

Electrical response of heterogeneous systems and Debye's problem

Liang Fu and Lorenzo Resca

Department of Physics, the Catholic University of America, Washington, D.C. 20064

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We study the linear and nonlinear electric response of heterogeneous systems containing inclusions of arbitrary structure and permanent multipole moments of all orders with $L = 0$ and $L = 1$ pair distributions, within mean field theory. We find that for these distributions only the dipole moments contribute to the effective dielectric function. In particular, we provide the results for inclusions without permanent dipole moments or polarizabilities, and spherical inclusions. We show that the Debye's effective dielectric function represents the linear part of the general result, in the special case of spherical inclusions with isotropic ($L = 0$) pair distributions.

I. INTRODUCTION

In this paper, we apply the mean field theory solution obtained in the preceding paper¹ to heterogeneous systems with $L = 0$ (isotropic) and 1 pair distributions for the positions of the inclusions. The inclusions in such systems are generally defined by their polarization coefficients and permanent multipole moments of arbitrary order. The detailed electrical interactions among all the inclusions and their images are thus exactly included. We find that for these cases of pair distributions, only the dipole moments (permanent and induced) contribute to the effective dielectric function. This supports previous theories that have included only the dipole-dipole interactions. However, we find that the contribution of the dipole moments of the surrounding inclusions to the local field on a given inclusion may be strongly affected by the pair distributions, whereas previous theories have only considered isotropic distributions.

For comparison, we then consider the macroscopic models of Debye² and Onsager,³ since they have been extensively studied, with various generalizations and implementations. Both models apply to polar fluids, assume isotropic molecules and (implicitly) distributions, consider only dipole moments and interactions, and provide only the linear part of the effective dielectric function. Our solution has none of those limitations, but is of course restricted to mean field theory.

To determine the local field acting on a given inclusion, both Debye and Onsager consider a spherical cavity with the average molecular volume in a surrounding medium treated macroscopically. However, Debye's cavity is the same as that used by Clausius in his derivation of the molecular Clausius-Mossotti relation (see, equivalently, Appendix A3 of Ref. 4): namely, a cavity in a medium which retains a uniform fixed polarization. In such a model, the charges in the medium do not respond to the given inclusion inside the cavity. On the other hand, Onsager's cavity is in a medium characterized by the dielectric constant: the charges in the medium readjust and react in response to both the cavity and the dipole moment in it, thus generating a so-called cavity

field and a reaction field (see, for instance, Secs. 5 and 6 of Ref. 4). Notice that when the two cavities are used on a macroscopic scale to account for the field produced by the inclusions outside a large sphere, they give the same result, given the same polarization [Eqs. (5.9) and (5.12) of Ref. 4]. The difference arises when the cavities are applied at a microscopic scale, as in Debye's and Onsager's model. On a microscopic scale, both models have well-recognized drawbacks. Most noticeably, Debye's model implies that the orientations of the surrounding inclusions do not respond to the instantaneous orientation of the given inclusion. Conversely, Onsager's model implies that the surrounding inclusions respond instantaneously and solely to the orientation of the given inclusion, generating a reaction field always along the dipole moment of the given inclusion. That is thought to be correct for fluctuation correlations.^{5,6} In fact, it has been noticed that the average period of a molecule free rotation is short compared with the relaxation time of a polar dielectric. If the rotations are thus so rapid that other molecules cannot follow them at all, the Lorentz model should be the truer picture (Ref. 7, p. 558). Also, it does not seem to have been previously noticed that if some molecules are ionic, i.e., they carry a net charge in addition to a permanent dipole moment, they would be constantly accelerated by Onsager's reaction field, even in the absence of any applied field, with paradoxical consequences on energy conservation and equilibrium. In reality, all molecules mutually interact, rather than all reacting to any one in particular as a medium surrounding a real cavity.

