Dielectric virial expansion of polarizable dipolar spheres

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The dielectric virial expansion is developed for composite systems with embedded interacting dielectric dipolar spheres. Introducing a multiple-scattering expansion for the polarization energy in the presence of an external field enables the derivation of a virial expansion for the polarizability. Substituting the polarizability into the Clausius-Mossotti relation yields the virial series for the effective medium permittivity. When the dipole moment of the particles or inclusions vanishes, the leading-order term in the series reduces to the Maxwell-Garnett mixing rule, whereas the higher-order terms provide corrections that become important at higher densities. The dielectric virial coefficients are readily evaluated by replacing the surface charge contributions with image lines. Numerical data are presented for the second virial coefficients to illustrate the effects of polarization. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5035551>

I. INTRODUCTION

The polarization is defined as the dipole moment per unit volume and, thus, characterizes the response of a dielectric material to an applied electric field. Given a static electric field $E_0(\mathbf{r})$, the major contributions to the polarization of dielectric materials arise from the distortion of the charge distribution and the reorientation of the polar constituents. In the linear regime, the polarization is proportional to the electric susceptibility $\chi(\mathbf{r})$ as $\mathbf{P}(\mathbf{r}) = \epsilon_0 \chi(\mathbf{r}) \mathbf{E}(\mathbf{r})$. The susceptibility $\chi(\mathbf{r})$ is in general a tensor, but reduces to a scalar for isotropic systems. In practice, the relative dielectric permittivity, which is defined by $\epsilon \equiv \chi + 1$, is widely used to parameterize how a dielectric material attenuates electric fields.¹

The present work focuses on the effective dielectric permittivity for composite containing polarizable spherical inclusions dispersed in a macroscopically homogeneous dielectric medium. Evaluating the effective dielectric permittivity for such a composite has played a central role in studies of composite dielectric capacitors² and with regards to the dielectric properties of various particulate fluids, such as the width of the depletion region in colloidal quantum dot films used for photovoltaics,³ the solvating capability of polar liquids,⁴ and the mechanical properties of electrorheological fluids.⁵

Theoretical studies of the effective dielectric permittivity have relied on the Maxwell-Garnett (M-G)⁶ or Rayleigh⁷ mixing rule and many of its empirical variants,^{8,9} such as the Bruggeman mixing rule.¹⁰ The M-G mixing rule is essentially the Debye expression for the dielectric permittivity of gases applied to non-polar molecules.¹¹ It is built on the Clausius-Mossotti¹ relation that links the inclusion polarizability to

the medium permittivity and approximates the polarizability with that of isolated particles. The original M-G mixing rule assumes spherical inclusions and neglects interactions between neighboring particles.

Various theoretical^{12,13} and numerical^{2,14} efforts have sought to explain impacts of molecular parameters, such as particle shape, density fluctuations, and dipole-dipole interaction. When the mismatch between host and inclusion permittivities is small, then regardless of the shape of inclusion, a 1/3 mixing rule (Sec. 9, Ref. 1) can be applied.

The first applications of more systematic density expansions have been devoted to the study of dielectric properties of polarizable molecular liquids. The statistical treatments of polarizable molecules and inclusions are analogous, as they are commonly parameterized by their size and polarizability. The early work of Kirkwood¹⁵ focuses on polarizable non-polar molecules and develops an expansion of the average dipole moment and medium permittivity in terms of the molecular polarizability. Along the same lines, Onsager¹⁶ and Kirkwood¹⁷ have further investigated the permittivity of fluids containing polar molecules.

Later on, Buckingham and Pople¹⁸ developed a dielectric virial expansion for non-polar molecules using an approach analogous to the virial expansion for low pressure liquids, which includes the contributions from interactions among polarized molecules. Buckingham and Joslin^{19,20} have carried out more extensive analyses in order to derive expressions for the second¹⁹ and the third²⁰ dielectric virial coefficients for non-polarizable dipolar hard-sphere fluids. Calculating the higher-order dielectric virial coefficients requires the evaluation of high-dimensional quadratures, a difficulty that can be alleviated by the use of a Monte Carlo sampling algorithm developed recently.²¹ However, most of these prior calculations are restricted to systems with non-polarizable molecules/inclusions. We provide a fully systemic

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analysis to evaluate the currently lacking contributions to the dielectric virial expansion for polarizable polar particles (with a nonzero size) through third-order in the density of the molecules/inclusions.

The present advances have become possible because of the recent development of a multiple-scattering formalism^{22,23} for studying interfacial polarization in a medium with sharp dielectric interfaces. The interfacial polarization has been shown to affect the aggregation of colloids^{24–26} and emulsions.²⁷ The multiple-scattering approach resolves polarization by iteratively solving the boundary value problem of Poisson's equation and provides a transparent protocol for decomposing the total interaction energy into sums of contributions from clusters of small numbers of particles. Furthermore, when the inclusions are spherical, the surface integrals representing the effects of interfacial charge polarization can be exactly and efficiently evaluated using image line charges. This formalism paves the way for developing virial expansions for the dielectric permittivity in media with polarizable polar inclusions.

With the aim of combining the multiple-scattering formalism and the dielectric virial expansion to study many-body systems of *polarizable* particles, this paper is organized as follows. First, we summarize the framework for developing the dielectric virial expansions in Sec. II. Second, we generalize the original multiple-scattering formalism for inclusions of polarizable dipolar particles to describe systems under an externally applied electrical field in Sec. III. Section IV provides explicit expressions for the first three dielectric virial coefficients and presents a comparison between theory and experimentally measured permittivities. The Sec. V summarizes our main findings.

II. DIELECTRIC VIRIAL EXPANSION: GENERAL PROCEDURE

The system studied consists of spherical polarizable particles embedded inside a medium with a dielectric permittivity ϵ_{out} , as illustrated in Fig. 1. Although the theory developed in the following applies to the more general case of heterogeneous particles, for simplicity, we treat all particles as identical. The radius of the particle and the permittivity are denoted by a and ϵ_{in} , respectively, which fully parameterizes the particle's

FIG. 1. A composite of spherical particles carrying point dipole at particle centers embedded in the continuum dielectric medium with permittivity ϵ_{out} . The particle has an internal permittivity ϵ_{in} . An average polarization $\mathbf{P}$ results from the application of an external field $\mathbf{E}_0$. The composite as a whole exhibits an effective medium permittivity ϵ_m .

polarizability. In practice, the polar particles may carry a net dipole moment μ , resulting in a dipolar fluid. The magnitude of the particle's dipole is fixed, but its orientation is allowed to change. Thus, a particle's orientation ω and position $\mathbf{R}$ constitute its internal degrees of freedom. This model is more general than that employed for polarizable *point* dipoles¹⁸ since it allows the multipolar surface charges to be spontaneously generated.

The effective medium dielectric permittivity ϵ_m depends on the overall polarization of the ensemble of interacting particles. This polarization includes contributions from the response of the permanent dipole moments and the induced surface charges at the interface between particles and the external medium. The existing studies^{18–20,28} on dipolar fluids have considered the contribution from permanent dipoles, by averaging over both configurational and orientational degrees of freedom. We focus now on the contribution from interfacial polarization arising from the discontinuity in the dielectric permittivity at the particle's interfaces.

