Electrical response of heterogeneous systems containing inclusions with permanent multipoles

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We provide the electrostatic solution in mean field theory to the electrical response of heterogeneous systems in which the inclusions have arbitrary structure and permanent multipole moments of all orders. The system is placed between two parallel electrode plates, and all the resulting multipole moments of the inclusions and their images are taken into account. By performing a statistical average over the orientations of the inclusions, we obtain the effective dielectric function, depending on temperature and applied potential at the electrode plates.

I. INTRODUCTION

The study of the electrical response of heterogeneous systems has played a substantial role in the development of modern physics, and it encompasses to this day a vast area with ramifications and applications in many fields. From the theoretical point of view, the complexity of the problem is inherent with its many-body structure. This has basically two aspects: one is the arrangement or the statistical distribution of the constituents, while the other is their detailed electrical interactions. Generally, the two are intertwined and influence each other.

The statistical aspect can be rigorously formulated to various orders of approximation, in terms of successive n-particle distribution functions.[1,2] We consider the so-called mean field theory (MFT), which involves only two-particle distributions. Its precise definition consists in replacing all the multipole moments of the inclusions surrounding a given one by their thermal averages, see Eq. (9) in the following. We have recently obtained solutions to all multipole orders of the electrical problem within MFT for heterogeneous systems without permanent multipole moments.[3–5] This has shown the crucial role played by nonspherical two-particle distributions and its precise connection to various orders of multipolar interactions. Previously, spherical distributions have often been implicitly assumed, although anisotropic distributions have been considered in applied fields that inherently deal with anisotropic systems, such as electrorheology[6] or ferrofluids.[7]

We have now succeeded in extending our first-principles MFT solution to the case where the inclusions have arbitrary structure and carry permanent multipole moments of arbitrary order, and in solving self-consistently the problem of the electrostatic interactions with that of the statistical distribution of the inclusion orientations. In this situation, the total multipole moments of the inclusions depend on both their permanent multipole moments and the polarization coefficients which describe their response to the local field.[5] Since the inclusions change their orientations (and distribution) under the influence of the applied field, the response of the system is inherently nonlinear, and the permanent multipole moments and the polarization coefficients contribute to both the linear and the nonlinear part of the effective dielectric function. With a nonlinear response, the choice of configuration that we have consistently made, namely that of a slab-shaped sample placed between two parallel electrode plates, has a decisive advantage, because the knowledge of the absolute value of the electric field inside the system is required. Previous theories have considered only the linear response and included only dipole moments (permanent and induced). We provide the effective dielectric function up to the first nonlinear order (higher orders can be obtained with the same procedure) and find again that the pair distribution of the inclusions determines the contribution from each order of the (permanent and induced) multipole moments. We present these results in this paper.

The results of this paper are quite general. They can be applied to systems containing inclusions of arbitrary structure and arbitrary order of permanent multipole moments. These may include composites where the inclusions are small particles yet containing many atoms or molecules, liquid crystals where the inclusions are large polar molecules or complexes, down to the systems where the inclusions are simple molecules. However, our results apply with precise restrictions. First, only electric classical interactions are considered (plus whatever core repulsions are inherently included in the distributions). Second, the inclusion volume fraction must be low enough to satisfy a nonoverlapping condition, namely that each inclusion is surrounded by a minimal sphere excluding any part of other inclusions (this equally applies to theories and computer simulations based on multipole expansion). Third, the inclusion volume fraction must be low enough to justify MFT. The last point is invariably hard to assess *a priori* for any particular system. Anyway, the knowledge of the rigorous MFT solution is always valuable in determining to what degree the experimental data reflect fluctuation effects, and in providing a reference or starting point for theoretical estimates of such effects.

The determination of the pair distribution may require

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a combination of experimental analysis and theoretical modeling.[2,6,7] The permanent multipole moments and the polarization coefficients of the inclusions must also be measured or calculated. With these input values, the application of the results derived in this paper is straightforward. In a following paper,[8] we apply our results to $L = 0$ and 1 pair distributions. In these cases, the multipole moments higher than dipoles have no contribution (within MFT). That allows us to compare our results with the macroscopic models of Debye and Onsager.

The rest of the paper is structured as follows. We first establish in Sec. II the equations for the total multipole moments of the inclusions, the interaction energy between an inclusion and the local field acting on it, and the effective dielectric function, in MFT. We then perform in Sec. III a thermal average over the orientations of the inclusions, including the interactions among all multipole moments. We thus obtain the effective dielectric function to the first nonlinear order, in terms of the polarization coefficients and the permanent multipole moments of the inclusions, the parameters describing the pair distribution, the temperature, and the applied potential at the electrode plates. We provide in Sec. IV the results for some particular systems, namely spherical inclusions, nonpolarizable inclusions, and polarizable inclusions without permanent multipole moments. All orders of multipole moments for all inclusions and their images are retained throughout. In Sec. V we draw our conclusions.

II. ELECTROSTATIC SOLUTION IN MEAN FIELD THEORY

Consider a heterogeneous system in which the inclusions have arbitrary structures and permanent multipole moments of arbitrary orders, defined as those of an inclusion when isolated. The system is placed between two parallel electrode plates at a distance d and subject to an alternating potential $V_0 e^{-j\omega t}$. We assume that the frequency is low enough that the system can be solved electrostatically. Let us denote by $\mathbf{r}_n$, $q^{(p)}_{nlm}$, and $\lambda^{l_1 m_1}_{nlm}$ the position, the permanent multipole moments, and the polarization coefficients[5] of the nth inclusion. We assume that the inclusions do not overlap, meaning that the minimum sphere circumscribing any given inclusion excludes any part of other inclusions. Then, the local potential acting on the nth inclusion can be written as [cf. Eq. (6) of Ref. 5]

$$U_{\text{local}}(\mathbf{r}) = (V_0/2 - \mathbf{E}_0 \cdot \mathbf{r}_n) - \sqrt{\frac{4\pi}{3}} E_0 |\mathbf{r} - \mathbf{r}_n| Y_{1,0}(\mathbf{r} - \mathbf{r}_n) + 4\pi \sum_{lm} \sum_{n_1 l_1 m_1} C^{l_1,m_1}_{l,m}(\mathbf{r}_{n_1} - \mathbf{r}_n) q_{n_1 l_1 m_1} |\mathbf{r} - \mathbf{r}_n|^l Y_{l,m}(\mathbf{r} - \mathbf{r}_n), \tag{1}$$

where $\mathbf{E}_0 = (V_0/d)\mathbf{e}_z$ is the applied field and the coefficients $C^{l_1,m_1}_{l,m}(\mathbf{r}_{n_1} - \mathbf{r}_n)$ are defined in Eq. (14) of Ref. 3. The total multipole moments of the nth inclusion q_{nlm} are simply the induced multipole moments, which are given by Eq. (7) of Ref. 5, plus its permanent multipole moments:

$$q_{nlm} = \sqrt{\frac{3}{4\pi}} \lambda^{10}_{nlm} E_0 - 3 \sum_{n_1 l_1 m_1} \sum_{l_2 m_2} \lambda^{l_2 m_2}_{nlm} C^{l_1,m_1}_{l_2,m_2}(\mathbf{r}_{n_1} - \mathbf{r}_n) q_{n_1 l_1 m_1} + q^{(p)}_{nlm}. \tag{2}$$

The permanent multipole moments $q^{(p)}_{nlm}$ and the polarization coefficients $\lambda^{l_1 m_1}_{nlm}$ depend on the orientation of the inclusion and have the rotational properties [cf. Eqs. (A13) and (A15) of Ref. 5]:

$$q^{(p)}_{lm}(\tau) = \sum_{m_1} \mathcal{D}^{lm_1 *}_{lm} q^{(p)}_{lm_1} \tag{3}$$

and

$$\lambda^{l_1 m_1}_{lm}(\tau)^* = \sum_{m_2 m_3} (\mathcal{D}^{-1})^{lm_2}_{lm} \lambda^{l_1 m_3 *}_{lm_2} \mathcal{D}^{l_1 m_1}_{l_1 m_3}. \tag{4}$$

In Eqs. (3) and (4), $\tau = (\alpha, \beta, \gamma)$ denotes the Euler angles of the rotation relative to the original orientation of the inclusion, with permanent multipole moments $q^{(p)}_{lm}$ and polarization coefficients $\lambda^{l_1 m_1}_{nlm}$. In particular[9]

$$D^{lm}_{l0}(\alpha,\beta,\gamma) = \sqrt{\frac{4\pi}{2l+1}} Y^*_{l,m}(\beta,\alpha),$$

$$D^{l0}_{lm}(\alpha,\beta,\gamma) = D^{lm}_{l0}(\gamma,\beta,\alpha) = \sqrt{\frac{4\pi}{2l+1}} Y^*_{l,m}(\beta,\gamma). \tag{5}$$

Hence,

$$q^{(p)}_{l0}(\tau) = \sqrt{\frac{4\pi}{2l+1}} \sum_m Y^*_{l,m}(\beta,\alpha) q^{(p)}_{lm} \tag{6}$$

and

$$\lambda^{l_1 0}_{l0}(\tau) = \frac{4\pi}{\sqrt{(2l+1)(2l_1+1)}} \sum_{mm_1} Y^*_{l,m}(\beta,\gamma) \lambda^{l_1 m_1}_{lm} Y_{l_1,m_1}(\beta,\gamma). \tag{7}$$

The electrostatical interaction energy between the nth inclusion and the local field is

$$w_n = \int \rho_n(\mathbf{r}) U_{\text{local}}(\mathbf{r}) d^3\mathbf{r}$$
$$= -\sqrt{\frac{4\pi}{3}} q_{n10} E_0 + 4\pi \sum_{lm} \sum_{n_1 l_1 m_1} q^*_{nlm} C^{l_1,m_1}_{l,m}(\mathbf{r}_{n_1} - \mathbf{r}_n) q_{n_1 l_1 m_1}, \quad (8)$$

where $\rho_n(\mathbf{r})$ is the total charge density on the nth inclusion. On the right-hand side of Eq. (8), the first term represents the electrical interaction between the nth inclusion and the applied field, while the rest represents the interactions between the nth inclusion and the other inclusions and all the images.