Theoretical progress has been made by applying Onsager's method to a macroscopic cavity, and then determining the microscopic interactions among the molecules within such a macroscopic cavity. General theorems have been developed [Secs. 7 and 8 of Ref. 4], and several microscopic results are more or less based on this idea.⁷⁻¹⁰ Also many computer simulations rest on it.¹¹⁻¹⁴

Debye's result predicts a Curie point, whereas Onsager's result does not. Since polar liquids do not exhibit generally a ferroelectric phase, Onsager's method has been previously regarded as superior.¹⁵⁻¹⁷ However,

recent computer simulations¹⁸ have shown that a system of spheres with only dipole-dipole interactions do form a stable orientationally ordered liquid state, after all. Similar results¹⁹ have also been related to specific polar liquid crystals. These results suggest that the absence of a Curie point may be due to other interactions which often dominate the dipole-dipole interactions at short range in polar liquids.¹⁸

Anyway, Debye's and Onsager's methods represent rather extreme starting points, that can hardly be reconciled. For example, in order to obtain Onsager's result from the general theorems reported in Sec. 7 of Ref. 4, one has to make approximations essentially in the same spirit as Onsager's approach. On the other hand, we shall see that the MFT solution reproduces the Debye's result in particular circumstances, whereas it never reproduces Onsager's result. Aside from all that, the major contribution of this paper consists in showing for the first time how all the multipolar interactions can be treated exactly in MFT, as well as the nonlinear response due to the rotations of the inclusions, and how all this is related to the pair distributions. That should provide at least a clear starting framework for numerical simulations and models which include only dipole-dipole interactions (which are virtually all). However, for $L > 1$ distributions, such multipolar contributions occur to correspond-

ing orders, and must be similarly determined from the preceding paper.¹

II. RESULTS FOR $L = 0$ AND $L = 1$ PAIR DISTRIBUTIONS

We consider identical inclusions characterized by polarization coefficients $\lambda_{lm}^{l_1 m_1}$ and permanent multipole moments $q_{lm}^{(p)}$ with respect to a given reference frame. The electrical interactions and thermal agitation determine the orientations of the inclusions, hence the average multipole moments. We have obtained the first three derivatives of the average multipole moments with respect to the applied field

$$\sum_{l_1} G_{l_1}^{l_1} \left. \frac{\partial^n \langle q_{l_0}(E_0) \rangle}{\partial E_0^n} \right|_0 = \sqrt{\frac{3}{4\pi}} H_l(n), \quad n = 1, 2, 3, \quad (1)$$

where the configuration matrix is

$$G_{l_1}^{l_1} = \delta_{l_1}^{l_1} - \left(\frac{4\pi}{3} \right) N \Delta_l (\delta_l^1 \delta_1^{l_1} + K_1^{l_1}) \quad (2)$$

and $H_l(n)$ are given in Ref. 1. The effective dielectric function is correspondingly

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

Let us consider in particular a heterogeneous system with an $L = 1$ pair distribution, whereby only $K_1^1 \neq 0$.²⁰ For such a system, Eq. (1) reduces to

$$\left. \frac{\partial^n \langle q_{10}(E_0) \rangle}{\partial E_0^n} \right|_0 - \left(\frac{4\pi}{3} \right) N(1 + K_1^1) \Delta_1(1) \left. \frac{\partial^n \langle q_{10}(E_0) \rangle}{\partial E_0^n} \right|_0 \delta_l^1 = \sqrt{\frac{3}{4\pi}} H_l(n). \quad (4)$$

In this case, we obtain from Eqs. (36), (42), and (48) of Ref. 1

$$H_l(1) = \Delta_1(1) \delta_l^1, \quad (5)$$

$$H_l(2) = 2\Delta_l(2) \left[1 + \left(\frac{4\pi}{3} \right) N(1 + K_1^1) \left. \frac{\partial \langle q_{10}(E_0) \rangle}{\partial E_0} \right|_0 \right]^2, \quad (6)$$

and

$$H_l(3) = 2\Delta_l(3) \left[1 + \left(\frac{4\pi}{3} \right) N(1 + K_1^1) \left. \frac{\partial \langle q_{10}(E_0) \rangle}{\partial E_0} \right|_0 \right]^3. \quad (7)$$

