example is only illustrative. In fact, we recall that our results hold exactly only as long as the minimum sphere circumscribing each cluster does not contain particles of any other cluster. Furthermore, in this numerical example we have assumed that the chains have a spherically symmetrical distribution. These conditions set an upper limit to the volume fractions, the second one being more stringent. To estimate this for linear chains of s identical spheres, we let the minimum spheres circumscribing the chains get as close as possible without intersecting. Then $v_s = 0.74/s^2$ is the corresponding volume fraction. Therefore, the results shown in Figs.1 and 2 should be virtually exact up to $s = 3$, while they may only be qualitatively correct for larger s. Nonetheless, the example clearly illustrates that the clustering has a significant effect. Nonspherical cluster pair distributions are clearly favored at relatively high concentrations, particularly for systems of aligned linear chains. In such cases, the effective dielectric function should be computed from Eq. (30), for any given nonspherical cluster pair distribution.

Nonspherical two-particle distributions for systems of spherical particles have been proposed, for example, in ferrofluids,[12] and also applied to electrorheological fluids.[13] Systems of clusters and the interactions involving multipole moments higher than dipoles have not been considered in these fluids so far.

V. CONCLUSIONS

We have developed an analytical approach to obtain the induced multipole moments, electric field, and effective dielectric function of a heterogeneous system containing clustered spherical particles. By introducing the quantities $\Lambda_{nlm}^{l''m''}$, which are completely determined by the configuration of the clusters and characterize their electrical properties, we have obtained exact results which parallel those for spherical particles. We have then obtained corresponding results for disordered systems in terms of cluster pair distributions, neglecting fluctuations. These results can be applied directly for any given pair distribution. As in the case of separate spheres, we have found that the pair distributions play a crucial role in determining the multipolar effects. In particular, for spherically symmetric pair distributions, the higher multipole moments of the clusters have no effect, although they are generally nonvanishing. The local field acting on each cluster remains uniform, and the effective dielectric function satisfies the Clausius-Mossotti's relation, with the cluster polarizabilities directly related to the cluster configurations. This relation holds exactly, whatever the radial dependence of the pair distributions (as long as the concentrations are not so high that the spherical symmetry of the pair distributions is broken). We have provided an illustrative example of particle chains. For metallic particles in an insulating host, we find large corrections to the Maxwell-Garnett result due to chaining, whereas only small corrections are induced in the opposite case of insulating particles in a conducting host.

APPENDIX

In this appendix we derive the formulas required in the text to express the multipole moments of the same charge distribution with respect to different expansion points. We consider a localized charge distribution, and expand the corresponding potential with respect to two different points $\mathbf{r}_1$ and $\mathbf{r}_2$. Outside two spheres of radii r_{10} and r_{20}, centered at $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively, each enclosing the entire charge distribution, we have

$$4\pi \sum_{l'm'} \frac{q^1_{l'm'}}{(2l'+1)} \frac{Y_{l',m'}(\mathbf{r}-\mathbf{r}_1)}{|\mathbf{r}-\mathbf{r}_1|^{l'+1}} = 4\pi \sum_{lm} \frac{q^2_{lm}}{(2l+1)} \frac{Y_{l,m}(\mathbf{r}-\mathbf{r}_2)}{|\mathbf{r}-\mathbf{r}_2|^{l+1}},$$

$$|\mathbf{r}-\mathbf{r}_1| > r_{10}, \quad |\mathbf{r}-\mathbf{r}_2| > r_{20}, \quad \text{(A1)}$$

where q^1_{lm} and q^2_{lm} are the multipole moments with respect to $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively. We have already obtained in Appendix A of Ref. 10 the expansion formula

$$\frac{Y_{l',m'}(\mathbf{r}-\mathbf{r}')}{(2l'+1)|\mathbf{r}-\mathbf{r}'|^{l'+1}} = \sum_{lm} A_{l,m}^{l',m'}(\mathbf{r}'-\mathbf{r}'')|\mathbf{r}-\mathbf{r}''|^l Y_{l,m}(\mathbf{r}-\mathbf{r}''), \quad |\mathbf{r}-\mathbf{r}''| < |\mathbf{r}'-\mathbf{r}''|, \quad \text{(A2)}$$