The results so far are exact, and can be applied to systems where the positions and orientations of the inclusions are known; for example, they can be used in molecular dynamics simulations. In the following, we concentrate on disordered systems treated statistically, and focus on orientation effects. Namely, we assume that the positions or the distribution of the inclusions do not vary with the applied field. For simplicity, we consider a single species system, in which all the inclusions are identical and distinguished only by their orientations.

The mean field approximation consists in replacing $q_{n_1 l_1 m_1}$ on the right-hand side of Eq. (2) by the averaged multipole moments $\langle q_{lm}(E_0)\rangle$. Averaging over the inclusions with same orientation, we obtain

$$q_{lm}(\tau, E_0) = \sqrt{\frac{3}{4\pi}} \lambda^{10}_{lm}(\tau) E_0 - 3 \sum_{l_1 m_1} \sum_{l_2 m_2} \lambda^{l_2 m_2}_{lm}(\tau) \left[\sum_{n_1} C^{l_1,m_1}_{l_2,m_2}(\mathbf{r}_{n_1} - \mathbf{r}_n)\right] \langle q_{l_1 m_1}(E_0)\rangle + q^{(p)}_{lm}(\tau). \quad (9)$$

The summation over n_1 in the bracket is now independent of $\mathbf{r}_n$. Similarly, we obtain the interaction energy for the inclusions with orientation τ

$$w(\tau, E_0) = -\sqrt{\frac{4\pi}{3}} q_{10}(\tau, E_0) E_0 + 4\pi \sum_{lm} \sum_{n_1 l_1 m_1} q^*_{lm}(\tau, E_0) C^{l_1,m_1}_{l,m}(\mathbf{r}_{n_1} - \mathbf{r}_n) \langle q_{l_1 m_1}(E_0)\rangle. \quad (10)$$

Finally, ensemble averaging over τ in Eq. (9), we obtain

$$\langle q_{lm}(E_0)\rangle = \sqrt{\frac{3}{4\pi}} \langle \lambda^{10}_{lm}(E_0)\rangle E_0 - 3 \sum_{l_1 m_1} \sum_{l_2 m_2} \langle \lambda^{l_2 m_2}_{nlm}(E_0)\rangle \left[\sum_{n_1} C^{l_1,m_1}_{l_2,m_2}(\mathbf{r}_{n_1} - \mathbf{r}_n)\right] \langle q_{l_1 m_1}(E_0)\rangle + \langle q^{(p)}_{lm}(E_0)\rangle. \quad (11)$$

The longitudinal effective dielectric function is

$$\epsilon_{ezz} = 1 + 4\pi N \sqrt{\frac{4\pi}{3}} \left.\frac{\partial \langle q_{10}(E_0)\rangle}{\partial E_0}\right|_0 + 4\pi N \sqrt{\frac{4\pi}{3}} \frac{1}{3!} \left.\frac{\partial^3 \langle q_{10}(E_0)\rangle}{\partial E_0^3}\right|_0 E_0^2 + O^*(E_0^4), \quad (12)$$

where $|_0$ denotes the corresponding quantity evaluated at $E_0 = 0$, and N is the average number density of the inclusions. We assume that the system has a macroscopic reflection symmetry on $z \longrightarrow -z$. In Appendix A we show that this leads to

$$\langle q_{lm}(-E_0)\rangle = (-1)^{l+m} \langle q_{lm}(E_0)\rangle,$$
$$\langle \lambda^{l_1 m_1}_{lm}(-E_0)\rangle = (-1)^{l+m+l_1+m_1} \langle \lambda^{l_1 m_1}_{nlm}(E_0)\rangle. \quad (13)$$

As a consequence, all the even order derivatives in Eq. (12) vanish.

Equations (9)–(11) are still expressed in terms of the positions of the inclusions, while disordered systems are described by the distribution of the inclusions. Given a positional pair distribution with azimuthal symmetry, we have previously obtained [cf. Eq. (A17) of Ref. 3]

$$\sum_{n_1} C^{l_1,m_1}_{l_2,m_2}(\mathbf{r}_{n_1} - \mathbf{r}_n) = -\frac{4\pi}{9}(\delta^1_{l_2}\delta^{l_1}_1 + K^{l_1}_{l_2})\delta^{m_1}_{m_2}, \quad (14)$$

where $K^{l_1}_{l_2}$ are the parameters describing the position distribution of the inclusions, as defined in Eq. (21) of Ref. 5. We then obtain

$$q_{l0}(\tau, E_0) - \left(\frac{4\pi}{3}\right) N \sum_{l_1} \lambda^{l_1 0}_{l0}(\tau)(Kq)_{l_1}$$
$$= \sqrt{\frac{3}{4\pi}} \lambda^{10}_{l0}(\tau) E_0 + q^{(p)}_{l0}(\tau), \quad (15)$$

$$w(\tau, E_0) = -\sqrt{\frac{4\pi}{3}} q_{10}(\tau, E_0) E_0$$
$$- \left(\frac{4\pi}{3}\right)^2 N \sum_l q_{l0}(\tau, E_0)(Kq)_l, \quad (16)$$

and

$$\langle q_{l0}(E_0)\rangle - \left(\frac{4\pi}{3}\right) N \sum_{l_1} \langle \lambda_{l0}^{l_1 0}(E_0)\rangle (Kq)_{l_1} = \sqrt{\frac{3}{4\pi}} \langle \lambda_{l0}^{10}(E_0)\rangle E_0 + \langle q_{l0}^{(p)}(E_0)\rangle. \quad (17)$$

In Eqs. (15)–(17), we have used the short notation

$$(Kq)_l = \sum_{l_1} (\delta_l^1 \delta_1^{l_1} + K_l^{l_1}) \langle q_{l_1 0}(E_0)\rangle. \quad (18)$$

Due to the macroscopic azimuthal symmetry, $\langle q_{lm}(E_0)\rangle = 0$ for $m \neq 0$, and the applied field (in the z direction) excites only the longitudinal response (12).

III. ENSEMBLE AVERAGE OVER ORIENTATIONS

We assume that the electrical interactions and the thermal fluctuations are the only effects acting on the system. The electrical interactions tend to align the inclusions as to minimize the total energy, while the thermal motion tends to make them randomly oriented. We assume in equilibrium the Boltzmann distribution for orientations

$$N(\tau, E_0) \propto e^{-w(\tau,E_0)/(kT)}. \quad (19)$$

Substituting Eq. (15) into Eq. (16), we obtain

$$w(\tau, E_0) = -\sqrt{\frac{4\pi}{3}} q_{10}^{(p)}(\tau) E_0 - \left(\frac{4\pi}{3}\right)^2 N \sum_l q_{l0}^{(p)}(\tau)(Kq)_l - \lambda_{10}^{10}(\tau) E_0^2 - \left(\frac{4\pi}{3}\right)^{3/2} N \sum_l [\lambda_{10}^{l0}(\tau) + \lambda_{l0}^{10}(\tau)](Kq)_l E_0 - \left(\frac{4\pi}{3}\right)^3 N^2 \sum_{ll_1} \lambda_{l0}^{l_1 0}(\tau)(Kq)_l (Kq)_{l_1}. \quad (20)$$

Equation (17) is now closed by

$$\langle \lambda_{l0}^{l_1 0}(E_0)\rangle = \frac{\int \lambda_{l0}^{l_1 0}(\tau) e^{-w(\tau,E_0)/(kT)} d\tau}{\int e^{-w(\tau,E_0)/(kT)} d\tau} \quad (21)$$

and

$$\langle q_{l0}^{(p)}(E_0)\rangle = \frac{\int q_{l0}^{(p)}(\tau) e^{-w(\tau,E_0)/(kT)} d\tau}{\int e^{-w(\tau,E_0)/(kT)} d\tau}, \quad (22)$$

where $d\tau = \sin\beta d\beta d\alpha d\gamma$. Equations (17) and (20)–(22) determine $\langle q_{l0}(E_0)\rangle$ implicitly as functions of E_0. However, $\langle q_{l0}(E_0)\rangle$ cannot be solved in closed form. On the other hand, it is possible to obtain the derivatives of $\langle q_{l0}(E_0)\rangle$ at $E_0 = 0$, hence the effective dielectric function (12), as follows.

