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Electrical response of heterogeneous systems of nonlinear inclusions

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We present an analytical approach to the electrical response of microscopically inhomogeneous systems consisting of inclusions with arbitrary structure and linear and nonlinear response, embedded in a linear host medium. By introducing linear and nonlinear polarization coefficients, which describe the electrical response of a single inclusion, we are able to take into account the contributions of all multipole moments of the inclusions and their images. We obtain the exact effective dielectric function for ordered systems to the first nonlinear order, in terms of the microscopic configuration. Higher nonlinear terms can be obtained similarly with this approach. We also obtain the mean-field result for disordered systems in terms of pair distributions. We find that the pair distribution of the inclusions plays a crucial role: it determines precisely the contribution from each order of the multipole moments. Particular results are provided for $L = 0, 1$ pair distributions; we prove that for these distributions the multipole moments higher than dipoles do not contribute to the effective dielectric function. We find that the mutual stimulation among the inclusions may significantly affect the effective dielectric function, especially the nonlinear part, depending on the concentration and the distribution of the inclusions. We illustrate numerically this multi-inclusion effect for a system of nonlinear spherical inclusions.

I. INTRODUCTION

Interest in nonlinear electrical properties of composites has dramatically increased in recent years. For a general perspective of the properties of macroscopically inhomogeneous media, we refer the readers to the review article by Bergman and Stroud.[1] In this paper, we focus on microscopically inhomogeneous (macroscopically homogeneous) systems formed by nonlinear inclusions dispersed in a linear host medium. The electrical response of such systems is much more complex than in the corresponding linear cases, due to the complicated interactions among the inclusions. Only approaches for inclusions of particularly simple shapes have been developed so far, with one of the following approximations: (1) single-particle approximation, which considers a single inclusion immersed in a uniform external field and a host medium;[2–4] (2) effective medium approximation, which also considers a single inclusion immersed in a host medium, but the host medium is replaced by an effective one;[2,5] (3) Clausius-Mossotti (or Maxwell-Garnett) approximation, which considers a single inclusion immersed in a uniform Lorentz field, as in the cavity used in the standard derivation of the Clausius-Mossotti relation.[2,6] None of these theories considers microscopically the detailed interactions among the inclusions. Computer simulations have also been carried out, which consider microscopic interactions, but only limited to dipole moments.[7]

We present a general rigorous approach to the electrical response of microscopically inhomogeneous systems of nonlinear inclusions based on a fully multipolar expansion method. By introducing linear and nonlinear polarization coefficients, we are able to treat inclusions with arbitrary shapes, structures, and response. Nonlinear systems require complete definiteness of the local field acting on each inclusion. So, the system configuration becomes crucial, and the one that we have consistently adopted is quite valuable: that consists of a slab sample placed between two parallel electrode plates with an alternating potential. We take into account the exact interactions among the inclusions by retaining all orders of the multipole moments of the inclusions and their images induced by the electrodes. Then, we expand the multipole moments as Taylor series in the applied field and solve the exact equations consecutively to each order of the derivatives of the multipole moments. The first three derivatives yield the effective dielectric function to the first nonlinear order. For inclusions with stronger nonlinearities, higher derivatives may be required, and those can be obtained by the same procedure. Some of the previous theories with the single-particle approximation have been carried out to nonlinear terms of higher order.[3,4] In Sec. II, we present the general results for ordered systems in terms of the microscopic configuration and the applied field. In Sec. III, we obtain the mean-field results for disordered systems, in terms of the pair distribution and the applied field. We show that it is the pair distribution of the inclusions that determines precisely the contribution from each order of the multipole moments. In Sec. IV, we provide the explicit results for systems with $L = 0, 1$ pair distributions. We show that for these distributions only the dipole moments contribute to the effective dielectric function. In Sec. V, we apply the results of Sec. IV to a system of nonlinear spherical inclusions and illustrate the effect due to the interactions among the inclusions with a numerical computation.

II. EXACT RESULTS FOR ORDERED SYSTEMS

We study a system containing inclusions with arbitrary form of nonlinear response embedded in a linear homogeneous medium with dielectric function ϵ_m. The system fills the space between two parallel electrode plates to which a low frequency alternating potential $V_0 e^{-j\omega t}$ is applied. We consider a system with fixed nonoverlapping inclusions, meaning that for each inclusion there is a minimum circumscribing sphere which encloses all the charges associated with the inclusion while excluding any charge associated with other inclusions.

To describe the electrical response of such systems, we need first a set of parameters describing completely the electrical response of a single inclusion, in a local potential of the most general form. Let us consider a single inclusion *fixed at the origin*, in an infinite linear medium of dielectric function ϵ_m, and subject to a local potential of the form (we omit the $e^{-j\omega t}$ time dependence throughout the paper)

$$U_{\text{local}}(\mathbf{r}) = -\sqrt{\frac{4\pi}{3}} \sum_{l_1 m_1} E_{l_1 m_1} r^{l_1} Y_{l_1, m_1}(\mathbf{r}). \tag{1}$$

Since the inclusions are nonoverlapping, Eq. (1) indeed represents the most general local potential. The total induced multipole moments q_{lm} on the inclusion, including the contribution of the host medium, are in general functions of all $E_{l_1 m_1}$. Expanding q_{lm} as a Taylor series in $E_{l_1 m_1}$, we obtain