When the particle number density is low, interactions between particles can be neglected, and the effective permittivity ϵ_m increases linearly with particle number and polarizability. At elevated densities, however, nonlinear terms become important. One way to account for the nonlinearity is to expand the permittivity in terms of the particle number density, analogous to the derivation of the virial expansion for the pressure. The details for obtaining such expansions have been extensively discussed in the literature for non-polarizable dipolar particles.^{18–20,28} To facilitate our discussion for polarizable particles, the key results for the dielectric virial expansion are summarized in the following.

A. Clausius-Mossotti relation for permittivity

The Clausius-Mossotti relation connects the dielectric permittivity of the effective medium ϵ_m with the polarizability α for non-polar particles. The dielectric composite, represented in Fig. 1, depicts the uniform external electric field $\mathbf{E}_0$ that induces the macroscopic polarization $\mathbf{P}$, which is the volume average of the dipole moment imparted to the dielectric particles, i.e., $\mathbf{P} = \rho \alpha \mathbf{E}_0$, where ρ is the particle number density and $\alpha \mathbf{E}_0$ is the induced moment. The particle is assumed to be isotropic, and consequently, the particle's polarizability is a scalar, indicating that $\mathbf{P}$ points along the direction of $\mathbf{E}_0$.

On the other hand, the polarization $\mathbf{P}$ can be calculated using the effective medium permittivity. To see this, consider a spherical cavity in the composite that is sufficiently large to ensure a macroscopic average. The average field strength $\mathbf{E}$ inside this cavity, i.e., the Lorentz field,²⁹ is $\mathbf{E} = \frac{3\epsilon_{\text{out}}}{\epsilon_m + 2\epsilon_{\text{out}}} \mathbf{E}_0$. This average field is further related to the polarization by $\mathbf{P} = (\epsilon_m - \epsilon_{\text{out}})\mathbf{E}$. Combining these equations with the definition of $\mathbf{P}$ in terms of the particle polarizability leads to

$$\frac{\epsilon_m - \epsilon_{\text{out}}}{\epsilon_m + 2\epsilon_{\text{out}}} = \frac{\rho}{3\epsilon_{\text{out}}} \alpha. \quad (1)$$

The above expression essentially relates the medium permittivity with particle polarizability α . If the inter-particle interactions are neglected, as is applicable for low inclusion

densities, the polarizability is given by $\alpha = 4\pi\epsilon_{\text{out}}a^3(\epsilon_{\text{in}} - \epsilon_{\text{out}})/(\epsilon_{\text{in}} + 2\epsilon_{\text{out}})$, and Eq. (1) is identical to the M-G mixing rule.³⁰

More generally, the inter-particle interactions cannot be neglected. In order to extend the Clausius-Mossotti relation, the macroscopic polarization must be evaluated by averaging over an ensemble of particles and then passing to the limit of vanishing field strength E_0 . The polarization can be obtained by differentiating the Helmholtz free energy $\mathcal{F}$ with respect to the external field E_0 ,

$$\mathbf{P} = -\frac{1}{V} \nabla_{E_0} \mathcal{F}|_{V,T}, \quad (2)$$

in the limit of low field strength, $E_0 \rightarrow 0$. Because the system is homogeneous, E_0 and $\mathbf{P}$ are collinear and point in the same direction. Hence, the derivative of $\mathbf{P}$ with respect to E_0 yields the particle polarizability in dipolar fluids.²⁸ After some algebra, the virial expansion for the effective dielectric permittivity emerges from that for the free energy as

$$\frac{\epsilon_{\text{m}} - \epsilon_{\text{out}}}{\epsilon_{\text{m}} + 2\epsilon_{\text{out}}} = A\tilde{\rho} + B\tilde{\rho}^2 + C\tilde{\rho}^3 + \dots \quad (3)$$

Here $\tilde{\rho} \equiv \rho a^3$ is the dimensionless number density and A , B , and C are the first, second, and third dielectric virial expansion coefficients.

B. Polarizability of interacting particles

The original formalism for determining the dielectric virial expansion only considers pairwise interactions, which suffices for treating non-polarizable particles. In order to understand what additions are necessary to describe the effects of polarization on the virial expansion, we detail the steps needed for deriving the dielectric virial expansion and demonstrate that the previous derivation²⁰ for non-polar molecules must be extended to incorporate contributions from the three-body and higher-order electrostatic interactions.²⁰ An auxiliary expression [Eq. (10) below] is also provided to simplify the evaluation of higher-order virial coefficients.

Section II A shows that the combination of the cluster expansion for free energy or the partition function^{31,32} with Eq. (2) naturally yields the dielectric virial expansion. The system is assumed to be subjected to a uniform external field, and the Hamiltonian can be expressed as a sum of contributions from one-, two-, three-body, etc. interactions. Using the notation of Ref. 20, the canonical ensemble partition function of an interacting system in an imposed external field E_0 is expressed as

$$Q_N(V, T, E_0) = \sum_{\{m_\ell\}} \sum_{\ell=1}^N \frac{1}{m_\ell!} \left(\frac{V}{\lambda^3} b_\ell \right)^{m_\ell}, \quad (4)$$

where

$$b_\ell = \frac{1}{\ell! \lambda^{3\ell-3} V} \left\langle \int d\mathbf{R}_1 \dots d\mathbf{R}_\ell U_\ell(1, 2, \dots, \ell) \right\rangle_{\omega_1 \omega_2 \dots \omega_\ell}.$$

Here, N , V , and T are the number of particles, the volume, and the temperature, respectively. The term $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$ is the thermal de Broglie wavelength. The partition index m_ℓ is chosen such that $\sum_\ell m_\ell = N$. The cluster integrals b_ℓ are expressed

in terms of the Ursell functions U_ℓ and involve integration over the full configuration degrees of freedom of the clusters. The terms $\mathbf{R}_1, \mathbf{R}_2$, etc. represent the positions of particles, and $\langle \cdot \rangle_{\omega_1, \omega_2, \dots, \omega_\ell}$ denotes the average over the orientations of the dipolar particles in the cluster. The average over ω is redundant for neutral particles.

The first three Ursell functions are given using the standard notation by

$$U_1(1) = e_1,$$

$$U_2(1, 2) = e_1 e_2 (e_{12} - 1), \quad (5)$$

$$U_3(1, 2, 3) = e_1 e_2 e_3 (e_{12} e_{23} e_{31} e_{123} - e_{12} - e_{23} - e_{31} + 2).$$

The Mayer- e functions provide the statistical weights for the one-, two-, and three-body potentials

$$e_1 \equiv \exp(-\beta u_1), \quad e_{12} \equiv \exp(-\beta u_{12}), \quad e_{123} \equiv \exp(-\beta u_{123}),$$

where $\beta = 1/(k_B T)$. The potentials u_1 , u_{12} , and u_{123} are uniquely specified by the configurations of one-, two-, and three-particle clusters, respectively. The Mayer- f function is defined by $f_{ij} = e_{ij} - 1$. The expression for U_3 differs from that in Ref. 20 by the presence of the extra factor e_{123} , which is absent for non-polarizable fluids. For a system containing non-polarizable dipolar particles, u_1 is $-\mu \cdot E_0$, while u_2 reduces to the interaction energy between a pair of dipoles. The more complicated description of polarizable particles is presented in Sec. II C, along with the exact forms for u_1 , u_{12} , and u_{123} .