Using Eqs. (6) and (7), we obtain

$$\int \lambda_{l0}^{l_1 0}(\tau) d\tau = 8\pi^2 \Gamma_l \delta_l^{l_1},$$

$$\int q_{l0}^{(p)}(\tau) d\tau = 0,$$

$$\int \lambda_{l0}^{l_1 0}(\tau) \lambda_{l_2 0}^{l_3 0}(\tau) d\tau = 8\pi^2 \eta_{ll_2}^{l_1 l_3},$$

$$\int \lambda_{l0}^{l_1 0}(\tau) q_{l_2 0}^{(p)}(\tau) d\tau = 4\pi^2 \sqrt{\frac{3}{4\pi}} \xi_{ll_2}^{l_1},$$

$$\int q_{l0}^{(p)}(\tau) q_{l_1 0}^{(p)}(\tau) d\tau = 2\pi \mu_l \delta_l^{l_1},$$

$$\int \lambda_{l0}^{l_1 0}(\tau) q_{l_2 0}^{(p)}(\tau) q_{l_3 0}^{(p)}(\tau) d\tau = 2\pi \beta_{ll_2 l_3}^{l_1},$$

$$\int q_{l0}^{(p)}(\tau) q_{l_1 0}^{(p)}(\tau) q_{l_2 0}^{(p)}(\tau) d\tau = 2\pi \sqrt{\frac{3}{4\pi}} \nu_{ll_1 l_2},$$

$$\int q_{l0}^{(p)}(\tau) q_{l_1 0}^{(p)}(\tau) q_{l_2 0}^{(p)}(\tau) q_{l_3 0}^{(p)}(\tau) d\tau = \kappa_{ll_1 l_2 l_3}, \quad (23)$$

where the integrals have been carried out in Appendix B. These results are used in the subsequent derivation.

Taking $E_0 = 0$ in Eq. (17), we have

$$\langle q_{l0}(E_0)\rangle|_0 - \left(\frac{4\pi}{3}\right) \sum_{l_1} \langle \lambda_{l0}^{l_1 0}(E_0)\rangle|_0 (Kq|_0)_{l_1} = \langle q_{l0}^{(p)}(E_0)\rangle|_0. \quad (24)$$

It is easy to verify that

$$\langle q_{l0}(E_0)\rangle|_0 = 0 \quad \text{for all } l \quad (25)$$

is a solution to Eq. (24): the left-hand side of Eq. (24) vanishes, and [from Eq. (20)]

$$w(\tau, E_0)|_0 = 0, \quad (26)$$

hence [from Eq. (23)]

$$\langle q_{l0}^{(p)}(E_0)\rangle|_0 = \frac{1}{8\pi^2} \int q_{l0}^{(p)}(\tau) d\tau = 0. \quad (27)$$

Equation (25) represents the situation when there is no spontaneous polarization. We assume that to be the case in this paper.

Using Eq. (26), we obtain the following results:

$$\left.\frac{\partial}{\partial E_0} e^{-w(\tau,E_0)/(kT)}\right|_0 = \frac{1}{kT}\left[\sqrt{\frac{4\pi}{3}}\, q_{10}^{(p)}(\tau) + \left(\frac{4\pi}{3}\right)^2 N \sum_l q_{l0}^{(p)}(\tau)\left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_l\right], \tag{28a}$$

$$\begin{aligned}\left.\frac{\partial^2}{\partial E_0^2} e^{-w(\tau,E_0)/(kT)}\right|_0 = {} & \frac{1}{kT}\left(\frac{4\pi}{3}\right)^2 N \sum_l q_{l0}^{(p)}(\tau)\left(K \left.\frac{\partial^2 q}{\partial E_0^2}\right|_0\right)_l + \frac{1}{kT}\left[2\lambda_{10}^{10}(\tau) + \frac{1}{kT}\left(\frac{4\pi}{3}\right) q_{10}^{(p)}(\tau) q_{10}^{(p)}(\tau)\right] \\ & + \frac{2}{kT}\left(\frac{4\pi}{3}\right)^{3/2} N \sum_l \left[\lambda_{10}^{l0}(\tau) + \lambda_{l0}^{10}(\tau) + \frac{1}{kT}\left(\frac{4\pi}{3}\right) q_{l0}^{(p)}(\tau) q_{10}^{(p)}(\tau)\right]\left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_l \\ & + \frac{1}{kT}\left(\frac{4\pi}{3}\right)^3 N^2 \sum_{ll_1}\left[2\lambda_{l0}^{l_10}(\tau) + \frac{1}{kT}\left(\frac{4\pi}{3}\right) q_{l0}^{(p)}(\tau) q_{l_10}^{(p)}(\tau)\right]\left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_l \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1}, \end{aligned} \tag{28b}$$

$$\begin{aligned}\left.\frac{\partial^3}{\partial E_0^3} e^{-w(\tau,E_0)/(kT)}\right|_0 = {} & \frac{1}{(kT)^2}\sqrt{\frac{4\pi}{3}}\left[6\lambda_{10}^{10}(\tau) q_{10}^{(p)}(\tau) + \frac{1}{kT}\left(\frac{4\pi}{3}\right) q_{10}^{(p)}(\tau) q_{10}^{(p)}(\tau) q_{10}^{(p)}(\tau)\right] \\ & + \frac{3}{(kT)^2}\left(\frac{4\pi}{3}\right)^2 N \sum_l \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_l \\ & \times\left[2\lambda_{10}^{l0}(\tau) q_{10}^{(p)}(\tau) + 2\lambda_{l0}^{10}(\tau) q_{10}^{(p)}(\tau) + 2\lambda_{10}^{10}(\tau) q_{l0}^{(p)}(\tau) + \frac{1}{kT}\left(\frac{4\pi}{3}\right) q_{l0}^{(p)}(\tau) q_{10}^{(p)}(\tau) q_{10}^{(p)}(\tau)\right] \\ & + \frac{3}{(kT)^2}\left(\frac{4\pi}{3}\right)^{7/2} N^2 \sum_{ll_1}\left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_l \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1} \\ & \times\left[2\lambda_{10}^{l0}(\tau) q_{l_10}^{(p)}(\tau) + 2\lambda_{l0}^{10}(\tau) q_{l_10}^{(p)}(\tau) + 2\lambda_{l0}^{l_10}(\tau) q_{10}^{(p)}(\tau) + \frac{1}{kT}\left(\frac{4\pi}{3}\right) q_{l0}^{(p)}(\tau) q_{l_10}^{(p)}(\tau) q_{10}^{(p)}(\tau)\right] \\ & + \frac{3}{kT}\left(\frac{4\pi}{3}\right)^{3/2} N \sum_l \left[\lambda_{10}^{l0}(\tau) + \lambda_{l0}^{10}(\tau) + \frac{1}{kT}\left(\frac{4\pi}{3}\right) q_{l0}^{(p)}(\tau) q_{10}^{(p)}(\tau)\right]\left(K \left.\frac{\partial^2 q}{\partial E_0^2}\right|_0\right)_l \\ & + \frac{3}{kT}\left(\frac{4\pi}{3}\right)^3 N^2 \sum_{ll_1}\left[\lambda_{l0}^{l_10}(\tau) + \lambda_{l_10}^{l0}(\tau) + \frac{1}{kT}\left(\frac{4\pi}{3}\right) q_{l0}^{(p)}(\tau) q_{l_10}^{(p)}(\tau)\right] \\ & \times\left(K \left.\frac{\partial^2 q}{\partial E_0^2}\right|_0\right)_l \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1} \\ & + \frac{1}{(kT)^2}\left(\frac{4\pi}{3}\right)^5 N^3 \sum_{ll_1l_2}\left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_l \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} \\ & \times\left[6\lambda_{l0}^{l_10}(\tau) q_{l_20}^{(p)}(\tau) + \frac{1}{kT}\left(\frac{4\pi}{3}\right) q_{l0}^{(p)}(\tau) q_{l_10}^{(p)}(\tau) q_{l_20}^{(p)}(\tau)\right] \\ & + \frac{1}{kT}\left(\frac{4\pi}{3}\right)^2 N \sum_l q_{l0}^{(p)}(\tau)\left(K \left.\frac{\partial^3 q}{\partial E_0^3}\right|_0\right)_l, \end{aligned} \tag{28c}$$

and so on. From Eq. (28a), we immediately obtain

$$\int \left.\frac{\partial}{\partial E_0} e^{-w(\tau,E_0)/(kT)}\right|_0 d\tau = 0. \tag{29}$$

Equations (28) and (29) will be needed in the subsequent derivation.

Taking the first-order derivative of Eq. (17), we have

$$\left.\frac{\partial\langle q_{10}(E_0)\rangle}{\partial E_0}\right|_0 - \left(\frac{4\pi}{3}\right) N \sum_{l_1}\langle\lambda_{l0}^{l_10}(E_0)\rangle|_0\left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1} = \sqrt{\frac{3}{4\pi}}\langle\lambda_{l0}^{10}(E_0)\rangle|_0 + \left.\frac{\partial\langle q_{l0}^{(p)}(E_0)\rangle}{\partial E_0}\right|_0, \tag{30}$$

where $(K\partial^k q/\partial E_0^k|_0)_l$ are defined similarly to Eq. (18). Using Eqs. (21), (23), and (26) we obtain

$$\langle\lambda_{l0}^{l_10}(E_0)\rangle|_0 = \frac{1}{8\pi^2}\int \lambda_{l0}^{l_10}(\tau)d\tau = \Gamma_l\delta_l^{l_1}. \tag{31}$$

Using Eqs. (22), (23), (28a), and (29), we obtain

$$\begin{aligned}\left.\frac{\partial\langle q_{l0}^{(p)}(E_0)\rangle}{\partial E_0}\right|_0 & = \frac{1}{8\pi^2}\int q_{l0}^{(p)}(\tau)\left.\frac{\partial}{\partial E_0} e^{-w(\tau,E_0)/(kT)}\right|_0 d\tau \\ & = \sqrt{\frac{3}{4\pi}}\frac{\mu_1}{3kT}\delta_l^1 + \frac{\mu_l}{3kT}\left(\frac{4\pi}{3}\right) N\left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_l. \end{aligned} \tag{32}$$