$$\begin{aligned} q_{lm} = {} & \sum_{l_1 m_1} \left. \frac{\partial q_{lm}}{\partial E_{l_1 m_1}} \right|_0 E_{l_1 m_1} + \frac{1}{2!} \sum_{l_1 m_1 l_2 m_2} \left. \frac{\partial^2 q_{lm}}{\partial E_{l_1 m_1} \partial E_{l_2 m_2}} \right|_0 E_{l_1 m_1} E_{l_2 m_2} \\ & + \frac{1}{3!} \sum_{l_1 m_1 l_2 m_2 l_3 m_3} \left. \frac{\partial^3 q_{lm}}{\partial E_{l_1 m_1} \partial E_{l_2 m_2} \partial E_{l_3 m_3}} \right|_0 E_{l_1 m_1} E_{l_2 m_2} E_{l_3 m_3} + \cdots = \sqrt{\frac{3}{4\pi}} \left[\sum_{l_1 m_1} \lambda_{lm}^{l_1 m_1} E_{l_1 m_1} \right. \\ & \left. + \frac{1}{2!} \sum_{l_1 m_1 l_2 m_2} \mu_{lm}^{l_1 m_1 l_2 m_2} E_{l_1 m_1} E_{l_2 m_2} + \frac{1}{3!} \sum_{l_1 m_1 l_2 m_2 l_3 m_3} \nu_{lm}^{l_1 m_1 l_2 m_2 l_3 m_3} E_{l_1 m_1} E_{l_2 m_2} E_{l_3 m_3} + \cdots \right], \end{aligned} \tag{2}$$

where $|_0$ denotes the corresponding quantity evaluated at all $E_{lm} = 0$, and we assume $q_{lm}|_0 = 0$ (i.e., no permanent multipole moments). The upper indices of $\mu_{lm}^{l_1 m_1 l_2 m_2}$ and $\nu_{lm}^{l_1 m_1 l_2 m_2 l_3 m_3}$ are interchangeable in pairs, namely

$$\begin{aligned} \mu_{lm}^{l_2 m_2 l_1 m_1} &= \mu_{lm}^{l_1 m_1 l_2 m_2}, \\ \nu_{lm}^{l_2 m_2 l_1 m_1 l_3 m_3} &= \nu_{lm}^{l_3 m_3 l_2 m_2 l_1 m_1} = \nu_{lm}^{l_1 m_1 l_2 m_2 l_3 m_3}, \ldots . \end{aligned} \tag{3}$$

In Eq. (2), $\lambda_{lm}^{l_1 m_1}$, $\mu_{lm}^{l_1 m_1 l_2 m_2}$, $\nu_{lm}^{l_1 m_1 l_2 m_2 l_3 m_3}$, ... represent the zero- (linear), first-, and second-order polarization coefficients. For inclusions formed of linear response materials, all the nonlinear polarization coefficients vanish. We have already investigated the electrical response of such systems.[8] We now generalize the theory to inclusions constituted of nonlinear materials. One can define the polarization coefficients to any desired order: here we retain up to $\nu_{lm}^{l_1 m_1 l_2 m_2 l_3 m_3}$. All polarization coefficients depend on the structure of the inclusion (shape and material), on ϵ_m, on ω, and on the orientation of the inclusion. Similar to the results of Appendix A in Ref. 8, we have the rotational properties

$$\lambda_{lm}^{l_1 m_1}(\tau)^* = \sum_{m_2 m_3} (D^{-1})_{lm}^{l m_2} \lambda_{l m_2}^{l_1 m_3 *} D_{l_1 m_3}^{l_1 m_1}, \tag{4a}$$

$$\mu_{lm}^{l_1 m_1 l_2 m_2}(\tau)^* = \sum_{m_3 l_4 m_4 m_5} (D^{-1})_{lm}^{l m_3} \mu_{l m_3}^{l_1 m_4 l_2 m_5 *} D_{l_1 m_4}^{l_1 m_1} \times D_{l_2 m_5}^{l_2 m_2}, \tag{4b}$$

$$\nu_{lm}^{l_1 m_1 l_2 m_2 l_3 m_3}(\tau)^* = \sum_{m_4 m_5 m_6 m_7} (D^{-1})_{lm}^{l m_4} \nu_{l m_4}^{l_1 m_5 l_2 m_6 l_3 m_7 *} \times D_{l_1 m_5}^{l_1 m_1} D_{l_2 m_6}^{l_2 m_2} D_{l_3 m_7}^{l_3 m_3}, \tag{4c}$$

etc. For specific systems, the polarization coefficients which represent the complete response of an isolated inclusion must be calculated by solving the corresponding boundary value problem (an example will be presented in Sec. V) or determined experimentally. In the following, we will assume that they are given.

We first consider an ordered system in which the positions and orientations of all the inclusions are known. Let $\mathbf{r}_n$ denote the position of the nth inclusion inside a heterogeneous system: the local potential acting on the nth inclusion is given by [cf. Eq. (6) of Ref. 8]

$$\begin{aligned} U_{\text{local}}(\mathbf{r}) = {} & (V_0/2 - \mathbf{r}_n \cdot \mathbf{E}_0) \\ & - \sqrt{\frac{4\pi}{3}} \sum_{lm} \left[E_0 \delta_l^1 \delta_m^0 - 3\sqrt{\frac{4\pi}{3}} \sum_{n_1 l_1 m_1} C_{l,m}^{l_1, m_1}(\mathbf{r}_{n_1} - \mathbf{r}_n) q_{n_1 l_1 m_1} \right] |\mathbf{r} - \mathbf{r}_n|^l Y_{l,m}(\mathbf{r} - \mathbf{r}_n), \end{aligned} \tag{5}$$

where the coefficients $C_{l,m}^{l_1,m_1}(\mathbf{r}_{n_1}-\mathbf{r}_n)$, defined in Eq. (1a) of Ref. 9, result from a reexpansion of the multipole potentials around $\mathbf{r}_n$ [cf. Eq. (12) of Ref. 9]. According to Eq. (2), the induced multipole moments on the nth inclusion are

$$\begin{aligned} q_{nlm} = &\sqrt{\frac{3}{4\pi}}\left(\lambda_{nlm}^{10}E_0+\frac{1}{2!}\mu_{nlm}^{1010}E_0^2+\frac{1}{3!}\nu_{nlm}^{101010}E_0^3\right)\\ &-3\sum_{l_1m_1}\left(\lambda_{nlm}^{l_1m_1}+\mu_{nlm}^{10l_1m_1}E_0+\frac{1}{2}\nu_{nlm}^{1010l_1m_1}E_0^2\right)(Cq)_{nl_1m_1}\\ &+\frac{9}{2!}\sqrt{\frac{4\pi}{3}}\sum_{l_1m_1l_2m_2}\left(\mu_{nlm}^{l_1m_1l_2m_2}+\nu_{nlm}^{10l_1m_1l_2m_2}E_0\right)(Cq)_{nl_1m_1}(Cq)_{nl_2m_2}\\ &-\frac{27}{3!}\left(\frac{4\pi}{3}\right)\sum_{l_1m_1l_2m_2l_3m_3}\nu_{nlm}^{l_1m_1l_2m_2l_3m_3}(Cq)_{nl_1m_1}(Cq)_{nl_2m_2}(Cq)_{nl_3m_3}+\cdots, \end{aligned} \tag{6}$$