The cluster expansion for the free energy follows readily from that for the partition function. Substituting this cluster expansion into Eqs. (1) and (2), the first three virial coefficients are found to be²⁰

$$A = \frac{k_B T}{3\epsilon_{\text{out}} a^3} \lim_{E_0 \rightarrow 0} \nabla_{E_0} b_1 / E_0, \quad (6)$$

$$B = \frac{k_B T}{3\epsilon_{\text{out}} a^3} \left(\frac{\lambda}{a} \right)^3 \lim_{E_0 \rightarrow 0} ([\nabla_{E_0} b_2 - 2b_2 \nabla_{E_0} b_1] / E_0), \quad (7)$$

$$C = \frac{k_B T}{3\epsilon_{\text{out}} a^3} \left(\frac{\lambda}{a} \right)^6 \lim_{E_0 \rightarrow 0} ([\nabla_{E_0} b_3 - 4b_2 \nabla_{E_0} b_2 + (8b_2^2 - 3b_3) \nabla_{E_0} b_1] / E_0). \quad (8)$$

Note that the vacuum permittivity in Ref. 20 has been replaced with the permittivity of the host ϵ_{out} , as required for treating polarizable particles. The equations for the virial coefficients A , B , and C are correct regardless the nature of the remainder of the Hamiltonian, and the details of the interactions enter in the expressions for b_1 , b_2 , and b_3 .

Before proceeding further, we note that formally dividing the gradient terms by a vector E_0 is permitted since the gradient ∇_{E_0} yields a vector pointing along the direction of E_0 . The gradients to be evaluated all have the following structures:

$$\beta \left\langle \left(\sum_{i=1}^m \mu_i \right) e^{\beta E_0 \cdot (\sum_{i=1}^m \mu_i)} \mathcal{K} \right\rangle_{\{\omega_i\}}, \quad (9)$$

where m is the number of particles involved. The average of the Mayer functions over spatial configurations is represented by the generic kernel $\mathcal{K} = \mathcal{K}(\{\mu_1, \mu_2, \dots, \mu_m\})$,

which is invariant with respect to arbitrary spatial rotations, but which depends on the orientations of the dipoles. Explicit examples for $\mathcal{K}$ are provided in Sec. II C when dielectric virial coefficients are evaluated for non-polarizable particles. In Appendix A, it is shown that introducing the limit $E_0 \rightarrow 0$ in the above simplifies the average to

$$\frac{m\beta^2}{3} \left\langle [\mu^2 + (m-1)\mu_1 \cdot \mu_2] \mathcal{K} \right\rangle_{\{\omega_i\}} \quad (10)$$

for an isotropic fluid, which is used below for evaluating the dielectric virial coefficients.

C. Non-polarizable particles

We provide explicit expressions for the lowest order dielectric virial coefficient, which has first been derived in Ref. 28, by applying the general expression presented above. The expressions for the first and the second virial coefficients are identical to the known results. The expression for the third virial coefficient differs because the three-body electrostatic interaction is included.

The first-order term depends on the one-particle cluster integral $b_1 = \langle e^{\beta\mu_1 \cdot E} \rangle_{\omega_1}$, which approaches unity as $E_0 \rightarrow 0$. With the aid of Eqs. (9) and (10), we find that the first-order virial coefficient reduces to

$$A = \frac{k_B T}{3\epsilon_{\text{out}} a^3} \lim_{E_0 \rightarrow 0} \nabla_{E_0} b_1 / E_0 = \frac{\beta}{9\epsilon_{\text{out}} a^3} \mu^2 \quad (11)$$

which has the same form as the Debye polarizability for dipolar molecules.

The second-order term depends on the average of the cluster integral of the form

$$b_2 = \frac{1}{2} \langle e^{\beta(\mu_1 + \mu_2) \cdot E_0} \mathcal{I}_{12} \rangle_{\omega_1, \omega_2}, \quad \mathcal{I}_{12} \equiv \frac{1}{\lambda^3} \int d\mathbf{R}_{12} f_{12}. \quad (12)$$

The zero-field limit is obviously $\frac{1}{2} \langle \mathcal{I}_{12} \rangle_{\omega_1}$. The spatial integral $\mathcal{I}_{12}$ yields a constant that depends on μ_1 and μ_2 , is symmetric with respect to exchange $\mu_1 \leftrightarrow \mu_2$, and is invariant with respect to the sign changes $\mu_1 \rightarrow -\mu_1$ and $\mu_2 \rightarrow -\mu_2$. Applying Eqs. (9) and (10) yields $\nabla_{E_0} b_2 / E_0 \rightarrow \frac{\beta^2}{3} [\mu^2 \langle \mathcal{I}_{12} \rangle_{\omega_2} + \langle \mu_1 \cdot \mu_2 \mathcal{I}_{12} \rangle_{\omega_1 \omega_2}]$ and $[\nabla_{E_0} b_2 - 2b_2 \nabla_{E_0} b_1] / E_0 \rightarrow \frac{\beta^2}{3} \langle \mu_1 \cdot \mu_2 \mathcal{I}_{12} \rangle_{\omega_1 \omega_2}$ in the limit $E_0 \rightarrow 0$. The contribution from “-1” in $\mathcal{I}_{12}$ vanishes since $\langle \mu_1 \cdot \mu_2 \rangle_{\omega_1 \omega_2} = 0$. Keeping it damps the integrand to 0 at large separations R_{12} . Combining these pieces with Eq. (7) yields the expression for the second virial coefficient as

$$B = \frac{4\pi}{9} \beta \left\langle \int d\mathbf{R}_{12} \mu_1 \cdot \mu_2 e_{12} \right\rangle_{\omega_1 \omega_2}. \quad (13)$$

It is evident that the second virial coefficient only depends on the form of two-body potentials through the term e_{12} . As derived in the following, the two-body potential, however, is allowed to contain additional contributions from polarization in our model.

The third-order term follows the same lines of analysis. The lengthy algebra is provided in Appendix B. The final

expression for the third-order virial coefficient is

$$C = \frac{4\pi}{9} \beta \left\langle (\mu_2 \cdot \mu_3) \int d\mathbf{R}_{12} d\mathbf{R}_{13} e_{23} \times (e_{12} e_{31} e_{123} - e_{12} - e_{31} + 1) \right\rangle_{\omega_1 \omega_2 \omega_3}. \quad (14)$$

When the three-body interaction vanishes, $e_{123} = 1$, and the last expression becomes identical to that derived previously for non-polarizable dipolar particles.²⁰ The above analysis also shows that three-body electrostatic interactions are relevant for the third virial coefficients.