Substituting Eqs. (31) and (32) into Eq. (30), we obtain

$$\sum_{l_1} G_l^{l_1} \left.\frac{\partial\langle q_{l_1 0}(E_0)\rangle}{\partial E_0}\right|_0 = \sqrt{\frac{3}{4\pi}} H_l(1), \tag{33}$$

where the system configuration matrix is defined as

$$G_l^{l_1} = \delta_l^{l_1} - \left(\frac{4\pi}{3}\right) N(\delta_l^1 \delta_1^{l_1} + K_l^{l_1})\Delta_l(1), \tag{34}$$

with

$$\Delta_l(1) = \Gamma_l + \frac{\mu_l}{3kT} \tag{35}$$

and

$$H_l(1) = \Delta_1(1)\delta_l^1. \tag{36}$$

Equation (33) has solution

$$\left.\frac{\partial\langle q_{l0}(E_0)\rangle}{\partial E_0}\right|_0 = \sqrt{\frac{3}{4\pi}} \sum_{l_1} (G^{-1})_l^{l_1} H_{l_1} = \sqrt{\frac{3}{4\pi}} (G^{-1})_l^1 \Delta_1(1). \tag{37}$$

Taking the second-order derivative in Eq. (17), we obtain

$$\left.\frac{\partial^2\langle q_{l0}(E_0)\rangle}{\partial E_0^2}\right|_0 - \left(\frac{4\pi}{3}\right) N \sum_{l_1} \langle \lambda_{l0}^{l_1 0}(E_0)\rangle|_0 \left(K \left.\frac{\partial^2 q}{\partial E_0^2}\right|_0\right)_{l_1} - 2\left(\frac{4\pi}{3}\right) N \sum_{l_1} \left.\frac{\partial\langle \lambda_{l0}^{l_1 0}(E_0)\rangle}{\partial E_0}\right|_0 \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1}$$

$$= 2\sqrt{\frac{3}{4\pi}} \left.\frac{\partial\langle \lambda_{l0}^{10}(E_0)\rangle}{\partial E_0}\right|_0 + \left.\frac{\partial^2\langle q_{l0}^{(p)}(E_0)\rangle}{\partial E_0^2}\right|_0. \tag{38}$$

Using Eqs. (21), (23), (28a) and (29), we obtain

$$\left.\frac{\partial\langle \lambda_{l0}^{l_1 0}(E_0)\rangle}{\partial E_0}\right|_0 = \frac{1}{8\pi^2} \int \lambda_{l0}^{l_1 0}(\tau) \left.\frac{\partial}{\partial E_0} e^{-w(\tau,E_0)/(kT)}\right|_0 d\tau$$
$$= \frac{1}{2kT} \xi_{l1}^{l_1} + \frac{1}{2kT} \left(\frac{4\pi}{3}\right)^{3/2} N \sum_{l_2} \xi_{ll_2}^{l_1} \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_2}. \tag{39}$$

From Eqs. (22), (23), (28b) and (29), we obtain

$$\left.\frac{\partial^2\langle q_{l0}^{(p)}(E_0)\rangle}{\partial E_0^2}\right|_0 = \frac{1}{8\pi^2} \int q_{l0}^{(p)}(\tau) \left.\frac{\partial^2}{\partial E_0^2} e^{-w(\tau,E_0)/(kT)}\right|_0 d\tau$$
$$= \frac{\mu_l}{3kT} \left(\frac{4\pi}{3}\right) N \left(K \left.\frac{\partial^2 q}{\partial E_0^2}\right|_0\right)_l + \sqrt{\frac{3}{4\pi}} \frac{1}{kT} \left(\xi_{1l}^1 + \frac{\nu_{l11}}{3kT}\right)$$
$$+ \frac{1}{kT} \left(\frac{4\pi}{3}\right) N \sum_{l_1} \left(\xi_{1l}^{l_1} + \xi_{l_1 l}^1 + 2\frac{\nu_{ll_1 1}}{3kT}\right) \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1}$$
$$+ \frac{1}{kT} \left(\frac{4\pi}{3}\right)^{5/2} N^2 \sum_{l_1 l_2} \left(\xi_{l_1 l}^{l_2} + \frac{\nu_{ll_1 l_2}}{3kT}\right) \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1} \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_2}. \tag{40}$$

Substituting Eqs. (39) and (40) into Eq. (38), we obtain

$$\sum_{l_1} G_l^{l_1} \left.\frac{\partial^2\langle q_{l_1 0}^{(p)}(E_0)\rangle}{\partial E_0^2}\right|_0 = \sqrt{\frac{3}{4\pi}} H_l(2), \tag{41}$$

where

$$H_l(2) = \frac{1}{kT}\left(\xi_{l1}^1 + \xi_{1l}^1 + \frac{\nu_{l11}}{3kT}\right) + \frac{1}{kT}\left(\frac{4\pi}{3}\right)^{3/2} N \sum_{l_1} \left(\xi_{ll_1}^1 + \xi_{l1}^{l_1} + \xi_{1l}^{l_1} + \xi_{l_1 l}^1 + 2\frac{\nu_{ll_1 1}}{3kT}\right) \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1}$$
$$+ \frac{1}{kT}\left(\frac{4\pi}{3}\right)^3 N^2 \sum_{l_1 l_2} \left(\xi_{l_1 l}^{l_2} + \xi_{ll_2}^{l_1} + \frac{\nu_{ll_1 l_2}}{3kT}\right) \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1} \left(K \left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_2}. \tag{42}$$

Hence, we obtain

$$\left.\frac{\partial^2\langle q_{l0}^{(p)}(E_0)\rangle}{\partial E_0^2}\right|_0 = \sqrt{\frac{3}{4\pi}} \sum_{l_1} (G^{-1})_l^{l_1} H_{l_1}(2). \tag{43}$$

Taking the third-order derivative in Eq. (17), we obtain

$$\frac{\partial^3\langle q_{l0}(E_0)\rangle}{\partial E_0^3}\bigg|_0 - \left(\frac{4\pi}{3}\right) N \sum_{l_1}\langle\lambda_{l0}^{l_1 0}(E_0)\rangle|_0 \left(K\,\frac{\partial^3 q}{\partial E_0^3}\bigg|_0\right)_{l_1} - 3\left(\frac{4\pi}{3}\right) N \sum_{l_1} \frac{\partial^2\langle\lambda_{l0}^{l_1 0}(E_0)\rangle}{\partial E_0^2}\bigg|_0 \left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_1}$$

$$-3\left(\frac{4\pi}{3}\right) N \sum_{l_1} \frac{\partial\langle\lambda_{l0}^{l_1 0}(E_0)\rangle}{\partial E_0}\bigg|_0 \left(K\,\frac{\partial^2 q}{\partial E_0^2}\bigg|_0\right)_{l_1} = 3\sqrt{\frac{3}{4\pi}}\,\frac{\partial^2\langle\lambda_{l0}^{10}(E_0)\rangle}{\partial E_0^2}\bigg|_0 + \frac{\partial^3\langle q_{l0}^{(p)}(E_0)\rangle}{\partial E_0^3}\bigg|_0 . \quad (44)$$

Using Eqs. (21), (23), (28b), and (29) we obtain

$$\frac{\partial^2\langle\lambda_{l0}^{l_1 0}(E_0)\rangle}{\partial E_0^2}\bigg|_0 = \frac{1}{8\pi^2}\int \lambda_{l0}^{l_1 0}(\tau)\,\frac{\partial^2}{\partial E_0^2} e^{-w(\tau,E_0)/(kT)}\bigg|_0 d\tau - \frac{1}{(8\pi^2)^2}\int \lambda_{l0}^{l_1 0}(\tau)d\tau \int \frac{\partial^2}{\partial E_0^2} e^{-w(\tau,E_0)/(kT)}\bigg|_0 d\tau$$

$$= -\frac{\Gamma_l}{kT}\left(2\Gamma_1 + \frac{\mu_1}{3kT}\right)\delta_l^{l_1} - 2\frac{\Gamma_l}{kT}\left(2\Gamma_1 + \frac{\mu_1}{3kT}\right)\left(\frac{4\pi}{3}\right)^{3/2} N \left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_1 \delta_l^{l_1}$$

$$-\frac{\Gamma_l}{kT}\left(\frac{4\pi}{3}\right)^3 N^2 \sum_{l_2}\left(2\Gamma_{l_2} + \frac{\mu_{l_2}}{3kT}\right)\left[\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_2}\right]^2 + \frac{1}{kT}\left(2\eta_{l1}^{l_1 1} + \frac{\beta_{l11}^{l_1}}{3kT}\right)$$

$$+\frac{2}{kT}\left(\frac{4\pi}{3}\right)^{3/2} N \sum_{l_2}\left(\eta_{l1}^{l_1 l_2} + \eta_{ll_2}^{l_1 1} + \frac{\beta_{ll_2 1}^{l_1}}{3kT}\right)\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_2}$$

$$+\frac{1}{kT}\left(\frac{4\pi}{3}\right)^3 N^2 \sum_{l_2 l_3}\left(2\eta_{ll_2}^{l_1 l_3} + \frac{\beta_{ll_2 l_3}^{l_1}}{3kT}\right)\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_2}\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_3}$$

$$+\frac{1}{2kT}\left(\frac{4\pi}{3}\right)^{3/2} N \sum_{l_2}\xi_{ll_2}^{l_1}\left(K\,\frac{\partial^2 q}{\partial E_0^2}\bigg|_0\right)_{l_2} . \quad (45)$$