where $(Cq)_{nlm}$ is an abbreviation for $\sum_{n_1l_1m_1}C_{l,m}^{l_1,m_1}(\mathbf{r}_{n_1}-\mathbf{r}_n)q_{n_1l_1m_1}$. The nonoverlapping condition for the inclusions is required for a multipolar expansion, or the local potential may not have the form (1). So, systems with aggregate topology, or systems with a nonlinear host medium, where the charges cannot be separated and contained within circumscribing spheres, cannot be treated by this technique.

Now, Eq. (6) provides q_{nlm} as functions of E_0. Expanding q_{nlm} in both sides of Eq. (6) as a Taylor series in E_0 and comparing the coefficients of the same power, we obtain

$$\sum_{n_1l_1m_1}G_{nlm}^{n_1l_1m_1}\left.\frac{\partial^k q_{n_1l_1m_1}}{\partial E_0^k}\right|_0=\sqrt{\frac{3}{4\pi}}H_{nlm}(k),\quad k=1,2,3,\ldots, \tag{7}$$

where the configuration matrix is

$$G_{nlm}^{n_1l_1m_1}=\delta_n^{n_1}\delta_l^{l_1}\delta_m^{m_1}+3\sum_{l_2m_2}\lambda_{nlm}^{l_2m_2}C_{l_2,m_2}^{l_1,m_1}(\mathbf{r}_{n_1}-\mathbf{r}_n), \tag{8}$$

and

$$H_{nlm}(1)=\lambda_{nlm}^{10}, \tag{9a}$$

$$\begin{aligned} H_{nlm}(2)=&\,\mu_{nlm}^{1010}-6\sqrt{\frac{4\pi}{3}}\sum_{l_1m_1}\mu_{nlm}^{10l_1m_1}\left(C\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{nl_1m_1}\\ &+9\left(\frac{4\pi}{3}\right)\sum_{l_1m_1l_2m_2}\mu_{nlm}^{l_1m_1l_2m_2}\left(C\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{nl_1m_1}\left(C\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{nl_2m_2}, \end{aligned} \tag{9b}$$

$$\begin{aligned} H_{nlm}(3)=&\,\nu_{nlm}^{101010}-9\sqrt{\frac{4\pi}{3}}\sum_{l_1m_1}\nu_{nlm}^{1010l_1m_1}\left(C\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{nl_1m_1}\\ &+27\left(\frac{4\pi}{3}\right)\sum_{l_1m_1l_2m_2}\nu_{nlm}^{10l_1m_1l_2m_2}\left(C\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{nl_1m_1}\left(C\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{nl_2m_2}\\ &-27\left(\frac{4\pi}{3}\right)^{3/2}\sum_{l_1m_1l_2m_2l_3m_3}\nu_{nlm}^{l_1m_1l_2m_2l_3m_3}\left(C\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{nl_1m_1}\left(C\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{nl_2m_2}\left(C\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{nl_3m_3}\\ &-9\sqrt{\frac{4\pi}{3}}\sum_{l_1m_1}\mu_{nlm}^{10l_1m_1}\left(C\left.\frac{\partial^2 q}{\partial E_0^2}\right|_0\right)_{nl_1m_1}\\ &+27\left(\frac{4\pi}{3}\right)\sum_{l_1m_1l_2m_2}\mu_{nlm}^{l_1m_1l_2m_2}\left(C\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{nl_1m_1}\left(C\left.\frac{\partial^2 q}{\partial E_0^2}\right|_0\right)_{nl_2m_2}, \end{aligned} \tag{9c}$$

etc. Equation (7) has the solution

$$\left.\frac{\partial^k q_{nlm}}{\partial E_0^k}\right|_0=\sqrt{\frac{3}{4\pi}}\sum_{n_1l_1m_1}(G^{-1})_{nlm}^{n_1l_1m_1}H_{n_1l_1m_1}(k),\quad k=1,2,3,\ldots. \tag{10}$$

We define the (longitudinal) effective dielectric function ϵ_e through the average displacement over the whole system as

$$\epsilon_e\langle E\rangle = \epsilon_m\langle E\rangle + \epsilon_m 4\pi N\sqrt{\frac{4\pi}{3}}\langle q_{10}\rangle$$
$$= \epsilon_m\langle E\rangle + \epsilon_m 4\pi N\sqrt{\frac{4\pi}{3}}\left.\frac{\partial\langle q_{10}\rangle}{\partial E_0}\right|_0 + \epsilon_m 4\pi N\sqrt{\frac{4\pi}{3}}\frac{1}{6}\left.\frac{\partial^3\langle q_{10}\rangle}{\partial E_0^3}\right|_0 E_0^3 + O^*\left(E_0^5\right), \tag{11}$$

where N is the average number density and $\langle q_{10}\rangle$ is the average dipole moment of the inclusions. This definition is the natural extension of that used for linear inclusions.[9] Using $\langle E\rangle = E_0$, which is evident in our configuration, we obtain

$$\epsilon_e = \epsilon_m + 4\pi N\sqrt{\frac{4\pi}{3}}\left.\frac{\partial\langle q_{10}\rangle}{\partial E_0}\right|_0 + \epsilon_m 4\pi N\sqrt{\frac{4\pi}{3}}\frac{1}{6}\left.\frac{\partial^3\langle q_{10}\rangle}{\partial E_0^3}\right|_0 E_0^2 + O^*\left(E_0^4\right)$$
$$= \epsilon_m + \epsilon_m\frac{4\pi}{V}\sum_{nn_1l_1m_1}(G^{-1})_{n10}^{n_1l_1m_1}\lambda_{n_1l_1m_1} + \epsilon_m\frac{4\pi}{V}\frac{1}{6}\sum_{nn_1l_1m_1}(G^{-1})_{n10}^{n_1l_1m_1}H_{n_1l_1m_1}(3)E_0^2 + O^*\left(E_0^4\right), \tag{12}$$