where

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

$$|m|\le l,\quad |m'|\le l'. \quad \text{(A3)}$$

Now

$$\frac{Y_{l',m'}(\mathbf{r}-\mathbf{r}')}{(2l'+1)|\mathbf{r}-\mathbf{r}'|^{l'+1}} = (-1)^{l'}\frac{Y_{l',m'}(\mathbf{r}'-\mathbf{r})}{(2l'+1)|\mathbf{r}'-\mathbf{r}|^{l'+1}} = (-1)^{l'}\sum_{lm} A_{l,m}^{l',m'}(\mathbf{r}-\mathbf{r}'')|\mathbf{r}'-\mathbf{r}''|^{l}Y_{l,m}(\mathbf{r}'-\mathbf{r}''),\quad |\mathbf{r}'-\mathbf{r}''|<|\mathbf{r}-\mathbf{r}''|. \quad \text{(A4)}$$

Renaming the summation indices l as $l-l'$ and m as $m'-m$, we obtain with some manipulations

$$\frac{Y_{l',m'}(\mathbf{r}-\mathbf{r}')}{(2l'+1)|\mathbf{r}-\mathbf{r}'|^{l'+1}} = \sum_{lm} t_{l,m}^{l',m'}(\mathbf{r}'-\mathbf{r}'')\frac{Y_{l,m}(\mathbf{r}-\mathbf{r}'')}{(2l+1)|\mathbf{r}-\mathbf{r}''|^{l+1}},\quad |\mathbf{r}'-\mathbf{r}''|<|\mathbf{r}-\mathbf{r}''| \quad \text{(A5)}$$

where

$$t_{l,m}^{l',m'}(\mathbf{r}'-\mathbf{r}'') = |\mathbf{r}'-\mathbf{r}''|^{l-l'}Y^*_{l-l',m-m'}(\mathbf{r}'-\mathbf{r}'') \times\left[\frac{4\pi(2l+1)(l+m)!(l-m)!}{(2l'+1)(2l-2l'+1)(l-l'+m-m')!(l-l'-m+m')!(l'+m')!(l'-m')!}\right]^{1/2}. \quad \text{(A6)}$$

Substituing Eq. (A5) into Eq. (A1), and comparing corresponding terms on each side, we obtain the relation between the two sets of multipole moments

$$q^2_{lm} = \sum_{l'm'} t_{l,m}^{l',m'}(\mathbf{r}_1-\mathbf{r}_2)q^1_{l'm'}. \quad \text{(A7)}$$

We now derive a second expansion formula. We write

$$|\mathbf{r}-\mathbf{r}'|^{l'}Y_{l',m'}(\mathbf{r}-\mathbf{r}') = \sum_{l''m''} B_{l'',m''}^{l',m'}(\mathbf{r}'-\mathbf{r}'')|\mathbf{r}-\mathbf{r}''|^{l''}Y_{l'',m''}(\mathbf{r}-\mathbf{r}''). \quad \text{(A8)}$$

First, apply $\partial^{l-m}/\partial z^{l-m}(\partial/\partial x \pm j\partial/\partial y)^m$ to Eq. (A8) and use the identities[10]

$$\frac{\partial^{l-m}}{\partial z^{l-m}}\left(\frac{\partial}{\partial x}\pm j\frac{\partial}{\partial y}\right)^m [r^{l'}Y_{l',m'}(\mathbf{r})\,] = (\pm 1)^m r^{l'-l}Y_{l'-l,m'\pm m}(\mathbf{r})\left[\frac{(2l'+1)(l'+m')!(l'-m')!}{(2l'-2l+1)(l'-l\pm m'+m)!(l'-l\mp m'-m)!}\right]^{1/2}. \quad \text{(A9)}$$

Then, take $\mathbf{r}\to\mathbf{r}''$. The only surviving term in the right-hand side has $l''=l,\ m''=-m$ for the upper sign, and $l''=l,\ m''=m$ for the lower sign; we find

$$B_{l,m}^{l',m'}(\mathbf{r}'-\mathbf{r}'') = t_{l',m'}^{l,m}(\mathbf{r}''-\mathbf{r}')^*. \quad \text{(A10)}$$

Hence, we have

$$|\mathbf{r}-\mathbf{r}'|^{l'}Y_{l',m'}(\mathbf{r}-\mathbf{r}') = \sum_{l''m''} t_{l',m'}^{l'',m''}(\mathbf{r}''-\mathbf{r}')^*|\mathbf{r}-\mathbf{r}''|^{l''}Y_{l'',m''}(\mathbf{r}-\mathbf{r}''). \quad \text{(A11)}$$

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