From Eqs. (22), (23), (28c), and (29), we obtain

$$\frac{\partial^3\langle q_{l0}^{(p)}(E_0)\rangle}{\partial E_0^3}\bigg|_0 = \frac{1}{8\pi^2}\int q_{l0}^{(p)}(\tau)\,\frac{\partial^3}{\partial E_0^3} e^{-w(\tau,E_0)/(kT)}\bigg|_0 d\tau$$

$$-\frac{3}{(8\pi^2)^2}\int q_{l0}^{(p)}(\tau)\,\frac{\partial}{\partial E_0} e^{-w(\tau,E_0)/(kT)}\bigg|_0 d\tau \int \frac{\partial^2}{\partial E_0^2} e^{-w(\tau,E_0)/(kT)}\bigg|_0 d\tau$$

$$= \frac{\mu_l}{3kT}\left(\frac{4\pi}{3}\right) N \left(K\,\frac{\partial^3 q}{\partial E_0^3}\bigg|_0\right)_l - \sqrt{\frac{3}{4\pi}}\frac{\mu_1}{(kT)^2}\left(2\Gamma_1 + \frac{\mu_1}{3kT}\right)\delta_l^1$$

$$-2\frac{\mu_1}{(kT)^2}\left(2\Gamma_1 + \frac{\mu_1}{3kT}\right)\left(\frac{4\pi}{3}\right) N \left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_1 \delta_l^1 - \frac{\mu_l}{(kT)^2}\left(2\Gamma_1 + \frac{\mu_1}{3kT}\right)\left(\frac{4\pi}{3}\right) N \left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_l$$

$$-2\frac{\mu_l}{(kT)^2}\left(2\Gamma_1 + \frac{\mu_1}{3kT}\right)\left(\frac{4\pi}{3}\right)^{5/2} N^2 \left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_1 \left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_l$$

$$-\frac{\mu_1}{(kT)^2}\left(\frac{4\pi}{3}\right)^{5/2} N^2 \sum_{l_1}\left(2\Gamma_{l_1} + \frac{\mu_{l_1}}{3kT}\right)\left[\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_1}\right]^2 \delta_l^1$$

$$-\frac{\mu_l}{(kT)^2}\left(\frac{4\pi}{3}\right)^4 N^3 \left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_l \sum_{l_1}\left(2\Gamma_{l_1} + \frac{\mu_{l_1}}{3kT}\right)\left[\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_1}\right]^2$$

$$+\frac{2}{(kT)^2}\sqrt{\frac{3}{4\pi}}\left(\beta_{1l1}^1 + \frac{\kappa_{l111}}{9kT}\right) + \frac{2}{(kT)^2}\left(\frac{4\pi}{3}\right) N \sum_{l_1}\left(\beta_{1l1}^{l_1} + \beta_{l_1 l1}^1 + \beta_{1ll_1}^1 + \frac{\kappa_{ll_1 11}}{3kT}\right)\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_1}$$

$$+\frac{2}{(kT)^2}\left(\frac{4\pi}{3}\right)^{5/2} N^2 \sum_{l_1 l_2}\left(\beta_{1ll_2}^{l_1} + \beta_{l_1 ll_2}^1 + \beta_{l_1 l1}^{l_2} + \frac{\kappa_{ll_1 l_2 1}}{3kT}\right)\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_1}\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_2}$$

$$+\frac{2}{(kT)^2}\left(\frac{4\pi}{3}\right)^4 N^3 \sum_{l_1 l_2 l_3}\left(\beta_{l_1 ll_3}^{l_2} + \frac{\kappa_{ll_1 l_2 l_3}}{9kT}\right)\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_1}\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_2}\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_3}$$

$$+\frac{3}{2kT}\left(\frac{4\pi}{3}\right) N \sum_{l_1}\left(\xi_{1l}^{l_1} + \xi_{l_1 l}^1 + 2\frac{\nu_{ll_1 1}}{3kT}\right)\left(K\,\frac{\partial^2 q}{\partial E_0^2}\bigg|_0\right)_{l_1}$$

$$+\frac{3}{2kT}\left(\frac{4\pi}{3}\right)^{5/2} N^2 \sum_{l_1 l_2}\left(\xi_{l_1 l}^{l_2} + \xi_{l_2 l}^{l_1} + 2\frac{\nu_{ll_1 l_2}}{3kT}\right)\left(K\,\frac{\partial^2 q}{\partial E_0^2}\bigg|_0\right)_{l_1}\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_2} . \quad (46)$$

Substituting Eqs. (45) and (46) into Eq. (44), we obtain

$$\sum_{l_1} G_l^{l_1} \left.\frac{\partial^3 \langle q_{l_1 0}^{(p)}(E_0)\rangle}{\partial E_0^3}\right|_0 = \sqrt{\frac{3}{4\pi}} H_l(3), \tag{47}$$

where

$$\begin{aligned}
H_l(3) = &-\frac{3}{kT}\left(\Gamma_1+\frac{\mu_1}{3kT}\right)\left(2\Gamma_1+\frac{\mu_1}{3kT}\right)\delta_l^1 - \frac{6}{kT}\left(\Gamma_1+\frac{\mu_1}{3kT}\right)\left(2\Gamma_1+\frac{\mu_1}{3kT}\right)\left(\frac{4\pi}{3}\right)^{3/2} N\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_1 \delta_l^1 \\
&-\frac{3}{kT}\left(\Gamma_l+\frac{\mu_l}{3kT}\right)\left(2\Gamma_1+\frac{\mu_1}{3kT}\right)\left(\frac{4\pi}{3}\right)^{3/2} N\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_l \\
&-\frac{6}{kT}\left(\Gamma_l+\frac{\mu_l}{3kT}\right)\left(2\Gamma_1+\frac{\mu_1}{3kT}\right)\left(\frac{4\pi}{3}\right)^{3} N^2\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_1\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_l \\
&-\frac{3}{kT}\left(\Gamma_1+\frac{\mu_1}{3kT}\right)\left(\frac{4\pi}{3}\right)^{3} N^2\sum_{l_1}\left(2\Gamma_{l_1}+\frac{\mu_{l_1}}{3kT}\right)\left[\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1}\right]^2 \delta_l^1 \\
&-\frac{3}{kT}\left(\Gamma_l+\frac{\mu_l}{3kT}\right)\left(\frac{4\pi}{3}\right)^{9/2} N^3\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_l\sum_{l_1}\left(2\Gamma_{l_1}+\frac{\mu_{l_1}}{3kT}\right)\left[\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1}\right]^2 \\
&+\frac{1}{kT}\left[6\eta_{l1}^{11}+2\frac{\beta_{1l1}^1}{kT}+\frac{\beta_{l11}^1}{kT}+2\frac{\kappa_{l111}}{9(kT)^2}\right]+\frac{1}{kT}\left(\frac{4\pi}{3}\right)^{3/2} N\sum_{l_1}\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1} \\
&\times\left[6\eta_{l1}^{1l_1}+6\eta_{ll_1}^{11}+6\eta_{l1}^{l_11}+2\frac{\beta_{1l1}^{l_1}}{kT}+2\frac{\beta_{l_1l1}^1}{kT}+2\frac{\beta_{1ll_1}^1}{kT}+2\frac{\beta_{ll_11}^1}{kT}+\frac{\beta_{l11}^{l_1}}{kT}+2\frac{\kappa_{ll_111}}{3(kT)^2}\right] \\
&+\frac{1}{kT}\left(\frac{4\pi}{3}\right)^{3} N^2\sum_{l_1l_2}\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} \\
&\times\left[6\eta_{ll_1}^{1l_2}+6\eta_{l1}^{l_1l_2}+6\eta_{ll_2}^{l_11}+2\frac{\beta_{1ll_2}^{l_1}}{kT}+2\frac{\beta_{l_1ll_2}^{1}}{kT}+2\frac{\beta_{l_1l1}^{l_2}}{kT}+2\frac{\beta_{ll_21}^{l_1}}{kT}+\frac{\beta_{ll_1l_2}^{1}}{kT}+2\frac{\kappa_{ll_1l_21}}{3(kT)^2}\right] \\
&+\frac{1}{kT}\left(\frac{4\pi}{3}\right)^{9/2} N^3\sum_{l_1l_2l_3}\left[6\eta_{ll_2}^{l_1l_3}+2\frac{\beta_{l_1ll_3}^{l_2}}{kT}+\frac{\beta_{ll_2l_3}^{l_1}}{kT}+2\frac{\kappa_{ll_1l_2l_3}}{9(kT)^2}\right] \\
&\times\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} \\
&+\frac{3}{2kT}\left(\frac{4\pi}{3}\right)^{3/2} N\sum_{l_1}\left(\xi_{1l}^{l_1}+\xi_{l_1l}^{1}+\xi_{ll_1}^{1}+\xi_{l1}^{l_1}+2\frac{\nu_{ll_11}}{3kT}\right)\left(K\left.\frac{\partial^2 q}{\partial E_0^2}\right|_0\right)_{l_1} \\
&+\frac{3}{2kT}\left(\frac{4\pi}{3}\right)^{3} N^2\sum_{l_1l_2}\left(\xi_{l_1l}^{l_2}+\xi_{l_2l}^{l_1}+\xi_{ll_2}^{l_1}+\xi_{ll_1}^{l_2}+2\frac{\nu_{ll_1l_2}}{3kT}\right)\left(K\left.\frac{\partial^2 q}{\partial E_0^2}\right|_0\right)_{l_1}\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_2}.
\end{aligned} \tag{48}$$

Hence, we obtain

$$\left.\frac{\partial^3 \langle q_{l0}(E_0)\rangle}{\partial E_0^3}\right|_0 = \sqrt{\frac{3}{4\pi}}\sum_{l_1}(G^{-1})_l^{l_1} H_{l_1}(3). \tag{49}$$

In principle, one can continue with this procedure to obtain even higher-order derivatives. They generally have the form

$$\left.\frac{\partial^n \langle q_{l0}(E_0)\rangle}{\partial E_0^n}\right|_0 = \sqrt{\frac{3}{4\pi}}\sum_{l_1}(G^{-1})_l^{l_1} H_{l_1}(n), \tag{50}$$

where $H_l(n)$ contains lower order derivatives. It is clear that the central quantities for the whole problem are the $H_l(n)$. With given $\lambda_{lm}^{l_1m_1}$, $q_{lm}^{(p)}$, and $K_l^{l_1}$, one calculates the derivatives of the averaged multipole moments recursively from Eq. (50).