The main results above, Eqs. (11), (13), and (14), are applicable to *non-polarizable* systems containing two-body, three-body, etc. electrostatic interactions. However, these results may *not* be applicable to polarizable systems. The Hamiltonian for the latter contains quadratic terms in E_0 , which affects the limiting procedure sketched above, as delineated in Secs. III and IV.

III. ENERGY OF POLARIZABLE PARTICLES IN AN EXTERNAL FIELD

The formalism of Sec. II C relies on the decomposition of system energy in terms of one-, two-, three-body interactions, etc. The recently established multiple-scattering formalism²² for the polarization energy of many-body dipolar particles²³ serves precisely this purpose. The formalism has been developed for a system in the absence of an externally applied field, which suffices for the purpose of evaluating the polarization energy, force, and torque. However, to obtain the virial expansion for the dielectric permittivity, the multiple-scattering formalism must be generalized to include the effects of a homogeneous external field E_0 .

The following begins with a brief review of necessary results from the multiple-scattering formalism for a polarizable dipolar fluid without an external field. Then the discussion passes onto the treatment of polarizable *neutral* particles in a background of a homogeneous external field E_0 . Subsection III C combines the results of the first two and provides the explicit expression to the two- and three-body potentials needed for evaluating the second and third-order dielectric virial coefficients.

A. Dipolar particles without external field

The multiple-scattering formalism for the energy of polarizable particles developed for monopolar²² and dipolar²³ particles is obtained by iteratively solving Poisson's equation. The key result is a series expansion for the total electrostatic energy of the system about the energy in the absence of an external field. The first-order contribution from this series yields the standard solvation energy, which measures the energy cost for inserting the polarizable particles into the dielectric continuum. The second-order contribution represents the direct interaction energy between two particles. The third-order contribution emerges from the interactions involving one polarized surface, etc. The electrostatic energy for a system with dipolar particles $\mathcal{E}(\{\hat{\mu}_i\}, E_0 = 0)$ is found to be expressible as the sum

FIG. 2. Multiple-scattering processes needed for evaluating energies. (a) The one-body energy. (b) The two-body energy, including the direct interaction $\{1; 2\}$ between charges Q_1 and Q_2 and an interaction involving one interfacial scattering, $\{2; 1; 2\}$. The term $\{2; 1; 2\}$ represents the interaction between charge $Q_2(\mathbf{r})$ and the surface charge σ_1 induced on particle 1. (c) The three-body energy: the interaction between charges Q_1 and Q_3 mediated by surface 2.

$$\begin{aligned} \mathcal{E} &= \mathcal{E}_1 + \mathcal{E}_2 + \mathcal{E}_3 + \mathcal{E}_4 + \cdots \\ &= \sum_i \frac{\mu_i^2}{8\pi a_i^3} \frac{2(\epsilon_r - 1)}{\epsilon_r + 2} \\ &\quad + \sum_{i \neq j} \left(\frac{3}{2 + \epsilon_r} \right)^2 \frac{\mu_j \mu_i}{8\pi \epsilon_{\text{out}}} \hat{\mu}_j \cdot \frac{\mathbf{I} - 3\hat{\mathbf{R}}_{ij}\hat{\mathbf{R}}_{ij}}{R_{ij}^3} \cdot \hat{\mu}_i \\ &\quad + \sum_{i \neq k_1, j \neq k_1} \left(\frac{3}{2 + \epsilon_r} \right)^2 \frac{\mu_j \mu_i}{8\pi \epsilon_{\text{out}}} \{j; k_1; i\} \\ &\quad + \sum_{i \neq k_1, k_1 \neq k_2, j \neq k_2} \left(\frac{3}{2 + \epsilon_r} \right)^2 \frac{\mu_j \mu_i}{8\pi \epsilon_{\text{out}}} \{j; k_2 k_1; i\} + \cdots \quad (15) \end{aligned}$$

Here the term $\mathcal{E}_1$ is the solvation energy, which is independent of particle coordinates. The higher-order terms $\mathcal{E}_2, \mathcal{E}_3, \mathcal{E}_4$, etc. by contrast depend on the relative configurations (see Fig. 2). The term μ_i is the dipole moment, and $\epsilon_r \equiv \epsilon_{\text{in}}/\epsilon_{\text{out}}$ is the ratio between the dielectric permittivities of the inclusion and the

host. The vector $\mathbf{R}_{ij}$ is the separation between two particles at the positions $\mathbf{R}_i$ and $\mathbf{R}_j$. The summation runs over all possible permutations of particle indices and no two neighboring indices can be identical.

The second-order term $\mathcal{E}_2$ is the direct interaction between dipoles. The third-order term $\mathcal{E}_3$ involves one polarized surface and is symbolized by the “string” notation.^{22,23} The string of the form $\{j; k; i\}$ can be understood as follows: The electric field emitted from particle i polarizes particle k and induces surface charges; these induced charges then act on particle j (Fig. 2). This string is evaluated using the line integral of the form²³

$$\begin{aligned} \{j; k_1; i\} &= \frac{\epsilon}{(R_{jk_1} R_{ki})^{3/2}} t_{k_1} \left[\delta_{s_{k_1}, 1} - g \int_0^1 ds_{k_1} s_{k_1}^{g-1} \right] \\ &\quad \times \hat{\mu}_j \cdot \mathbf{D}_{ji}^{(k_1)}(s_{k_1} t_{k_1}^2) \cdot \hat{\mu}_i, \quad (16) \end{aligned}$$

in which $t_{k_1}^2 = a_{k_1}^2 / (R_{jk_1} R_{ki})$. The factor $\epsilon \equiv (\epsilon_{\text{out}} - \epsilon_{\text{in}}) / (\epsilon_{\text{in}} + \epsilon_{\text{out}})$ quantifies the relative dielectric discontinuity at the surface of particle k_1 . The terms in the bracket are contributions from the Kelvin image point and Neumann image line,²³ which collectively represent the effects of the interfacial charge polarization on the k_1 surface. The expression for the interaction kernel $\mathbf{D}_{ji}^{(k_1)}$ and those for the higher-order strings are provided in Ref. 23. By analogy, the strings involving two surface scatterings needed by the fourth-order term $\mathcal{E}_4$ is given by

$$\begin{aligned} \{j; k_2 k_1; i\} &= \frac{\epsilon^2}{(R_{jk_2} R_{ki})^{3/2}} \\ &\quad \times \mathcal{I}_{k_2} \mathcal{I}_{k_1} \hat{\mu}_j \cdot \mathbf{D}_{ji}^{(k_2, k_1)}(\{s_k t_k^2\}) \cdot \hat{\mu}_i, \quad (17) \end{aligned}$$

where $\mathcal{I}_k \equiv t_k [\delta_{s_k, 1} - g \int_0^1 ds_k s_k^{g-1}]$ represents the contribution of the surface charge on the k th interface. More generally, an $(n + 2)$ th-order interaction kernel $\mathbf{D}_{ji}^{(k_n, k_{n-1}, \dots, k_2, k_1)}$ is related to the string of the type by

$$\{j; k_n k_{n-1} \cdots k_2 k_1; i\} = \frac{\epsilon^n}{(R_{jk_n} R_{ki})^{3/2}} \mathcal{I}_{k_n} \mathcal{I}_{k_{n-1}} \cdots \mathcal{I}_{k_2} \mathcal{I}_{k_1} \hat{\mu}_j \cdot \mathbf{D}_{ji}^{(k_n, k_{n-1}, \dots, k_2, k_1)}(\{s_k t_k^2\}) \cdot \hat{\mu}_i. \quad (18)$$