In Eqs. (4)–(7)

$$\begin{aligned} \Delta_l(1) &= \Gamma_l + \frac{\mu_l}{3kT}, \\ \Delta_l(2) &= \frac{1}{2kT} \left(\xi_{l1}^1 + \xi_{l1}^1 + \frac{\nu_{l11}}{3kT} \right), \\ \Delta_l(3) &= \frac{1}{kT} \left\{ 3\eta_{l1}^{11} + \frac{\beta_{l11}^1}{kT} + \frac{\beta_{l11}^1}{2kT} + \frac{\kappa_{l111}}{9(kT)^2} \right. \\ &\quad \left. - [3\Gamma_1^2 + 3\frac{\Gamma_1 \mu_1}{2kT} + \frac{\mu_1^2}{6(kT)^2}] \delta_l^1 \right\}, \end{aligned} \quad (8)$$

where Γ_l , μ_l , $\xi_{ll_2}^{l_1}$, $\nu_{ll_1 l_2}$, $\eta_{ll_2}^{l_1 l_3}$, $\beta_{ll_2 l_3}^{l_1}$, and $\kappa_{ll_1 l_2 l_3}$ are defined in Eqs. (23) of Ref. 1. In particular, we have (see also the Appendix in this paper)

$$\begin{aligned} \Gamma_1 &= \frac{1}{3} (\gamma_{xx} + \gamma_{yy} + \gamma_{zz}) \equiv \bar{\gamma}, \\ \mu_1 &= p_x^2 + p_y^2 + p_z^2 \equiv \mu^2, \\ \xi_{11}^1 &= 0, \\ \nu_{111} &= 0, \\ \eta_{11}^{11} &= \frac{1}{15} [(\gamma_{xx}^2 + \gamma_{yy}^2 + \gamma_{zz}^2) + (\gamma_{xx} + \gamma_{yy})^2 \\ &\quad + (\gamma_{xx} + \gamma_{zz})^2 + (\gamma_{yy} + \gamma_{zz})^2 \\ &\quad + (\gamma_{xy} + \gamma_{yx})^2 + (\gamma_{xz} + \gamma_{zx})^2 + (\gamma_{yz} + \gamma_{zy})^2], \\ \beta_{111}^1 &= \frac{1}{5} [(\gamma_{xx} + \gamma_{yy} + \gamma_{zz})(2p_x^2 + 2p_y^2 + p_z^2) + 2\gamma_{zz} p_z^2], \\ \kappa_{1111} &= \frac{9}{10} \mu^4. \end{aligned} \quad (9)$$

In Eqs. (9), γ_{ij} and p_i ($i, j = x, y, z$) are the Cartesian components of the tensor polarizability and the permanent dipole moment of the inclusions, respectively. Hence, we have

$$\begin{aligned}\Delta_1(1) &= \bar{\gamma} + \frac{\mu^2}{3kT}, \\ \Delta_1(2) &= 0, \\ \Delta_1(3) &= \frac{1}{45kT} \left\{ 2 [(\gamma_{xx} - \gamma_{yy})^2 + (\gamma_{xx} - \gamma_{zz})^2 + (\gamma_{yy} - \gamma_{zz})^2] \right. \\ &\quad \left. + 3 [(\gamma_{xy} + \gamma_{yx})^2 + (\gamma_{xz} + \gamma_{zx})^2 + (\gamma_{yz} + \gamma_{zy})^2 + (2\gamma_{zz} - \gamma_{xx} - \gamma_{yy})(2p_z^2 - p_x^2 - p_y^2) - \mu^4] \right\}. \quad (10)\end{aligned}$$

From Eqs. (4)–(7), we see that all derivatives of the $(l, 0)$ -order average multipole moments are coupled to the derivative of the dipole moment only. As a consequence, the higher multipole moments do not contribute to the effective dielectric function in systems with $L = 1$ pair distributions.