Substituting Eqs. (37) and (49) into Eq. (12), we obtain the effective dielectric function

$$\epsilon_e = 1 + 4\pi N (G^{-1})_1^1 \Delta_1(1) + 4\pi N \frac{1}{6} \sum_{l_1} (G^{-1})_1^{l_1} H_{l_1}(3) E_0^2 + O^*(E_0^4), \tag{51}$$

which represents the central result of this paper.

IV. RESULTS FOR SOME PARTICULAR SYSTEMS

A. Nonpolarizable inclusions

If all the inclusions are nonpolarizable, $\lambda_{nlm}^{l_1 m_1} = 0$. This results in

$$\Gamma_l = \eta_{ll_2}^{l_1 l_3} = \xi_{ll_2}^{l_1} = \beta_{ll_2 l_3}^{l_1} = 0 \tag{52}$$

and

$$\Delta_l(1) = \frac{\mu_l}{3kT}. \tag{53}$$

Then, from Eqs. (36), (42), and (48)

$$H_l(1) = \frac{\mu_l}{3kT}\delta_l^1, \tag{54}$$

$$H_l(2) = \frac{\nu_{l11}}{3(kT)^2} + \frac{2}{3(kT)^2}\left(\frac{4\pi}{3}\right)^{3/2} N \sum_{l_1} \nu_{ll_1 1}\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1} + \frac{1}{3(kT)^2}\left(\frac{4\pi}{3}\right)^3 N^2 \sum_{l_1 l_2} \nu_{ll_1 l_2}\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1}\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_2}, \tag{55}$$

$$\begin{aligned} H_l(3) = &-\frac{\mu_1^2}{3(kT)^3}\delta_l^1 - \frac{2\mu_1^2}{3(kT)^3}\left(\frac{4\pi}{3}\right)^{3/2} N\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_1 \delta_l^1 - \frac{\mu_1^2}{3(kT)^3}\left(\frac{4\pi}{3}\right)^{3/2} N\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_l \\ &-\frac{2\mu_1^2}{3(kT)^3}\left(\frac{4\pi}{3}\right)^3 N^2\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_1\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_l - \frac{\mu_1}{3(kT)^3}\left(\frac{4\pi}{3}\right)^3 N^2 \sum_{l_1}\mu_{l_1}\left[\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1}\right]^2 \delta_l^1 \\ &-\frac{\mu_l}{3(kT)^3}\left(\frac{4\pi}{3}\right)^{9/2} N^3\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_l \sum_{l_1}\mu_{l_1}\left[\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1}\right]^2 \\ &+\frac{2\kappa_{l111}}{9(kT)^3} + \frac{2}{3(kT)^3}\left(\frac{4\pi}{3}\right)^{3/2} N \sum_{l_1}\kappa_{ll_1 11}\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1} \\ &+\frac{2}{3(kT)^3}\left(\frac{4\pi}{3}\right)^3 N^2 \sum_{l_1 l_2}\kappa_{ll_1 l_2 1}\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1}\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_2} \\ &+\frac{2}{9(kT)^3}\left(\frac{4\pi}{3}\right)^{9/2} N^3 \sum_{l_1 l_2 l_3}\kappa_{ll_1 l_2 l_3}\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1}\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_2}\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_3} \\ &+\frac{1}{(kT)^2}\left(\frac{4\pi}{3}\right)^{3/2} N \sum_{l_1}\nu_{ll_1 1}\left(K\left.\frac{\partial^2 q}{\partial E_0^2}\right|_0\right)_{l_1} + \frac{1}{(kT)^2}\left(\frac{4\pi}{3}\right)^3 N^2 \sum_{l_1 l_2}\nu_{ll_1 l_2}\left(K\left.\frac{\partial^2 q}{\partial E_0^2}\right|_0\right)_{l_1}\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_2}. \end{aligned} \tag{56}$$

In this case, the electrical response purely arises from the rotations of the permanent multipole moments.

B. Inclusions without permanent multipole moments

In this case $q_{nlm}^{(p)} = 0$, and we have

$$\nu_l = \beta_{ll_2 l_3}^{l_1} = \kappa_{ll_1 l_2 l_3} = \xi_{ll_2}^{l_1} = \nu_{ll_1 l_2} = 0, \tag{57}$$

$$\Delta_l(1) = \Gamma_l. \tag{58}$$

Then, from Eqs. (36), (42), and (48)

$$H_l(1) = \Gamma_l \delta_l^1, \tag{59}$$

$$H_l(2) = 0, \tag{60}$$

and

$$\begin{aligned} H_l(3) = & -\frac{6\Gamma_1^2}{kT}\delta_l^1 - \frac{12\Gamma_1^2}{kT}\left(\frac{4\pi}{3}\right)^{3/2} N\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_1 \delta_l^1 - \frac{6\Gamma_1\Gamma_l}{kT}\left(\frac{4\pi}{3}\right)^{3/2} N\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_l \\ & -\frac{12\Gamma_1\Gamma_l}{kT}\left(\frac{4\pi}{3}\right)^3 N^2\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_1\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_l - \frac{6\Gamma_1}{3(kT)^3}\left(\frac{4\pi}{3}\right)^3 N^2 \sum_{l_1}\Gamma_{l_1}\left[\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_1}\right]^2 \delta_l^1 \\ & -\frac{6\Gamma_l}{kT}\left(\frac{4\pi}{3}\right)^{9/2} N^3\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_l \sum_{l_1}\Gamma_{l_1}\left[\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_1}\right]^2 \\ & +\frac{6\eta_{l1}^{11}}{kT} + \frac{6}{kT}\left(\frac{4\pi}{3}\right)^{3/2} N\sum_{l_1}(\eta_{l1}^{1l_1} + \eta_{ll_1}^{11} + \eta_{l1}^{l_11})\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_1} \\ & +\frac{6}{kT}\left(\frac{4\pi}{3}\right)^3 N^2\sum_{l_1l_2}(\eta_{ll_1}^{1l_2} + \eta_{l1}^{l_1l_2} + \eta_{ll_2}^{l_11})\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_1}\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_2} \\ & +\frac{6}{kT}\left(\frac{4\pi}{3}\right)^{9/2} N^3\sum_{l_1l_2l_3}\eta_{ll_2}^{l_1l_3}\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_1}\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_2}\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_3}. \end{aligned} \tag{61}$$

In this case, the electrical response arises from both the direct polarization and the rotation of the inclusions (for nonspherical inclusions).

C. Spherical inclusions

Let us consider now spherical inclusions with radius a and dielectric function ϵ_p. The corresponding polarization coefficients are [cf. Eq. (4) of Ref. 5]

$$\lambda_{lm}^{l_1m_1} = \frac{1}{3}l(2l+1)\left[\frac{\epsilon_p - 1}{l\epsilon_p + (l+1)}\right] a^{2l+1}\delta_l^{l_1}\delta_m^{m_1}. \tag{62}$$

Then

$$\begin{aligned} \Gamma_l &= l\left[\frac{\epsilon_p - 1}{l\epsilon_p + (l+1)}\right] a^{2l+1}, \\ \eta_{ll_2}^{l_1l_3} &= \Gamma_l\Gamma_{l_2}\delta_l^{l_1}\delta_{l_2}^{l_3}, \\ \xi_{ll_2}^{l_1} &= 0, \\ \beta_{ll_2l_3}^{l_1} &= \Gamma_l\mu_{l_2}\delta_l^{l_1}\delta_{l_2}^{l_3}. \end{aligned} \tag{63}$$