The one-dimensional s -integrals involved in the definition of strings and $\mathcal{I}_k$ terms can be evaluated using a convenient quadrature rule. Retaining terms from the Taylor series of the integrand through twentieth order in s ensures convergence.²³

This multiple-scattering formalism naturally decomposes the total energy for a given configuration into a sum of interactions among a small number of particles, making it possible to develop the cluster expansion for the free energy in the absence of an external field. Next, we show how this formalism is generalized when the external field is present. The results are presented first for neutral particles and then for dipolar particles. The notation follows closely that used in the discussion above.

B. Polarizable neutral particles in an external field

For the sake of clarity, we set the dipole moments in the system sketched in Fig. 1 to zero and consider the energy of the system under a uniform electric field $\mathbf{E}_0$. The polarization energy resulting from embedding the dielectric particles into the matrix is given by the difference of the total energy after and before particle embedding (Sec. 9, Ref. 1),

$$\mathcal{E} - \mathcal{E}_0 = -\frac{1}{2} \mathbf{E}_0 \cdot \int d\mathbf{r} (\mathbf{D}(\mathbf{r}) - \epsilon_{\text{out}} \mathbf{E}(\mathbf{r})). \quad (19)$$

Here the integration range is the whole system. The displacement $\mathbf{D}(\mathbf{r})$ is the product of the local field strength $\mathbf{E}(\mathbf{r})$ and the local dielectric permittivity $\epsilon(\mathbf{r})$. Since dielectric heterogeneity in the system is caused by particulate inclusion, the above

energy difference can be written as

$$\mathcal{E} - \mathcal{E}_0 = -\frac{1}{2} \sum_i (\epsilon_{\text{in}} - \epsilon_{\text{out}}) \mathbf{E}_0 \cdot \int_i d\mathbf{r} \mathbf{E}(\mathbf{r}). \quad (20)$$

Here the summation over i runs over all particles in the system and “ $\int_i$ ” means integration over the volume of particle i . Since $\mathcal{E}_0$ amounts to a constant shift in energy, for notational simplicity, let $\mathcal{E}$ denote $\mathcal{E} - \mathcal{E}_0$ from now on. This shift does not affect any statistical property of interest. Since $\mathbf{E}_0$ is a given constant, a multiple-scattering expansion is required only for the field $\mathbf{E}(\mathbf{r})$.

In full analogy with the expansion for the potential of monopolar and dipolar particles, the electric field $\mathbf{E}(\mathbf{r})$ can be written as a sum of the source field $\mathbf{E}_0$ and contributions due to interfacial polarization at the surface of each sphere. The interfacial polarization may be caused by one or multiple intermediate “scattering” events. Consequently, the required field strength at a point inside a particle j , which is needed by Eq. (20), may be written in the string notation as

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0 + \{\mathbf{r}; j; \mathbf{E}_0\} + \sum_{i; i \neq j} \{\mathbf{r}; i; \mathbf{E}_0\} + \sum_{k, i; k \neq j, k \neq i} \{\mathbf{r}; ki; \mathbf{E}_0\} + \cdots \quad (21)$$

The first term is the source field. The second term is the electric field due to the induced surface charge on particle j , i.e., the one containing the position vector $\mathbf{r}$. The third term is the electric field due to the surface charge on particle i ($i \neq j$) that has been polarized by the field $\mathbf{E}_0$. The fourth term follows the same logic and, in principle, any number of intermediate scattering surfaces is allowed. Note that, following the convention of our previous work,²³ the summation over repeated scattering on the same surface is implicit in the above. Therefore, for instance, $\{\mathbf{r}; i; \mathbf{E}_0\}$ represents the sum of all terms of the nature $\{\mathbf{r}; i; \mathbf{E}_0\}$, $\{\mathbf{r}; ii; \mathbf{E}_0\}$, $\{\mathbf{r}; iii; \mathbf{E}_0\}$, etc. The leading terms contributing to the field at $\mathbf{r}$ are illustrated in Fig. 3.

1. One particle polarized by an external field

The string of the form $\{\mathbf{r}; i; \mathbf{E}_0\}$ gives the electric field produced by the polarized surface i . When $\mathbf{r}$ is outside sphere i , the electric field produced by surface charge on particle i is

FIG. 3. Multiple-scattering processes needed for evaluating an electric field inside particle j , symbolized by the terms in Eq. (21). (a) The source and the field scattered by surface j and (b) the field from the neighboring polarized surface i .

the same as that produced by a dipole $\mathbf{p}$ placed at the center of particle i .²⁹ The dipole $\mathbf{p}$ is parallel to $\mathbf{E}_0$,

$$\mathbf{p} = \alpha \mathbf{E}_0, \quad \alpha = 4\pi\epsilon_{\text{out}} a^3 \frac{\epsilon_r - 1}{\epsilon_r + 2}, \quad (22)$$

where α is the polarizability of particle i . The field produced by the induced dipole is

$$\{\mathbf{r}; i; \mathbf{E}_0\} = -\frac{1}{4\pi\epsilon_{\text{out}}} \frac{(\mathbf{r} - \mathbf{R}_i)^2 - 3(\mathbf{r} - \mathbf{R}_i)(\mathbf{r} - \mathbf{R}_i)}{|\mathbf{r} - \mathbf{R}_i|^5} \cdot \mathbf{p}. \quad (23)$$

On the other hand, if $\mathbf{r}$ is inside the polarized sphere, the electric field is a constant

$$\{\mathbf{r}; j; \mathbf{E}_0\} = \frac{3}{\epsilon_r + 2} \mathbf{E}_0. \quad (24)$$

The above two expressions show how the second and the third terms in Eq. (21) are evaluated. Appendix C verifies these known results using the multiple-scattering formalism.

2. Polarization energy of one particle

The energy due to polarization on one particle can be evaluated using Eq. (20). The required information is the dot product of the external field $\mathbf{E}_0$ and the integral of the electrical field inside the particle of interest. If the field is caused by surface charge induced directly by $\mathbf{E}_0$, Eq. (24) is used, producing

$$-\frac{1}{2}(\epsilon_{\text{in}} - \epsilon_{\text{out}}) \mathbf{E}_0 \cdot \int d\mathbf{r} \{\mathbf{r}; j; \mathbf{E}_0\} = -\frac{1}{2} \alpha \mathbf{E}_0^2, \quad (25)$$

which is the self-energy caused by creating the dipole in the medium.