where V is the volume of the system. We assume the system has macroscopic reflection symmetry in $z \longrightarrow -z$, which leads to[10]

$$\langle q_{lm}(-E_0)\rangle = (-1)^{l+m}\langle q_{lm}(E_0)\rangle. \tag{13}$$

Thus, we dropped the even derivatives in Eq. (11). We show in the Appendix that this symmetry also leads to

$$\langle\lambda_{lm}^{l_1m_1}\rangle = (-1)^{l+m+l_1+m_1}\langle\lambda_{lm}^{l_1m_1}\rangle,$$
$$\langle\mu_{lm}^{l_1m_1l_2m_2}\rangle = (-1)^{l+m+l_1+m_1+l_2+m_2}\langle\mu_{lm}^{l_1m_1l_2m_2}\rangle,$$
$$\langle\nu_{lm}^{l_1m_1l_2m_2l_3m_3}\rangle = (-1)^{l+m+l_1+m_1+l_2+m_2+l_3+m_3}\langle\nu_{lm}^{l_1m_1l_2m_2l_3m_3}\rangle, \tag{14}$$

etc. Hence, an average polarization coefficient vanishes if its indices add up to an odd integer. The nonlinear response is then characterized by[11]

$$\frac{\Delta\epsilon_e}{E_0^2} = \frac{\epsilon_e(E_0) - \epsilon_e(0)}{E_0^2} = \epsilon_m 4\pi N\sqrt{\frac{4\pi}{3}}\frac{1}{6}\left.\frac{\partial^3\langle q_{10}\rangle}{\partial E_0^3}\right|_0 + O^*\left(E_0^2\right)$$
$$= \epsilon_m\frac{4\pi}{V}\frac{1}{6}\sum_{nn_1l_1m_1}(G^{-1})_{n10}^{n_1l_1m_1}H_{n_1l_1m_1}(3) + O^*\left(E_0^2\right). \tag{15}$$

Up to now, we have expressed all the results in terms of the polarization coefficients of the inclusions, the system configuration matrix G, and the applied potential at the electrode plates. For example, these results can be applied to periodic systems with inclusions on a lattice, or used in computer simulations. These results are exact to first order in the nonlinear response for ordered systems. For inclusions with strong nonlinearities, higher terms in Eq. (2) may be required, and one can define similarly the higher polarization coefficients. The expressions for higher-order derivatives of the multipole moments have the same form as in Eq. (10), with corresponding $H_{nlm}(k)$ $(k > 3)$ containing lower-order derivatives.

III. MEAN-FIELD RESULTS FOR DISORDERED SYSTEMS

In this section, we derive the mean-field results for disordered systems. First, we replace in Eq. (6) the individual multipole moments $q_{n_1l_1m_1}$ of the surrounding inclusions and all images by the ensemble average multipole moments $\langle q_{lm}\rangle$. Then, we average the equations over all the inclusions (i.e., over n). This represents the mean-field approximation, which ignores fluctuation effects. We assume that the system has also macroscopic azimuthal symmetry, hence $\langle q_{lm}\rangle = 0$ for $m \neq 0$, and

$$\sum_{n_1} C_{l,0}^{l_1,0}(\mathbf{r}_{n_1} - \mathbf{r}_n)q_{n_1l_10} = -\frac{4\pi}{9}N\left(\delta_l^1\delta_1^{l_1} + K_l^{l_1}\right)\langle q_{l_10}\rangle, \tag{16}$$

where Eq. (A17) of Ref. 9 has been used, and the coefficients $K_l^{l_1}$ are defined in Eq. (21) of Ref. 8, in terms of the pair distributions of the inclusions. Here, $K_l^{l_1} = 0$ for $l + l_1 =$ odd integers, due to reflection symmetry. To convert the results in the previous section to disordered systems, we drop the index n, set $m, m_1, m_2, \ldots = 0$, replace the polarization coefficients and multipole moments for individual inclusions with the corresponding averages, and let

$$\left(C\left.\frac{\partial^k q}{\partial E_0^k}\right|_0\right)_l \longrightarrow -\frac{4\pi}{9}N\sum_{l_1}(\delta_l^1\delta_1^{l_1} + K_l^{l_1})\left.\frac{\partial^k\langle q_{l_10}\rangle}{\partial E_0^k}\right|_0$$
$$\equiv -\frac{4\pi}{9}N\left(K\left.\frac{\partial^k q}{\partial E_0^k}\right|_0\right)_l. \tag{17}$$

According to these rules, we have

$$\left.\frac{\partial^k \langle q_{l0}\rangle}{\partial E_0^k}\right|_0 - \left(\frac{4\pi}{3}\right) N \sum_{l_1} \langle \lambda_{l0}^{l_2 0}\rangle (\delta_{l_2}^1 \delta_1^{l_1} + K_{l_2}^{l_1}) \left.\frac{\partial^k \langle q_{l_1 0}\rangle}{\partial E_0^k}\right|_0$$

$$= \sqrt{\frac{3}{4\pi}} H_l(k), \quad k = 1, 2, 3, \ldots, \quad (18)$$

or

$$\left.\frac{\partial^k \langle q_{l0}\rangle}{\partial E_0^k}\right|_0 = \sqrt{\frac{3}{4\pi}} \sum_{l_1} (G^{-1})_l^{l_1} H_{l_1}(k), \quad k = 1, 2, 3, \ldots, \quad (19)$$

where

$$G_l^{l_1} = \delta_l^{l_1} - \left(\frac{4\pi}{3}\right) N \sum_{l_2} \langle \lambda_{l0}^{l_2 0}\rangle (\delta_{l_2}^1 \delta_1^{l_1} + K_{l_2}^{l_1}) \quad (20)$$