From Eq. (4), we immediately obtain

$$\left. \frac{\partial \langle q_{l0}(E_0) \rangle}{\partial E_0} \right|_0 = \sqrt{\frac{3}{4\pi}} \frac{\Delta_1(1)}{1 - \left(\frac{4\pi}{3}\right) N(1 + K_1^1)\Delta_1(1)} \delta_l^1. \quad (11)$$

The first derivatives vanish for average multipole moments higher than dipoles. Substituting Eq. (11) into Eqs. (6) and (7), respectively, we obtain

$$H_l(2) = \frac{\Delta_l(2)}{\left[1 - \left(\frac{4\pi}{3}\right) N(1 + K_1^1)\Delta_1(1)\right]^2}, \quad (12)$$

and

$$H_l(3) = 2 \frac{\Delta_l(3)}{\left[1 - \left(\frac{4\pi}{3}\right) N(1 + K_1^1)\Delta_1(1)\right]^3}. \quad (13)$$

$$\epsilon_e = \frac{1 + \left(\frac{4\pi}{3}\right) N(2 - K_1^1)\Delta_1(1)}{1 - \left(\frac{4\pi}{3}\right) N(1 + K_1^1)\Delta_1(1)} + \left(\frac{4\pi}{3}\right) N \frac{\Delta_1(3)}{\left[1 - \left(\frac{4\pi}{3}\right) N(1 + K_1^1)\Delta_1(1)\right]^4} E_0^2 + O^*(E_0^4). \quad (16)$$

Equation (16) is the central result of this paper. It can be immediately applied to any system in which the $L = 1$ distribution has been determined (K_1^1), as well as the polarizabilities (γ_{ij}) and the permanent dipole moment (μ) of the inclusions. The denominators in Eq. (16) reflect a multi-inclusion effect, namely the dipole-dipole interactions among the inclusions. This multi-inclusion effect can significantly enhance the effective dielectric function, especially the nonlinear part, depending on the concentration (N) and distribution (K_1^1). The range of K_1^1 is limited by N , since the inclusions occupy a finite volume of the system. For point particles, K_1^1 can vary from -1

Substituting Eqs. (12) and (13), respectively, into Eq. (4), we obtain

$$\left. \frac{\partial^2 \langle q_{10}(E_0) \rangle}{\partial E_0^2} \right|_0 = 0, \quad (14a)$$

$$\left. \frac{\partial^2 \langle q_{l0}(E_0) \rangle}{\partial E_0^2} \right|_0 = 2\sqrt{\frac{3}{4\pi}} \frac{\Delta_l(2)}{\left[1 - \left(\frac{4\pi}{3}\right) N(1 + K_1^1)\Delta_1(1)\right]^2}$$

for $l > 1$, (14b)

and

$$\left. \frac{\partial^3 \langle q_{10}(E_0) \rangle}{\partial E_0^3} \right|_0 = 2\sqrt{\frac{3}{4\pi}} \frac{\Delta_l(3)}{\left[1 - \left(\frac{4\pi}{3}\right) N(1 + K_1^1)\Delta_1(1)\right]^4}, \quad (15a)$$

$$\left. \frac{\partial^3 \langle q_{l0}(E_0) \rangle}{\partial E_0^3} \right|_0 = 2\sqrt{\frac{3}{4\pi}} \frac{\Delta_l(3)}{\left[1 - \left(\frac{4\pi}{3}\right) N(1 + K_1^1)\Delta_1(1)\right]^3}$$

for $l > 1$. (15b)

Finally, substituting Eqs. (11) (with $l = 1$) and (15a) into Eq. (3), we obtain

to 2 [cf. Eq. (44) of Ref. 20]. The distribution effect has not been found in previous theories, since only isotropic distributions have been assumed. In the next section, we apply Eq. (16) to various cases.