If the field is caused instead by surface charges on a different particle, we may consider the effect of all the point sources outside separately. The polarization on sphere j due to a charge q at position $\mathbf{R}$ is given by strings of the form

$$-\frac{1}{2}(\epsilon_{\text{in}} - \epsilon_{\text{out}}) \mathbf{E}_0 \cdot \int d\mathbf{r} (\{\mathbf{r}; \mathbf{R}\} + \{\mathbf{r}; j; \mathbf{R}\} + \{\mathbf{r}; jj; \mathbf{R}\} \cdots). \quad (26)$$

The first term in the bracket is the field produced by the source charge q at $\mathbf{R}$, i.e., $\{\mathbf{r}; \mathbf{R}\} = \frac{q}{4\pi\epsilon_{\text{out}}} \frac{\mathbf{r} - \mathbf{R}}{|\mathbf{r} - \mathbf{R}|^3}$. The second term is the primary surface charge on particle j induced by source charge at $\mathbf{R}$. The third term is the secondary surface charge on particle j induced by the primary surface charges. The higher-order terms are defined by analogy. As described by Eqs. (23)–(25) of Ref. 23, the electric field generated by the sum of all repeated interfacial polarization, i.e., $\{\mathbf{r}; j; \mathbf{R}\} + \{\mathbf{r}; jj; \mathbf{R}\} + \cdots$, can be written as

$$\frac{q}{4\pi\epsilon_{\text{out}}} \frac{1 - \epsilon_r}{1 + \epsilon_r} \left(\delta_{f,1} - g \int_0^1 df f g^{f-1} \right) \frac{f(f\mathbf{r} - \mathbf{R})}{|f\mathbf{r} - \mathbf{R}|^3}. \quad (27)$$

The integration over “ $\mathbf{r}$ ” can be processed by noticing that the integration of the electrical field inside a sphere produced by point sources outside the sphere equals the field evaluated at the center of the sphere multiplied by the volume of the sphere. Therefore, the integration “ $\int d\mathbf{r}$ ” in Eq. (26) can be completed first, producing

$$\frac{q}{4\pi\epsilon_{\text{out}}} \frac{4\pi a^3}{3} \left[1 + \frac{1 - \epsilon_r}{1 + \epsilon_r} \left(\delta_{f,1} - g \int_0^1 df f g^{f-1} \right) f \right] \frac{\mathbf{R}_j - \mathbf{R}}{|\mathbf{R}_j - \mathbf{R}|^3}. \quad (28)$$

The integral in the square bracket can be explicitly combined. Further contraction with the external field $\mathbf{E}_0$, as needed by Eq. (26), leads to

$$-\frac{1}{2}(\alpha\mathbf{E}_0) \cdot \left(\frac{q}{4\pi\epsilon_{\text{out}}} \frac{\mathbf{R}_j - \mathbf{R}}{|\mathbf{R}_j - \mathbf{R}|^3} \right). \quad (29)$$

This result implies that the polarization energy of particle j is effectively the energy of a dipole $\mathbf{p} = \alpha\mathbf{E}_0$ placed at the center of the particle in the field produced by the sources outside the particle. Equations (23), (25), and (29) are the main results needed to treat the virial coefficients of polarizable spherical particles in an external field. This finding further demonstrates that the interaction between the external field and the spherical particles can be exactly represented by the interaction between the imposed electric field and the particle's polarizability α .

C. Polarizable dipolar particles in an external field

The above discussion suggests that, within the multiple-scattering formalism, a spherical particle polarized by homogeneous field $\mathbf{E}_0$ behaves as a dipole $\mathbf{p} = \alpha\mathbf{E}_0$ placed at the particle center. This is true both when the particle serves as the source of a polarizing field (the right end of a string) and serves as the evaluation point for the polarization energy (the left end of a string). Consequently, the multiple-scattering formulation for the total energy of polarizable dipolar particles in an external field can be formally written as

$$\mathcal{E}(\{\hat{\mu}_i\}, \mathbf{E}_0) = \mathcal{U}_1 + \mathcal{U}_2 + \mathcal{U}_3 + \cdots \quad (30)$$

The leading term $\mathcal{U}_1$ is the one-body, or solvation energy, which includes contributions from polarization of one particle by the external field Eq. (25), the interaction between the embedded dipole and Eq. (24) and the self-energy of the dipole [Eq. (32), Ref. 23],

$$\mathcal{U}_1 = - \sum_i \left(\frac{\alpha_i}{2} \mathbf{E}_0^2 + \frac{3}{\epsilon_r + 2} \boldsymbol{\mu}_i \cdot \mathbf{E}_0 \right) + \sum_i \left(\frac{\mu_i^2}{4\pi a^3 \epsilon_{\text{in}}} \frac{\epsilon_r - 1}{\epsilon_r + 2} \right). \quad (31)$$

The index i runs over all particles, and the subscript on α_i is relevant for the consideration of heterogeneous spherical particles. The first sum depending on the external field describes the dielectric response, while the second sum amounts to a constant shift in the total energy and can be neglected.

The two-body and higher-order interactions are formally described by the same expression as in the absence of external field, apart from the replacement

$$\boldsymbol{\mu} \rightarrow \tilde{\boldsymbol{\mu}} \equiv \frac{3}{\epsilon_r + 2} \boldsymbol{\mu} + \alpha\mathbf{E}_0. \quad (32)$$

Thus the two-body energy reads

$$\mathcal{U}_2 = \sum_{(i,j)}^{i \neq j} (\{i; j\} + \{i; j; i\} + \{j; i; j\} + \{j; i; j; i\} \cdots). \quad (33)$$

The term $\{i; j\}$ is the interaction between dipoles $\tilde{\boldsymbol{\mu}}_i$ and $\tilde{\boldsymbol{\mu}}_j$, and the term $\{i; j; i\}$ is the interaction between $\tilde{\boldsymbol{\mu}}_i$ and itself,

mediated by the surface of particle j . By analogy, the three-body energy reads

$$\mathcal{U}_3 = \sum_{(i,j,k)}^{i \neq j, i \neq k, j \neq k} (\{i; k; j\} + \{j; i; k\} + \{k; j; i\} + \cdots). \quad (34)$$

The higher-order interactions are constructed similarly. Note that, compared to Eq. (15), the factors preceding the strings have been absorbed into the definition of $\tilde{\boldsymbol{\mu}}$. The exact expressions needed for evaluating these strings are provided in Sec. IV. We note that $\mathcal{U}_2$ and $\mathcal{U}_3$ are distinct from $\mathcal{E}_2$ and $\mathcal{E}_3$: the latter is grouped according to the number of polarized interfaces, whereas the former is grouped according to the number of particles needed to specify the configuration.

IV. DIELECTRIC VIRIAL EXPANSION: POLARIZABLE PARTICLES

The multiple-scattering formalism for the energy of a many-body system of polarizable dipolar particles provides a convenient starting point for deriving the first three coefficients of the dielectric virial expansion. Subsection IV A explains how the dielectric virial coefficients are evaluated by applying Eqs. (11), (13), and (14). Numerical results are provided for illustrative purpose.