and

$$H_l(1) = \langle \lambda_{l0}^{10}\rangle, \quad (21a)$$

$$H_l(2) = \langle \mu_{l0}^{1010}\rangle + 2\left(\frac{4\pi}{3}\right)^{3/2} N \sum_{l_1} \langle \mu_{l0}^{10 l_1 0}\rangle \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1} + \left(\frac{4\pi}{3}\right)^3 N^2 \sum_{l_1 l_2} \langle \mu_{l0}^{l_1 0 l_2 0}\rangle \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1} \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_2}, \quad (21b)$$

$$\begin{aligned} H_l(3) = {} & \langle \nu_{l0}^{101010}\rangle + 3\left(\frac{4\pi}{3}\right)^{3/2} N \sum_{l_1} \langle \nu_{l0}^{1010 l_1 0}\rangle \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1} \\ & + 3\left(\frac{4\pi}{3}\right)^3 N^2 \sum_{l_1 l_2} \langle \nu_{l0}^{10 l_1 0 l_2 0}\rangle \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1} \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_2} \\ & + \left(\frac{4\pi}{3}\right)^{9/2} N^3 \sum_{l_1 l_2 l_3} \langle \nu_{l0}^{l_1 0 l_2 0 l_3 0}\rangle \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1} \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_2} \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_3} \\ & + 3\left(\frac{4\pi}{3}\right)^{3/2} N \sum_{l_1} \langle \mu_{l0}^{10 l_1 0}\rangle \left(K \left.\frac{\partial^2 q}{\partial E_0^2}\right|_0\right)_{l_1} \\ & + 3\left(\frac{4\pi}{3}\right)^3 N^2 \sum_{l_1} \langle \mu_{l0}^{l_1 0 l_2 0}\rangle \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1} \left(K \left.\frac{\partial^2 q}{\partial E_0^2}\right|_0\right)_{l_2}, \quad \text{etc.} \end{aligned} \quad (21c)$$

The macroscopic reflection symmetry requires [cf. Eq. (17)]

$$\left(K \left.\frac{\partial^k q}{\partial E_0^k}\right|_0\right)_l = 0 \quad \text{if } l + k = \text{ odd integers}, \quad (22)$$

and also $\partial^k \langle q_{l0}\rangle / \partial E_0^k$ with odd l and k are decoupled from those with even l and k. To obtain the effective dielectric function, we need only the former ones, which are given by

$$\sum_{l_1} \mathcal{G}_l^{l_1} \left.\frac{\partial^k \langle q_{2l_1-1,0}\rangle}{\partial E_0^k}\right|_0 = \sqrt{\frac{3}{4\pi}} H_{2l-1}(k), \quad k = 1, 3, \ldots, \quad (23)$$

where

$$\mathcal{G}_l^{l_1} = G_{2l-1}^{2l_1-1} = \delta_l^{l_1} - \left(\frac{4\pi}{3}\right) N \sum_{l_2} \langle \lambda_{2l-1,0}^{2l_2-1,0}\rangle (\delta_{l_2}^1 \delta_1^{l_1} + K_{2l_2-1}^{2l_1-1}). \quad (24)$$

Then, $\mathcal{G}$ reduces to about half the size of G. The effective dielectric function now is given by

$$\begin{aligned} \frac{\epsilon_e}{\epsilon_m} &= 1 + 4\pi N \sqrt{\frac{4\pi}{3}} \left.\frac{\partial \langle q_{10}\rangle}{\partial E_0}\right|_0 + 4\pi N \sqrt{\frac{4\pi}{3}} \frac{1}{6} \left.\frac{\partial^3 \langle q_{10}\rangle}{\partial E_0^3}\right|_0 E_0^2 + O^*(E_0^4) \\ &= 1 + 4\pi N \sum_{l_1} (\mathcal{G}^{-1})_1^{l_1} \langle \lambda_{2l_1-1,0}^{1,0}\rangle + \frac{1}{2}\left(\frac{4\pi}{3}\right) N \sum_{l_1} (\mathcal{G}^{-1})_1^{l_1} H_{2l_1-1}(3) E_0^2 + O^*(E_0^4), \end{aligned} \quad (25)$$

and the applied field (in the z direction) excites only the longitudinal component, due to the macroscopic azimuthal symmetry. We have thus expressed all the results for disordered systems in terms of the averaged polarization coefficients of the inclusions, the pair distribution of the positions of the inclusions ($K_l^{l_1}$), and the applied field. As in the linear systems,[8] it is the pair distribution ($K_l^{l_1}$) that determines precisely the contribution from each order of the multipole moments.

In general, the interactions among the inclusions, especially the contributions from the multipole moments higher than dipoles, increase with the concentration of the inclusions. This may produce significant corrections to previous results based on single particle, Clausius-Mossotti or dipole approximation. On the other hand, as we have shown, these interactions strongly depend on the form of the pair distribution. We will show in the next section that some of these previous results remain valid in the case of isotropic pair distributions, regardless of the concentration, as long as mean-field theory and the nonoverlapping condition are applicable.