III. INCLUSIONS WITHOUT PERMANENT DIPOLE MOMENT

If the inclusions do not have a permanent dipole moment, $q_{1m}^{(p)} = 0$, we have

$$\Delta_1(1) = \bar{\gamma},$$

$$\Delta_1(3) = \frac{1}{45kT} \left\{ 2 [(\gamma_{xx} - \gamma_{yy})^2 + (\gamma_{xx} - \gamma_{zz})^2 + (\gamma_{yy} - \gamma_{zz})^2] + 3 [(\gamma_{xy} + \gamma_{yx})^2 + (\gamma_{xz} + \gamma_{zx})^2 + (\gamma_{yz} + \gamma_{zy})^2] \right\}, \quad (17)$$

and Eq. (16) reduces to

$$\epsilon_e = \frac{1 + \left(\frac{4\pi}{3}\right) N(2 - K_1^1)\bar{\gamma}}{1 - \left(\frac{4\pi}{3}\right) N(1 + K_1^1)\bar{\gamma}} + \left(\frac{4\pi}{3}\right) N \frac{\Delta_1(3)}{\left[1 - \left(\frac{4\pi}{3}\right) N(1 + K_1^1)\bar{\gamma}\right]^4} E_0^2 + O^*(E_0^4). \quad (18)$$

Furthermore, if the pair distribution is isotropic ($L = 0$), $K_1^1 = 0$, and Eq. (18) reduces to

$$\epsilon_e = \frac{1 + \left(\frac{8\pi}{3}\right) N\bar{\gamma}}{1 - \left(\frac{4\pi}{3}\right) N\bar{\gamma}} + \left(\frac{4\pi}{3}\right) N \frac{\Delta_1(3)}{\left[1 - \left(\frac{4\pi}{3}\right) N\bar{\gamma}\right]^4} E_0^2 + O^*(E_0^4). \quad (19)$$

The linear part of Eq. (19) coincides with the Clausius-Mossotti relation. The nonlinear part in Eqs. (18) and (19) exists only for nonspherical inclusions, it is temperature dependent and due to the fact that nonspherical inclusions have a preferred direction to align with the applied field.

IV. INCLUSIONS WITHOUT POLARIZABILITIES

If the inclusions do not have polarizabilities, $\lambda_{1m}^{1m} = 0$, we have

$$\Delta_1(1) = \frac{\mu^2}{3kT}, \quad \Delta_1(3) = -\frac{\mu^4}{15kT}, \quad (20)$$

and Eq. (16) reduces to

$$\epsilon_e = \frac{1 + \left(\frac{4\pi}{3}\right) N(2 - K_1^1) \frac{\mu^2}{3kT}}{1 - \left(\frac{4\pi}{3}\right) N(1 + K_1^1) \frac{\mu^2}{3kT}} - \left(\frac{4\pi}{3}\right) N \frac{\mu^4}{15(kT)^3} \frac{1}{\left[1 - \left(\frac{4\pi}{3}\right) N(1 + K_1^1) \frac{\mu^2}{3kT}\right]^4} E_0^2 + O^*(E_0^4). \quad (21)$$

In this case, the electrical response arises purely from the rotation of the permanent dipole moments. The linear part in Eq. (21) yields the Curie-Weiss-type susceptibility²¹

$$\chi_e = \frac{C}{T - T_c}, \quad (22a)$$

with

$$C = \frac{N\mu^2}{3k} \quad (22b)$$

and

$$T_c = \left(\frac{4\pi}{3}\right) N(1 + K_1^1) \frac{\mu^2}{3k}. \quad (22c)$$

Equation (22c) shows that the critical temperature T_c largely depends on the pair distribution (K_1^1), and even vanishes for pointlike particles with an extreme distribution $K_1^1 = -1$. Also notice that the nonlinear part becomes increasingly important as T_c is approached.