A. The first virial coefficient

The first virial coefficient is determined by the one-body potential u_1 . Since the inconsequential self-energy of a dipole is dropped, the one-body energy u_1 can be extracted from Eq. (31) which yields the cluster function b_1 as

$$b_1 = \left\langle \frac{1}{V} \int d\mathbf{R}_1 \exp(-\beta u_1) \right\rangle_{\omega_1} = \left\langle \exp \left(\frac{\beta}{2} \alpha \mathbf{E}_0^2 + \frac{3\beta}{\epsilon_r + 2} \boldsymbol{\mu}_1 \cdot \mathbf{E}_0 \right) \right\rangle_{\omega_1}. \quad (35)$$

An average is performed over the orientations ω_1 of the permanent dipole. The limiting value of b_1 apparently equals unity, and the first dielectric virial coefficient becomes [Eq. (6)]

$$A = \frac{1}{3\epsilon_{\text{out}} a^3} \left[\alpha + \frac{\beta}{3} \left(\frac{3}{\epsilon_r + 2} \right)^2 \mu^2 \right]. \quad (36)$$

Apart from the factor $3/(\epsilon_r + 2)$, this result was first derived by Debye for gases.^{11,16} The first term in the square brackets is recognized as the M-G mixing rule. The second term is the polarizability produced by the permanent dipoles, which scales inversely with temperature. The factor ϵ_r depends on relative permittivity and measures the degree of screening of the dipole moment by its own surface.²³

B. The second virial coefficient

The second dielectric virial coefficient depends on both one-body and two-body potentials. The cluster integral to be evaluated is

$$b_2 = \frac{1}{2\lambda^3} \left\langle e^{-\beta u_1} e^{-\beta u_2} \int d\mathbf{R}_{12} (e^{-\beta u_{12}} - 1) \right\rangle_{\omega_1 \omega_2}, \quad (37)$$

where the one-body energies for particles 1 and 2 are u_1 and u_2 , respectively, and they have the same form as for the first-order virial coefficient above. The two-body energy contains

both dipole-dipole interactions and the contributions from the polarization of the dipoles, which are obtained from Eq. (33) and can be expressed as

$$u_{12} = \{1; 2\} + \{1; 2; 1\} + \{2; 1; 2\} + \cdots \quad (38)$$

The first term contains the direct dipole-dipole interaction. The second and the third terms are the corrections to the self-energy due to the presence of the second particle. For simplicity, contributions are retained only of strings containing one interfacial scattering. The higher-order corrections, e.g., $\{1; 2; 1; 2\}$, etc., can be safely omitted at low densities where the dielectric virial expansion is practical for application.

The direct dipole-dipole interaction term has the standard form

$$\{1; 2\} = \tilde{\mu}_1 \cdot \mathcal{D}_{12} \cdot \tilde{\mu}_2, \quad \mathcal{D}_{12} \equiv \frac{\mathbf{I} - 3\hat{\mathbf{R}}_{12}\hat{\mathbf{R}}_{12}}{4\pi\epsilon_{\text{out}}R_{12}^3}, \quad (39)$$

in which $\mathcal{D}_{12}$ is the interaction kernel between two dipoles. The leading-order polarization corrections $\{1; 2; 1\}$ and $\{2; 1; 2\}$ are of nearly identical forms and are given by²³

$$\begin{aligned} \{1; 2; 1\} &= \tilde{\mu}_1 \cdot \mathcal{D}_{121} \cdot \tilde{\mu}_1, \\ \mathcal{D}_{121} &\equiv \frac{a\epsilon}{8\pi\epsilon_{\text{out}}R_{12}^4} \\ &\times \left[\frac{t^2\mathbf{I} + \hat{\mathbf{R}}_{12}\hat{\mathbf{R}}_{12}}{(1-t^2)^3} - g \int_0^1 ds s^{g-1} \frac{st^2\mathbf{I} + \hat{\mathbf{R}}_{12}\hat{\mathbf{R}}_{12}}{(1-st^2)^3} \right], \end{aligned} \quad (40)$$

where $t^2 = a^2/(R_{12}^2)$. The interaction kernel $\mathcal{D}_{121}$ now contains the effects of the intermediate scattering function. The line integral can be conveniently handled by using a truncated Taylor series, as we have demonstrated previously.²³

1. Neutral particle

The evaluation of the virial coefficient for neutral particles is simpler for the following reasons: The effective dipoles are reduced to $\alpha\mathbf{E}_0$, the Boltzmann factors are reduced to unity in the zero-field limit, and averages over the orientational degree of freedom are unnecessary. It is straightforward to verify that $b_1 = e^{\beta\alpha E_0^2/2}$, $\nabla_{E_0} b_1/E_0 = \beta\alpha$, and $\lim_{E_0 \rightarrow 0} b_2 = 0$. The limit of the response described in b_2 can be simplified as follows. First write the two particle interaction formally as $\alpha^2\mathbf{E}_0 \cdot \mathcal{D} \cdot \mathbf{E}_0$. The total interaction kernel is $\mathcal{D} = \mathcal{D}_{12} + 2\mathcal{D}_{121}$, where the factor 2 for the term $\mathcal{D}_{121}$ includes the contribution from a

similar term $\mathcal{D}_{212}$. At the limit $E_0 \rightarrow 0$, the response function becomes

$$\lim_{E_0 \rightarrow 0} \nabla_{E_0} b_2/E_0 = -\frac{\beta\alpha^2}{\lambda^3} \int d\mathbf{R}_{12} \hat{\mathbf{E}}_0 \cdot \mathcal{D} \cdot \hat{\mathbf{E}}_0. \quad (41)$$

The second dielectric virial coefficient then follows, from Eq. (7), as

$$B_0 = -\frac{\alpha^2}{3\epsilon_{\text{out}}a^6} \int d\mathbf{R}_{12} \hat{\mathbf{E}}_0 \cdot \mathcal{D} \cdot \hat{\mathbf{E}}_0, \quad (42)$$

where $\hat{\mathbf{E}}_0$ is the direction of the external field and can be any arbitrary direction in the isotropic composite. The subscript “0” in B_0 indicates that it is applicable to neutral systems. The contribution from $\mathcal{D}_{12}$ vanishes since the term $\mathbf{I} - 3\hat{\mathbf{R}}_{12}\hat{\mathbf{R}}_{12}$ vanishes after averaging over the orientation of the separation vector $\mathbf{R}_{12}$. Thus, the dominant contribution to the second dielectric virial coefficient comes from interactions of the type $\{1; 2; 1\}$. This term also provides the first non-trivial correction to the M-G mixing rule. The correction scales with dielectric discontinuity as $(\epsilon_r - 1)^3$, with two such factors coming from α^2 and one from $\mathcal{D}$. This strong dependence partially explains why the M-G model in practice is a good approximation. Section IV B 3 demonstrates that B_0 is always positive if $\epsilon_r > 1$ and is negative otherwise. The latter case is applicable to porous materials, whereas the former one is applicable to, e.g., ceramic-polymer composites.