IV. EXPLICIT RESULTS FOR $L = 0, 1$ PAIR DISTRIBUTIONS

For an $L = 1$ pair distribution, only K_1^1 is nonvanishing.[8] In this case, only the dipole moments of the other inclusions and the images contribute. We solve Eq. (18) with $l = 1$, which corresponds to a one-dimensional $\mathcal{G}$ matrix

$$\mathcal{G}_1^1 = G_1^1 = 1 - \left(\frac{4\pi}{3}\right) N(1 + K_1^1)\langle\lambda_{10}^{10}\rangle. \tag{26}$$

Hence, we obtain

$$\left.\frac{\partial\langle q_{10}\rangle}{\partial E_0}\right|_0 = \sqrt{\frac{3}{4\pi}} \frac{\langle\lambda_{10}^{10}\rangle}{1 - \left(\frac{4\pi}{3}\right) N(1 + K_1^1)\langle\lambda_{10}^{10}\rangle}. \tag{27}$$

From Eq. (21c), considering Eqs. (14) and (22), we obtain

$$H_1(3) = \frac{\langle\nu_{10}^{101010}\rangle}{\left[1 - \left(\frac{4\pi}{3}\right) N(1 + K_1^1)\langle\lambda_{10}^{10}\rangle\right]^3}, \tag{28}$$

hence

$$\left.\frac{\partial^3\langle q_{10}\rangle}{\partial E_0^3}\right|_0 = \sqrt{\frac{3}{4\pi}} \frac{\langle\nu_{10}^{101010}\rangle}{\left[1 - \left(\frac{4\pi}{3}\right) N(1 + K_1^1)\langle\lambda_{10}^{10}\rangle\right]^4}. \tag{29}$$

Substituting Eqs. (27) and (29) into Eq. (25), we obtain the effective dielectric function for $L = 1$ pair distributions

$$\frac{\epsilon_e}{\epsilon_m} = \frac{1 + \left(\frac{4\pi}{3}\right) N(2 - K_1^1)\langle\lambda_{10}^{10}\rangle}{1 - \left(\frac{4\pi}{3}\right) N(1 + K_1^1)\langle\lambda_{10}^{10}\rangle} + \frac{1}{2}\left(\frac{4\pi}{3}\right) \times N \frac{\langle\nu_{10}^{101010}\rangle}{\left[1 - \left(\frac{4\pi}{3}\right) N(1 + K_1^1)\langle\lambda_{10}^{10}\rangle\right]^4} E_0^2 + O^*(E_0^4). \tag{30}$$

The linear part has already been obtained.[8] The denominators in Eq. (30) arise from interactions among the inclusions, and depend on their concentration and distribution. It is clear from Eq. (30) that the pair distribution can significantly affect the effective dielectric function, and especially the nonlinear part.

For $L = 0$ (isotropic) pair distributions, all $K_l^{l_1} = 0$. Then,

$$\frac{\epsilon_e}{\epsilon_m} = \frac{1 + \left(\frac{8\pi}{3}\right) N\langle\lambda_{10}^{10}\rangle}{1 - \left(\frac{4\pi}{3}\right) N\langle\lambda_{10}^{10}\rangle} + \frac{1}{2}\left(\frac{4\pi}{3}\right) \times N \frac{\langle\nu_{10}^{101010}\rangle}{\left[1 - \left(\frac{4\pi}{3}\right) N\langle\lambda_{10}^{10}\rangle\right]^4} E_0^2 + O^*(E_0^4). \tag{31}$$

The linear part coincides with the Clausius-Mossotti relation, as previously established.[8]

V. NONLINEAR SPHERICAL INCLUSIONS IN A LINEAR MEDIUM

We have so far obtained the general results for systems with nonlinear inclusions in a linear host medium, and particularly the explicit results for systems with $L = 0, 1$ pair distributions. In order to obtain the results for any specific system, one needs only to find the polarization coefficients $\langle\lambda_{10}^{10}\rangle$ and $\langle\nu_{10}^{101010}\rangle$. We consider as an example a system containing nonlinear spherical inclusions immersed in a linear medium with dielectric function ϵ_m. For simplicity, we assume identical spheres with radius a and a response

$$\mathbf{D} = \epsilon_p \mathbf{E} + \eta_p E^2 \mathbf{E}. \tag{32}$$

We now need to find the dipole moment induced on such an inclusion by a local potential corresponding to a uniform field $\mathbf{E}_{10}$

$$U_{\text{local}}(\mathbf{r}) = -\sqrt{\frac{4\pi}{3}} E_{10} r Y_{1,0}(\mathbf{r}), \tag{33}$$

to the order of E_{10}^3. This boundary value problem has already been solved,[12] whereby

$$q_{10} = \sqrt{\frac{3}{4\pi}} \left(\alpha a^3 E_{10} + \frac{1}{3}\frac{\eta_p}{\epsilon_m}\xi^4 a^3 E_{10}^3 + \cdots\right), \tag{34}$$

with

$$\alpha = \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m}, \quad \xi = \frac{3\epsilon_m}{\epsilon_p + 2\epsilon_m}. \tag{35}$$

Then,

$$\lambda_{10}^{10} = \alpha a^3, \quad \nu_{10}^{101010} = 2\frac{\eta_p}{\epsilon_m}\xi^4 a^3, \tag{36}$$

and

$$\epsilon_e = \epsilon_m \frac{1 + (2 - K_1^1)v\alpha}{1 - (1 + K_1^1)v\alpha} + \frac{v\eta_p\xi^4}{[1 - (1 + K_1^1)v\alpha]^4}E_0^2 + O^*(E_0^4), \tag{37}$$

where $v = (4\pi/3)Na^3$ is the volume fraction of the spheres. Taking $K_1^1 = 0$ in Eq. (37), we obtain the effective dielectric function for spherically symmetric pair distributions:

$$\epsilon_e = \epsilon_m \frac{1 + 2v\alpha}{1 - v\alpha} + \frac{v\eta_p\xi^4}{(1 - v\alpha)^4}E_0^2 + O^*(E_0^4). \tag{38}$$

This agrees with the result previously obtained using the Clausius-Mossotti approximation [see, for example, Eq. (16) of Ref. 6], which is expected: for $L = 0$ pair distributions, the higher multipole moments do not contribute to the effective dielectric function and the Lorentz cavity model is confirmed as in the linear case.[8] At low concentrations, Eq. (38) can be expanded. Retaining only the first order in v, we obtain

$$\epsilon_e \approx \epsilon_m(1 + 3v\alpha) + v\eta_p\xi^4. \tag{39}$$

This agrees with previous results obtained using the single-particle approximation [cf. Eqs. (32) and (38) of Ref. 4(b)].