$H_l(1)$ formally remains the same as in Eq. (36), while $H_l(2)$ and $H_l(3)$ reduce to

$$\begin{aligned} H_l(2) = & \frac{\nu_{l11}}{3(kT)^2} + \frac{2}{3(kT)^2}\left(\frac{4\pi}{3}\right)^{3/2} N\sum_{l_1}\nu_{ll_11}\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_1} \\ & +\frac{1}{3(kT)^2}\left(\frac{4\pi}{3}\right)^3 N^2\sum_{l_1l_2}\nu_{ll_1l_2}\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_1}\left(K\,\frac{\partial q}{\partial E_0}\bigg|_0\right)_{l_2}, \end{aligned} \tag{64}$$

and

$$H_l(3) = -\frac{\mu_1^2}{3(kT)^3}\delta_l^1 - \frac{2\mu_1^2}{3(kT)^3}\left(\frac{4\pi}{3}\right)^{3/2} N\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_1 \delta_l^1 - \frac{\mu_1\mu_l}{3(kT)^3}\left(\frac{4\pi}{3}\right)^{3/2} N\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_l$$
$$-\frac{2\mu_1\mu_l}{3(kT)^3}\left(\frac{4\pi}{3}\right)^3 N^2\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_1\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_l - \frac{\mu_1}{3(kT)^3}\left(\frac{4\pi}{3}\right)^3 N^2\sum_{l_1}\mu_{l_1}\left[\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1}\right]^2\delta_l^1$$
$$-\frac{\mu_l}{3(kT)^3}\left(\frac{4\pi}{3}\right)^{9/2} N^3\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_l\sum_{l_1}\mu_{l_1}\left[\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1}\right]^2 + \frac{2\kappa_{l111}}{9(kT)^3}$$
$$+\frac{2}{3(kT)^3}\left(\frac{4\pi}{3}\right)^{3/2} N\sum_{l_1}\kappa_{ll_111}\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1}$$
$$+\frac{2}{3(kT)^3}\left(\frac{4\pi}{3}\right)^3 N^2\sum_{l_1l_2}\kappa_{ll_1l_21}\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1}\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_2}$$
$$+\frac{2}{9(kT)^3}\left(\frac{4\pi}{3}\right)^{9/2} N^3\sum_{l_1l_2l_3}\kappa_{ll_1l_2l_3}\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_1}\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_2}\left(K\left.\frac{\partial q}{\partial E_0}\right|_0\right)_{l_3}$$
$$+\frac{1}{(kT)^2}\left(\frac{4\pi}{3}\right)^{3/2} N\sum_{l_1}\nu_{ll_11}\left(K\left.\frac{\partial^2 q}{\partial E_0^2}\right|_0\right)_{l_1} + \frac{1}{(kT)^2}\left(\frac{4\pi}{3}\right)^3 N^2\sum_{l_1l_2}\nu_{ll_1l_2}\left(K\left.\frac{\partial^2 q}{\partial E_0^2}\right|_0\right)_{l_1}\left(K\left.\frac{\partial^2 q}{\partial E_0^2}\right|_0\right)_{l_2}. \quad (65)$$

In this case, the electrical response arises from the direct polarization and the rotation of the permanent multipoles.

V. CONCLUSIONS

We have presented the mean field theory solution to the electrical response of heterogeneous systems, where the inclusions have arbitrary structures and permanent multipole moments of arbitrary orders. All orders of the total multipole moments of all the inclusions and their images have been taken into account. We have obtained explicitly the first three derivatives of the average multipole moments with respect to the applied field. Higher derivatives can be obtained with the same procedure. We have then obtained the effective dielectric function. These results are readily applied to disordered systems with given $\lambda_{lm}^{l_1m_1}$, $q_{lm}^{(p)}$, and $K_l^{l_1}$ (position pair distribution for the inclusions). With these input values, one calculates recursively the quantities $H_l(n)$ and the derivatives of the averaged multipole moments with respect to the applied field, and thus obtains the effective dielectric function. We have also provided the particular results for spherical inclusions, inclusions with only the permanent multipole moments, inclusions without permanent multipole moments.

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APPENDIX A

In this appendix, we prove Eqs. (13) for systems with macroscopic reflection symmetry. When the applied field is reversed $E_0 \longrightarrow -E_0$, inclusions change their orientations until a new equilibrium is reached. A system with macroscopic reflection symmetry is such that, when the applied field is reversed, the inclusions rotate and readjust so that any macroscopic quantity obeys

$$Q(-E_0,\mathbf{r}) = Q(E_0,\bar{\mathbf{r}}), \quad (A1)$$

where $\bar{\mathbf{r}} = (x,y,-z)$ is the mirror image of $\mathbf{r}$ about the $z = 0$ plane. To prove Eqs. (13), it is possible to construct a virtual system, equivalent to our original system in any macroscopic aspect, but also endowed with *microscopic* reflection symmetry. Taking the nth inclusion at the origin, its multipole moments are given by

$$q_{nlm}(E_0) = \sqrt{\frac{3}{4\pi}}\lambda_{nlm}^{10}(E_0)E_0 - 3\sum_{l_1m_1}\sum_{l_2m_2}\lambda_{nlm}^{l_2m_2}(E_0)\sum_{n_1}C_{l_2,m_2}^{l_1,m_1}(\mathbf{r}_{n_1})q_{n_1l_1m_1}(E_0) + q_{nlm}^{(p)}(E_0). \quad (A2)$$

Since the system has microscopic reflection symmetry, we have from Eqs. (13) and (14) of Ref. 3

$$\sum_{n_1}C_{l_2,m_2}^{l_1,m_1}(\mathbf{r}_{n_1}) = \sum_{n_1}C_{l_2,m_2}^{l_1,m_1}(\bar{\mathbf{r}}_{n_1}) = (-1)^{l_1+m_1+l_2+m_2}\sum_{n_1}C_{l_2,m_2}^{l_1,m_1}(\mathbf{r}_{n_1}). \quad (A3)$$

After the applied field is reversed, the multipole moments are given by

$$q_{nlm}(-E_0) = -\sqrt{\frac{3}{4\pi}}\lambda^{10}_{nlm}(-E_0)E_0 \\ -3\sum_{l_1m_1}\sum_{l_2m_2}(-1)^{l_2+m_2}\lambda^{l_2m_2}_{nlm}(-E_0)\sum_{n_1}C^{l_1,m_1}_{l_2,m_2}(\mathbf{r}_{n_1})(-1)^{l_1+m_1}q_{n_1l_1m_1}(-E_0) + q^{(p)}_{nlm}(-E_0), \quad (A4)$$

where we have used Eq. (A3). Since the system has microscopic reflection symmetry, when the applied field is reversed, each inclusion rotates and readjusts so that the charge distribution on each inclusion satisfies

$$\rho_n(-E_0,\mathbf{r}) = \rho_n(E_0,\bar{\mathbf{r}}). \quad (A5)$$

Hence, we obtain

$$q_{nlm}(-E_0) = \int \rho_n(-E_0,\mathbf{r})r^l Y^*_{l,m}(\mathbf{r})d^3\mathbf{r} \\ = \int \rho_n(E_0,\bar{\mathbf{r}})r^l Y^*_{l,m}(\mathbf{r})d^3\mathbf{r}. \quad (A6)$$

Changing the integration variable to $\bar{\mathbf{r}}$ and noticing that

$$\bar{r} = r, \quad d^3\bar{\mathbf{r}} = d^3\mathbf{r}, \quad \text{and} \quad Y^*_{l,m}(\bar{\mathbf{r}}) = (-1)^{l+m}Y^*_{l,m}(\mathbf{r}), \quad (A7)$$

we obtain

$$q_{nlm}(-E_0) = (-1)^{l+m}q_{nlm}(E_0). \quad (A8)$$

Substituting Eq. (A8) into Eq. (A4), we obtain

$$q_{nlm}(E_0) = \sqrt{\frac{3}{4\pi}}(-1)^{l+m+1}\lambda^{10}_{nlm}(-E_0)E_0 \\ -3\sum_{l_1m_1}\sum_{l_2m_2}(-1)^{l+m+l_2+m_2}\lambda^{l_2m_2}_{nlm}(-E_0)\sum_{n_1}C^{l_1,m_1}_{l_2,m_2}(\mathbf{r}_{n_1})q_{n_1l_1m_1}(E_0) + q^{(p)}_{nlm}(E_0). \quad (A9)$$

In order to recover Eq. (A2), it is necessary and sufficient that

$$\lambda^{l_1m_1}_{nlm}(-E_0) = (-1)^{l+m+l_1+m_1}\lambda^{l_1m_1}_{nlm}(E_0). \quad (A10)$$

Averaging Eqs. (A8) and (A10) over all inclusions, we obtain the corresponding equations for macroscopic quantities as in Eqs. (13), which hold for our original system.

APPENDIX B

In this appendix we carry out the integrals in Eq. (23). We use the relation

$$Y_{l,m}(\Omega)Y_{l_1,m_1}(\Omega) = \sum_{LM}(l,m,l_1,m_1|L,M)Y^*_{L,M}(\Omega), \quad (B1)$$

where the coefficients are expressed in terms of the $3j$ symbols:

$$(l,m,l_1,m_1|L,M) = \left[\frac{(2l+1)(2l_1+1)(2L+1)}{4\pi}\right]^{1/2}\begin{pmatrix} l & l_1 & L \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l & l_1 & L \\ m & m_1 & M\end{pmatrix}. \quad (B2)$$