V. SPHERICAL INCLUSIONS

For spherical inclusions with radius a and dielectric function ϵ_p , we have

$$\gamma_{xx} = \gamma_{yy} = \gamma_{zz} = \gamma = \left(\frac{\epsilon_p - 1}{\epsilon_p + 2}\right) a^3$$

and

$$\gamma_{ij} = 0 \quad \text{for } i \neq j. \quad (23)$$

Hence, we have

$$\Delta_1(1) = \gamma + \frac{\mu^2}{3kT}, \quad \Delta_1(3) = -\frac{\mu^4}{15(kT)^3}. \quad (24)$$

In this case, Eq. (16) reduces to

$$\epsilon_e = \frac{1 + \left(\frac{4\pi}{3}\right) N(1 + K_1^1) \left(\gamma + \frac{\mu^2}{3kT}\right)}{1 - \left(\frac{4\pi}{3}\right) N(1 + K_1^1) \left(\gamma + \frac{\mu^2}{3kT}\right)} - \left(\frac{4\pi}{3}\right) N \frac{\mu^4}{15(kT)^3} \frac{1}{\left[1 - \left(\frac{4\pi}{3}\right) N(1 + K_1^1) \left(\gamma + \frac{\mu^2}{3kT}\right)\right]^4} E_0^2 + O^*(E_0^4). \quad (25)$$

If the pair distribution is isotropic, $K_1^1 = 0$, and Eq. (25) further reduces to

$$\epsilon_e = \frac{1 + \left(\frac{8\pi}{3}\right) N \left(\gamma + \frac{\mu^2}{3kT}\right)}{1 - \left(\frac{4\pi}{3}\right) N \left(\gamma + \frac{\mu^2}{3kT}\right)} - \left(\frac{4\pi}{3}\right) N \frac{\mu^4}{15(kT)^3} \frac{1}{\left[1 - \left(\frac{4\pi}{3}\right) N \left(\gamma + \frac{\mu^2}{3kT}\right)\right]^4} E_0^2 + O^*(E_0^4). \quad (26)$$

The linear part in Eq. (26) coincides with Debye's effective dielectric function. This shows that Debye's result is correct to the first order in E_0 and consistent with MFT for isotropic pair distributions. Our result (16) generalizes Debye's effective dielectric function to cases of nonspherical inclusions with anisotropic $L = 1$ pair distribution, and includes the nonlinear response. On the other hand, the results of the cavity model introduced by Onsager are never recovered in MFT.

VI. CONCLUSIONS

We have provided the rigorous mean field theory result for the electrical response of heterogeneous systems in which the inclusions have arbitrary structure and permanent multipole moments of all orders, with $L = 0$ and $L = 1$ pair distributions in their positions. We have shown that in such systems the higher multipole moments do not contribute to the effective dielectric function. We have provided the explicit expression for both the linear and the nonlinear part of effective dielectric function, in terms of the applied electric field and temperature. Our results show that the pair distribution can affect the effective dielectric function significantly. We have

also provided results for particular systems, generalizing the Clausius-Mossotti relation, the Curie-Weiss law, and Debye's effective dielectric function, to account for nonspherical inclusions, nonspherical pair distributions, and nonlinear response. Debye's original effective dielectric function coincides in particular with the linear part of our result, in the case of spherical inclusions and isotropic pair distributions. We do not recover Onsager's result in mean field theory.