To estimate the multi-inclusion effect for $L = 1$ or $L = 0$ pair distributions, consider the quantity

$$Q = \frac{\eta_p\xi^4}{[1 - (1 + K_1^1)v\alpha]^4} \equiv \frac{\eta_p\xi^4}{[1 - F\alpha]^4}, \tag{40}$$

which represents the contribution to $\Delta\epsilon_e/E_0^2$ per inclusion. For definiteness, we assume Drude model to describe the linear dielectric function for both the host medium and the inclusions

$$\epsilon = 1 - \frac{\Omega^2}{\omega(\omega + j\gamma)}, \tag{41}$$

where Ω and γ are the plasma frequency and the damping constant, respectively. For $\omega \longrightarrow 0$, Q is real, approaching

$$Q \longrightarrow \frac{3\eta_p\sigma_m^4}{[(1 - F)\sigma_p + (2 + F)\sigma_m]^4}, \tag{42}$$

where $\sigma_{p,m} = \Omega_{p,m}^2/(4\pi\gamma_{p,m})$ are the dc conductivities for the inclusions and the host medium.

Now, the nonoverlapping condition places certain limits to the values of v and K_1^1 allowed, hence to the factor F defined in Eq. (40). Rather than assuming a specific range for v, given K_1^1, or vice versa, we provide here a simple estimate. The close-packed volume fraction for identical spheres is 0.74 and the range for K_1^1 is between -1 and 2 for point particles.[8] Considering the simplest case of a spherically symmetric pair distribution ($K_1^1 = 0$), the volume fraction must be somewhat lower than that. So, we may take $F = v = 0.6$ as a reasonable estimate. However, for anisotropic pair distributions, certain values for v and K_1^1 may not be allowed even when the resulting F may be smaller than 0.6. We also need to point out that for relatively high volume fractions the corrections due to fluctuation effects become more significant. Nevertheless, such corrections are at least one order higher (in the volume fraction) than those obtained here.

We plot Q versus the parameter F for the case $\sigma_p/\sigma_m = 1000$ in Fig. 1, and for the case $\sigma_m/\sigma_p = 1000$ in Fig. 2. In both cases, Q strongly depends on F. In the first case Q increases with F, but its overall value is small, while in the second case Q decreases with F, and its overall value is large. This is easily understood. For $\sigma_p \gg \sigma_m$, each inclusion already has a large induced dipole moment parallel to $\mathbf{E}_0$ due to the linear response

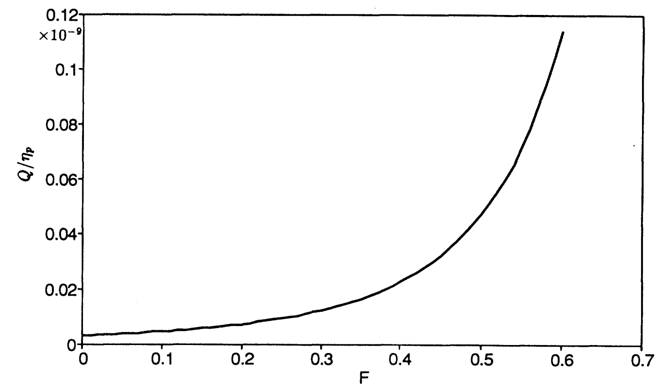

FIG. 1. Q/η_p vs F at $\omega = 0$ for $\sigma_p/\sigma_m = 1000$.

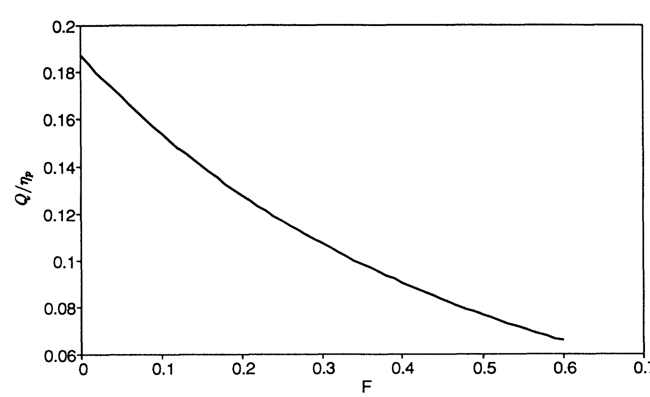

FIG. 2. Q/η_p vs F at $\omega = 0$ for $\sigma_m/\sigma_p = 1000$.

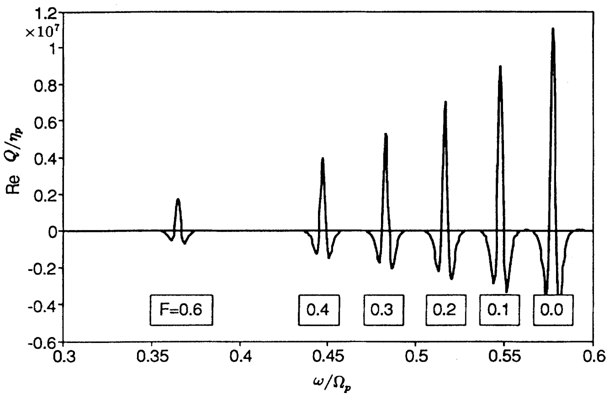

FIG. 3. Real part of Q/η_p vs ω/Ω_p, for $\Omega_p = 8.65 \times 10^{15}$ sec^{-1}, $\gamma_p = 0.01\Omega_p$, and $\epsilon_m = 1$.

of the inclusion: this dipole moment tends to increase the field inside other inclusions, hence the multi-inclusion effect is constructive; however, this large dipole moment reduces significantly the field inside the inclusion itself, hence the overall nonlinear response is small. The other case is just the opposite. Another simple situation occurs when both the medium and the inclusions are nonconducting. The response of the inclusions becomes frequency independent, and σ_m and σ_p in Eq. (42) are simply replaced by ϵ_m and ϵ_p, respectively.