Using Eqs. (6), (7), and (B1), we obtain

$$\int \lambda^{l_1 0}_{l0}(\tau)d\tau = \frac{8\pi^2}{\sqrt{(2l+1)(2l_1+1)}}\sum_{mm_1}\lambda^{l_1m_1}_{lm}\int Y^*_{l,m}(\Omega)Y_{l_1,m_1}(\Omega)d\Omega \\ = 8\pi^2\left(\frac{1}{2l+1}\sum_m \lambda^{lm}_{lm}\right)\delta^{l_1}_l \equiv 8\pi^2\Gamma_l\delta^{l_1}_l, \quad (B3)$$

$$\int q^{(p)}_{l0}(\tau)d\tau = 2\pi\sum_m q^{(p)}_{lm}\int Y^*_{l,m}(\Omega)d\Omega = 0, \quad \text{since } l \geq 1, \quad (B4)$$

$$\int \lambda^{l_1 0}_{l0}(\tau)\lambda^{l_3 0}_{l_2 0}(\tau)d\tau = \frac{8\pi^2}{\sqrt{(2l+1)(2l_1+1)(2l_2+1)(2l_3+1)}}\sum_{mm_1}\lambda^{l_1m_1}_{lm}\sum_{m_2m_3}\lambda^{l_3m_3}_{l_2m_2} \\ \times\int Y^*_{l,m}(\Omega)Y_{l_1,m_1}(\Omega)Y^*_{l_2,m_2}(\Omega)Y_{l_3,m_3}(\Omega)d\Omega \\ = \frac{8\pi^2}{\sqrt{(2l+1)(2l_1+1)(2l_2+1)(2l_3+1)}}\sum_{mm_1}\lambda^{l_1m_1}_{lm}\sum_{m_2m_3}\lambda^{l_3m_3}_{l_2m_2} \\ \times\sum_{LM}(l,m,l_2,m_2|L,M)\sum_{L_1M_1}(l_1,m_1,l_3,m_3|L_1,M_1)\int Y_{L,M}(\Omega)Y_{L_1,M_1}(\Omega)d\Omega \\ = \frac{8\pi^2}{\sqrt{(2l+1)(2l_1+1)(2l_2+1)(2l_3+1)}}\sum_{mm_1}\lambda^{l_1m_1}_{lm}\sum_{m_2m_3}\lambda^{l_3m_3}_{l_2m_2} \\ \times\sum_{LM}(l,m,l_2,m_2|L,M)(l_1,m_1,l_3,m_3|L,M) \equiv 8\pi^2\eta^{l_1l_3}_{ll_2}, \quad (B5)$$

$$\int \lambda_{l0}^{l_1 0}(\tau) q_{l_2 0}^{(p)}(\tau) d\tau$$

$$= 4\pi\sqrt{\frac{4\pi}{(2l+1)(2l_1+1)(2l_2+1)}} \sum_{mm_1} \lambda_{lm}^{l_1 m_1} \sum_{m_2} q_{l_2 m_2}^{(p)} \int Y_{l,m}^*(\beta,\gamma) Y_{l_1,m_1}(\beta,\gamma) Y_{l_2,m_2}^*(\beta,\alpha) d(\cos\beta) d\gamma d\alpha$$

$$= 8\pi\sqrt{\frac{4\pi}{(2l+1)(2l_1+1)(2l_2+1)}} \sum_{m} \lambda_{lm}^{l_1 m} q_{l_2 0}^{(p)} \int Y_{l,m}^*(\Omega) Y_{l_1,m}(\Omega) Y_{l_2,0}(\Omega) d\Omega$$

$$= 8\pi\sqrt{\frac{4\pi}{(2l+1)(2l_1+1)(2l_2+1)}} \sum_{m} (-1)^m \lambda_{lm}^{l_1 m} q_{l_2 0}^{(p)} \sum_{LM} (l,-m,l_1,m|L,M) \int Y_{L,M}^*(\Omega) Y_{l_2,0}(\Omega) d\Omega$$

$$= 8\pi\sqrt{\frac{4\pi}{(2l+1)(2l_1+1)(2l_2+1)}} \sum_{m} (-1)^m \lambda_{lm}^{l_1 m} q_{l_2 0}^{(p)} (l,-m,l_1,m|l_2,0) \equiv 4\pi^2 \sqrt{\frac{3}{4\pi}} \xi_{ll_2}^{l_1}, \tag{B6}$$

$$\int q_{l0}(\tau) q_{l_1 0}(\tau) d\tau = \frac{8\pi^2}{\sqrt{(2l+1)(2l_1+1)}} \sum_{mm_1} q_{lm}^{(p)} q_{l_1 m_1}^{(p)*} \int Y_{l,m}^*(\Omega) Y_{l_1,m_1}(\Omega) d\Omega$$

$$= \frac{8\pi^2}{2l+1} \delta_l^{l_1} \sum_{m} q_{lm}^{(p)} q_{lm}^{(p)*} \equiv 2\pi \mu_l \delta_l^{l_1}, \tag{B7}$$

$$\int \lambda_{l0}^{l_1 0}(\tau) q_{l_2 0}^{(p)}(\tau) q_{l_3 0}^{(p)}(\tau) d\tau = \frac{(4\pi)^2}{\sqrt{(2l+1)(2l_1+1)(2l_2+1)(2l_3+1)}} \sum_{mm_1m_2m_3} (-1)^m \lambda_{lm}^{l_1 m_1} q_{l_2 m_2}^{(p)} q_{l_3 m_3}^{(p)}$$

$$\times \int Y_{l,-m}(\beta,\gamma) Y_{l_1,m_1}(\beta,\gamma) Y_{l_2,m_2}^*(\beta,\alpha) Y_{l_3,m_3}^*(\beta,\alpha) d(\cos\beta) d\gamma d\alpha$$

$$= \frac{2\pi(4\pi)^2}{\sqrt{(2l+1)(2l_1+1)(2l_2+1)(2l_3+1)}} \sum_{mm_2} (-1)^{m+m_2} \lambda_{lm}^{l_1 m} q_{l_2 m_2}^{(p)} q_{l_3 m_2}^{(p)*}$$

$$\times \sum_{LL_1} (l,-m,l_1,m|L,0)(l_2,m_2,l_3,-m_2|L_1,0) \int Y_{L,0}^*(\Omega) Y_{L_1,0}(\Omega) d\Omega$$

$$= \frac{2\pi(4\pi)^2}{\sqrt{(2l+1)(2l_1+1)(2l_2+1)(2l_3+1)}} \sum_{mm_2} (-1)^{m+m_2} \lambda_{lm}^{l_1 m} q_{l_2 m_2}^{(p)} q_{l_3 m_2}^{(p)*}$$

$$\times \sum_{L} (l,-m,l_1,m|L,0)(l_2,m_2,l_3,-m_2|L,0) \equiv 2\pi \beta_{ll_2l_3}^{l_1}, \tag{B8}$$

$$\int q_{l0}^{(p)}(\tau) q_{l_1 0}^{(p)}(\tau) q_{l_2 0}^{(p)}(\tau) d\tau$$

$$= \frac{2\pi(4\pi)^{3/2}}{\sqrt{(2l+1)(2l_1+1)(2l_2+1)}} \sum_{mm_1m_2} q_{lm}^{(p)*} q_{l_1 m_1}^{(p)*} q_{l_2 m_2}^{(p)*} \int Y_{l,m}(\Omega) Y_{l_1,m_1}(\Omega) Y_{l_2,m_2}(\Omega) d\Omega$$

$$= \frac{2\pi(4\pi)^{3/2}}{\sqrt{(2l+1)(2l_1+1)(2l_2+1)}} \sum_{mm_1m_2} q_{lm}^{(p)*} q_{l_1 m_1}^{(p)*} q_{l_2 m_2}^{(p)*} \sum_{LM} (l,m,l_1,m_1|L,M) \int Y_{L,M}^*(\Omega) Y_{l_2,m_2}(\Omega) d\Omega$$

$$= \frac{2\pi(4\pi)^{3/2}}{\sqrt{(2l+1)(2l_1+1)(2l_2+1)}} \sum_{mm_1m_2} q_{lm}^{(p)*} q_{l_1 m_1}^{(p)*} q_{l_2 m_2}^{(p)*} (l,m,l_1,m_1|l_2,m_2) \equiv 2\pi \sqrt{\frac{3}{4\pi}} \nu_{ll_1l_2}, \tag{B9}$$

$$\int q_{l0}^{(p)}(\tau)q_{l_10}^{(p)}(\tau)q_{l_20}^{(p)}(\tau)q_{l_20}^{(p)}(\tau)d\tau = \frac{2\pi(4\pi)^2}{\sqrt{(2l+1)(2l_1+1)(2l_2+1)(2l_3+1)}}$$
$$\times \sum_{mm_1m_2m_3} q_{lm}^{(p)*}q_{l_1m_1}^{(p)*}q_{l_2m_2}^{(p)}q_{l_3m_3}^{(p)} \int Y_{l,m}(\Omega)Y_{l_1,m_1}(\Omega)Y_{l_2,m_2}^*(\Omega)Y_{l_3,m_3}^*(\Omega)d\Omega$$
$$= \frac{2\pi(4\pi)^2}{\sqrt{(2l+1)(2l_1+1)(2l_2+1)(2l_3+1)}} \sum_{mm_1m_2m_3} q_{lm}^{(p)*}q_{l_1m_1}^{(p)*}q_{l_2m_2}^{(p)}q_{l_3m_3}^{(p)}$$
$$\times \sum_{LML_1M_1} (l,m,l_1,m_1|L,M)(l_2,m_2,l_3,m_3|L_1,M_1) \int Y_{L,M}^*(\Omega)Y_{L_1,M_1}(\Omega)d\Omega$$
$$= \frac{2\pi(4\pi)^2}{\sqrt{(2l+1)(2l_1+1)(2l_2+1)(2l_3+1)}} \sum_{mm_1m_2m_3} q_{lm}^{(p)*}q_{l_1m_1}^{(p)*}q_{l_2m_2}^{(p)}q_{l_2m_2}^{(p)}$$
$$\times \sum_{LM}(l,m,l_1,m_1|L,M)(l_2,m_2,l_3,m_3|L,M) \equiv \kappa_{ll_1l_2l_3}. \tag{B10}$$

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