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APPENDIX

The results in Eq. (9) can be either deduced from the general expressions in Appendix B of Ref. 1, or obtained directly from the definition as follows. Using Eqs. (6), (7), and (23) of Ref. 1, we obtain

$$\begin{aligned} \Gamma_1 &= \frac{1}{8\pi^2} \int \lambda_{10}^{10}(\tau) d\tau = \frac{1}{8\pi^2} \left(\frac{4\pi}{3}\right) \sum_{m_1 m_2} (-1)^{m_1} \lambda_{1-m_1}^{1m_2} \int Y_{1,m_1}(\beta, \gamma) Y_{1,m_2}(\beta, \gamma) d\tau \\ &= \frac{1}{3} \sum_m \lambda_{1m}^{1m} = 8\pi^2 \frac{1}{3} (\gamma_{xx} + \gamma_{yy} + \gamma_{zz}) \equiv 8\pi^2 \bar{\gamma}, \end{aligned} \quad (A1)$$

$$\begin{aligned} \mu_1 &= \frac{1}{2\pi} \int [q_{10}^{(p)}(\tau)]^2 d\tau = \left(\frac{4\pi}{3}\right) \sum_{m_1} q_{1m_1}^{(p)*} \sum_{m_2} q_{1m_2}^{(p)*} \int Y_{1,m_1}(\beta, \alpha) Y_{1,m_2}(\beta, \alpha) d\tau \\ &= 4\pi \frac{1}{3} \sum_m q_{1m} q_{1m}^* = (p_x^2 + p_y^2 + p_z^2) \equiv \mu^2, \end{aligned} \quad (A2)$$

$$\begin{aligned} \xi_{11}^1 &= \frac{1}{4\pi^2} \sqrt{\frac{4\pi}{3}} \int \lambda_{10}^{10}(\tau) q_{10}^{(p)}(\tau) d\tau \\ &= \frac{4}{9} \sum_{m m_1} \lambda_{1m}^{1m_1} \sum_{m_2} q_{1m_2}^{(p)} \int Y_{1,m}^*(\beta, \gamma) Y_{1,m_1}(\beta, \gamma) Y_{1,m_2}^*(\beta, \alpha) d(\cos \beta) d\gamma d\alpha \\ &= \frac{8\pi}{9} \sum_m \lambda_{1m}^{1m} q_{10}^{(p)} \int Y_{1,m}^*(\Omega) Y_{1,m}(\Omega) Y_{1,0}(\Omega) d\Omega = 0, \end{aligned} \quad (A3)$$

$$\begin{aligned} \nu_{111} &= \frac{1}{2\pi} \sqrt{\frac{4\pi}{3}} \int [q_{10}^{(p)}(\tau)]^3 d\tau \\ &= \left(\frac{4\pi}{3}\right) \sum_{m m_1 m_2} q_{1m}^{(p)} q_{1m_1}^{(p)} q_{1m_2}^{(p)} \int Y_{1,m}^*(\Omega) Y_{1,m_1}^*(\Omega) Y_{1,m_2}^*(\Omega) d\Omega = 0, \end{aligned} \quad (A4)$$

$$\begin{aligned}
\eta_{11}^{11} &= \frac{1}{8\pi^2} \int [\lambda_{10}^{10}(\tau)]^2 d\tau = \frac{4\pi}{9} \sum_{m_1 m_2} \lambda_{1m_1}^{1m_2} \sum_{m_3 m_4} \lambda_{1m_3}^{1m_4} \times \int Y_{1,m_1}^*(\Omega) Y_{1,m_2}(\Omega) Y_{1,m_3}^*(\Omega) Y_{1,m_4}(\Omega) d\Omega \\
&= \frac{1}{15} \left(3\lambda_{10}^{10} \lambda_{10}^{10} + 2\lambda_{10}^{10} \lambda_{1-1}^{1-1} + 2\lambda_{10}^{10} \lambda_{11}^{11} - 2\lambda_{10}^{11} \lambda_{10}^{1-1} + 2\lambda_{10}^{11} \lambda_{11}^{10} \right. \\
&\quad \left. + 2\lambda_{10}^{1-1} \lambda_{1-1}^{10} - 2\lambda_{11}^{10} \lambda_{1-1}^{10} + 4\lambda_{1-1}^{11} \lambda_{11}^{1-1} + 2\lambda_{1-1}^{1-1} \lambda_{1-1}^{1-1} + 4\lambda_{11}^{11} \lambda_{1-1}^{1-1} + 2\lambda_{11}^{11} \lambda_{11}^{11} \right) \\
&= \frac{1}{15} \left[3(\gamma_{xx}^2 + \gamma_{yy}^2 + \gamma_{zz}^2) + 2(\gamma_{xx}\gamma_{yy} + \gamma_{xx}\gamma_{zz} + \gamma_{yy}\gamma_{zz}) \right. \\
&\quad \left. + 2\gamma_{xy}\gamma_{yx} + 2\gamma_{xz}\gamma_{zx} + 2\gamma_{yz}\gamma_{zy} + \gamma_{xy}^2 + \gamma_{yx}^2 + \gamma_{xz}^2 + \gamma_{zx}^2 + \gamma_{yz}^2 + \gamma_{zy}^2 \right], \tag{A5}
\end{aligned}$$