We also compute the spectrum of Q and plot it in Figs. 3 and 4, using sodium data for the linear response of the inclusions ($\Omega_p = 8.65 \times 10^{15}$ sec^{-1} and $\gamma_p = 0.01\Omega_p$) and assuming the host medium is the vacuum. We see for this particular case that the interactions among the inclusions tend to reduce the nonlinear response of the system. The reason is that the resonance peaks of the factors $1/(1-F\alpha)$ and $1/(1-F\alpha)^4$ increase with F, but also are shifted away from the linear resonance (represented by α) and the nonlinear resonance (represented by ξ^4) of an isolated sphere (both α and ξ^4 have their resonance peak at about $0.577\omega_p$), towards the low frequency end. Since

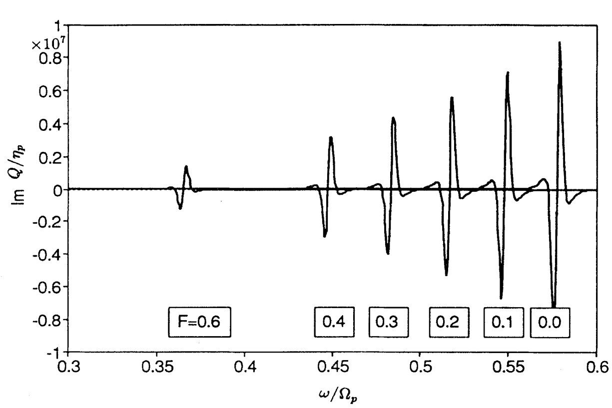

FIG. 4. Imaginary part of Q/η_p vs ω/Ω_p, $\Omega_p = 8.65 \times 10^{15}$ sec^{-1}, $\gamma_p = 0.01\Omega_p$, and $\epsilon_m = 1$.

both $1/(1-F\alpha)$ and α have a relatively wide resonance peak, the linear part of ϵ_e is still enhanced effectively when F increases. But both $1/(1-F\alpha)^4$ and ξ^4 have a much narrower resonance peak, hence the nonlinear part of ϵ_e is actually reduced when F increases. However, this result may not be general: in other systems the opposite situation may occur and Q may increase with F.

VI. CONCLUSIONS

We have obtained analytical results for the electrical response of nonlinear inclusions in a linear medium. The introduction of linear and nonlinear polarization coefficients of the inclusions enables us to retain the multipole moments of the inclusions and their images to all orders, making our results applicable to systems with inclusions of arbitrary structure and response. The results for ordered systems (Sec. II) are exact to first order in the nonlinear response. For inclusions with stronger nonlinearity, higher terms may be required and obtained similarly.

We have then obtained the mean-field results for disordered systems. The pair distribution plays a crucial role, determining how each order of the multipole moments contribute. We have provided explicit results for $L = 1$ and $L = 0$ pair distributions, where only the dipole moments contribute. We have found significant effects on the nonlinear response, depending on the concentration and distribution of the inclusions, due to the interactions among the inclusions.

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APPENDIX

Here, we prove Eq. (14). Let us imagine that there is a set of inclusions, each of them with reflection symmetry $z \longrightarrow -z$, but otherwise arbitrary (an easy way to envision that is to consider an arbitrary inclusion and its reflection image as a whole). We can further assume that these inclusions yield exactly the same average polarization coefficients as those in a real system with macroscopic reflection symmetry.

Apply the "mirror" potential of Eq. (1) to any given inclusion (assumed at the origin)

$$\bar{U}_{\text{local}}(\mathbf{r}) = U_{\text{local}}(\bar{\mathbf{r}}) = -\sqrt{\frac{4\pi}{3}} \sum_{l_1 m_1} E_{l_1 m_1} \bar{r}^{l_1} Y_{l_1, m_1}(\bar{\mathbf{r}})$$

$$= -\sqrt{\frac{4\pi}{3}} \sum_{l_1 m_1} (-1)^{l_1 + m_1} E_{l_1 m_1} r^{l_1} Y_{l_1, m_1}(\mathbf{r}), \tag{A1}$$

where $\bar{\mathbf{r}} = (x, y, -z)$ is the mirror image of $\mathbf{r}$. Since the inclusion has reflection symmetry, we have for the induced charge distribution

$$\bar{\rho}(\mathbf{r}) = \rho(\bar{\mathbf{r}}), \tag{A2}$$

where $\rho(\mathbf{r})$ is the charge distribution for the same inclusion under the local potential (1). Equation (A2) leads to

$$\bar{q}_{lm} = (-1)^{l+m} q_{lm}. \tag{A3}$$

Then, from the definition of the polarization coefficients, we have

$$\bar{q}_{lm} = \sqrt{\frac{3}{4\pi}} \left[\sum_{l_1 m_1} (-1)^{l_1+m_1} \lambda_{lm}^{l_1 m_1} E_{l_1 m_1} + \frac{1}{2!} \sum_{l_1 m_1 l_2 m_2} (-1)^{l_1+m_1+l_2+m_2} \mu_{lm}^{l_1 m_1 l_2 m_2} E_{l_1 m_1} E_{l_2 m_2} + \frac{1}{3!} \sum_{l_1 m_1 l_2 m_2 l_3 m_3} (-1)^{l_1+m_1+l_2+m_2+l_3+m_3} \nu_{lm}^{l_1 m_1 l_2 m_2 l_3 m_3} E_{l_1 m_1} E_{l_2 m_2} E_{l_3 m_3} + \cdots \right]. \tag{A4}$$

Substituting Eq. (A3) into Eq. (A4) and comparing the result with Eq. (2), we obtain

$$\begin{aligned} \lambda_{lm}^{l_1 m_1} &= (-1)^{l+m+l_1+m_1} \lambda_{lm}^{l_1 m_1}, \\ \mu_{lm}^{l_1 m_1 l_2 m_2} &= (-1)^{l+m+l_1+m_1+l_2+m_2} \mu_{lm}^{l_1 m_1 l_2 m_2}, \\ \nu_{lm}^{l_1 m_1 l_2 m_2 l_3 m_3} &= (-1)^{l+m+l_1+m_1+l_2+m_2+l_3+m_3} \nu_{lm}^{l_1 m_1 l_2 m_2 l_3 m_3}, \end{aligned} \tag{A5}$$

etc. Averaging these equations over all the inclusions, we obtain Eq. (14).

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