$$\begin{aligned}
\beta_{111}^{11} &= \frac{1}{2\pi} \int \lambda_{10}^{10}(\tau) [q_{10}^{(p)}(\tau)]^2 d\tau = \frac{8\pi}{9} \sum_{m_1 m_2} \lambda_{1m_1}^{1m_2} \sum_{m_3} q_{1m_3}^{(p)} \sum_{m_4} q_{1m_4}^{(p)} \\
&\quad \times \int Y_{1,m_1}^*(\beta, \gamma) Y_{1,m_2}(\beta, \gamma) Y_{1,m_3}^*(\beta, \alpha) Y_{1,m_4}^*(\beta, \alpha) d\cos\beta d\gamma d\alpha = \frac{4\pi}{15} \\
&\quad \times \left[3\lambda_{10}^{10} q_{10}^{(p)} q_{10}^{(p)} - 2\lambda_{10}^{10} q_{11}^{(p)} q_{1-1}^{(p)} + \lambda_{1-1}^{1-1} q_{10}^{(p)} q_{10}^{(p)} + \lambda_{11}^{11} q_{10}^{(p)} q_{10}^{(p)} - 4\lambda_{1-1}^{1-1} q_{11}^{(p)} q_{1-1}^{(p)} - 4\lambda_{11}^{11} q_{11}^{(p)} q_{1-1}^{(p)} \right] \\
&= \frac{1}{5} \left[(\gamma_{xx} + \gamma_{yy} + 3\gamma_{zz}) p_z^2 + (2\gamma_{xx} + 2\gamma_{yy} + \gamma_{zz}) (p_x^2 + p_y^2) \right], \tag{A6}
\end{aligned}$$

$$\begin{aligned}
\kappa_{1111} &= \int [q_{10}^{(p)}(\tau)]^4 d\tau = 2\pi \left(\frac{4\pi}{3} \right)^2 \sum_{m_1} q_{1m_1}^{(p)} \sum_{m_2} q_{1m_2}^{(p)} \sum_{m_3} q_{1m_3}^{(p)} \sum_{m_4} q_{1m_4}^{(p)} \\
&\quad \times \int Y_{1,m_1}^*(\Omega) Y_{1,m_2}^*(\Omega) Y_{1,m_3}^*(\Omega) Y_{1,m_4}^*(\Omega) d\Omega \\
&= \frac{8\pi^2}{5} \left\{ [q_{10}^{(p)}]^4 - [q_{10}^{(p)}]^2 q_{11}^{(p)} q_{1-1}^{(p)} + 12 [q_{11}^{(p)}]^2 [q_{1-1}^{(p)}]^2 \right\} \\
&= \frac{9}{10} [p_x^4 + p_y^4 + p_z^4 + 2(p_x^2 p_y^2 + p_x^2 p_z^2 + p_y^2 p_z^2)] = \frac{9\mu^4}{10}. \tag{A7}
\end{aligned}$$

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