2. Dipolar particle

The algebra becomes more challenging when a permanent dipole is present because of the coupling between the permanent dipole and fields mediated by polarization. Noting that the contribution from the permanent dipole μ to the effective dipole $\tilde{\mu}$ always contains the screening factor, $\frac{3}{\epsilon_r+2}$, for convenience, we introduce the compact notation, $\mu' \equiv \frac{3}{\epsilon_r+2}\mu$, which gives $\tilde{\mu} = \alpha\mathbf{E}_0 + \mu'$. Then the cluster integral b_2 is transformed by this notation into

$$b_2 = \frac{1}{2\lambda^3} \left\langle \int d\mathbf{R}_{12} e^{\beta\alpha E_0^2} e^{\beta(\mu'_1 + \mu'_2) \cdot \mathbf{E}_0} (e^{-\beta u_{12}} - 1) \right\rangle_{\omega_1 \omega_2}, \quad (43)$$

in which ($\mathcal{D} = \mathcal{D}_{12} + 2\mathcal{D}_{121}$ as before)

$$\begin{aligned} u_{12} &= \tilde{\mu}_1 \cdot \mathcal{D}_{121} \cdot \tilde{\mu}_1 + \tilde{\mu}_2 \cdot \mathcal{D}_{121} \cdot \tilde{\mu}_2 + \tilde{\mu}_1 \cdot \mathcal{D}_{12} \cdot \tilde{\mu}_2 \\ &= \alpha^2 \mathbf{E}_0 \cdot \mathcal{D} \cdot \mathbf{E}_0 + \alpha(\mu'_1 + \mu'_2) \cdot \mathcal{D} \cdot \mathbf{E}_0 + u_{12}(0) \end{aligned} \quad (44)$$

and $u_{12}(0)$ is the value of u_{12} in the absence of an external field, $\mathbf{E}_0$. The gradient term $\nabla_{E_0} b_2$ then becomes

$$\frac{\beta}{2\lambda^3} \left\langle \int d\mathbf{R}_{12} e^{\beta\alpha E_0^2} e^{\beta(\mu'_1 + \mu'_2) \cdot \mathbf{E}_0} \left[(2\alpha\mathbf{E}_0 + (\mu'_1 + \mu'_2)) (e^{-\beta u_{12}} - 1) - (2\alpha^2 \mathcal{D} \cdot \mathbf{E}_0 + \alpha \mathcal{D} \cdot (\mu'_1 + \mu'_2)) e^{-\beta u_{12}} \right] \right\rangle_{\omega_1 \omega_2}. \quad (45)$$

The terms linear in $\mathbf{E}_0$ in the integrand contribute to the quantity $\lim_{E_0 \rightarrow 0} \nabla_{E_0} b_2$ as

$$\frac{\beta\alpha}{\lambda^3} \left\langle \int d\mathbf{R}_{12} (\hat{\mathbf{E}}_0 \cdot (\mathbf{I} - \alpha\mathcal{D}) \cdot \hat{\mathbf{E}}_0 e^{-\beta u_{12}(0)} - 1) \right\rangle_{\omega_1 \omega_2}. \quad (46)$$

In order to evaluate the limit $\mathbf{E}_0 \rightarrow 0$, the remaining terms are combined with the contribution linear in $\mathbf{E}_0$ from the Boltzmann factors, which collectively yield

$$\frac{\beta^2}{2\lambda^3} \left\langle \int d\mathbf{R}_{12} \hat{\mathbf{E}}_0 \cdot (\mathbf{I} - \alpha \mathcal{D}) \cdot (\boldsymbol{\mu}'_1 + \boldsymbol{\mu}'_2)(\boldsymbol{\mu}'_1 + \boldsymbol{\mu}'_2) \cdot (\mathbf{I} - \alpha \mathcal{D}) \cdot \hat{\mathbf{E}}_0 e^{-\beta u_{12}(0)} \right\rangle_{\omega_1 \omega_2} - \frac{\beta^2}{2\lambda^3} \left\langle \int d\mathbf{R}_{12} \hat{\mathbf{E}}_0 \cdot (\boldsymbol{\mu}'_1 + \boldsymbol{\mu}'_2)(\boldsymbol{\mu}'_1 + \boldsymbol{\mu}'_2) \cdot \hat{\mathbf{E}}_0 \right\rangle_{\omega_1 \omega_2}. \quad (47)$$

Applying Eqs. (A2) and (A3) further simplifies the above to

$$\frac{\beta^2}{3\lambda^3} \left\langle \int d\mathbf{R}_{12} [\hat{\mathbf{E}}_0 \cdot (\mathbf{I} - \alpha \mathcal{D})^2 \cdot \hat{\mathbf{E}}_0 e^{-\beta u_{12}(0)} - 1] (\boldsymbol{\mu}'^2 + \boldsymbol{\mu}'_1 \cdot \boldsymbol{\mu}'_2) \right\rangle_{\omega_1 \omega_2}. \quad (48)$$

The last piece needed to evaluate the second virial coefficient is the limiting expression

$$\lim_{E_0 \rightarrow 0} 2b_2 \nabla_{E_0} b_1 / E_0 = \frac{1}{\lambda^3} \left\langle \int d\mathbf{R}_{12} (e^{-\beta u_{12}(0)} - 1) \left(\beta \alpha + \frac{\beta^2}{3} \boldsymbol{\mu}'^2 \right) \right\rangle_{\omega_1 \omega_2}. \quad (49)$$

Combining the above with Eqs. (46), (48), and (7), we arrive at the second virial coefficient for a system of polarizable dipolar particles as

$$B = -\frac{\alpha^2}{3\epsilon_{\text{out}} a^6} \left\langle \int d\mathbf{R}_{12} \hat{\mathbf{E}}_0 \cdot \mathcal{D} \cdot \hat{\mathbf{E}}_0 e^{-\beta u_{12}(0)} \right\rangle_{\omega_1 \omega_2} - \frac{\alpha \beta \boldsymbol{\mu}'^2}{9\epsilon_{\text{out}} a^6} \left\langle \int d\mathbf{R}_{12} \hat{\mathbf{E}}_0 \cdot (2\mathcal{D} - \alpha \mathcal{D}^2) \cdot \hat{\mathbf{E}}_0 e^{-\beta u_{12}(0)} \right\rangle_{\omega_1 \omega_2} + \frac{\beta}{9\epsilon_{\text{out}} a^6} \left\langle \int d\mathbf{R}_{12} [\hat{\mathbf{E}}_0 \cdot (\mathbf{I} - \alpha \mathcal{D})^2 \cdot \hat{\mathbf{E}}_0 e^{-\beta u_{12}(0)} - 1] (\boldsymbol{\mu}'_1 \cdot \boldsymbol{\mu}'_2) \right\rangle_{\omega_1 \omega_2}. \quad (50)$$

The unit vector $\hat{\mathbf{E}}_0$ has an arbitrary orientation. It is reassuring to notice that this expression reduces to that of the neutral particles when $\boldsymbol{\mu}' = 0$. The contribution from the “−1” term in the third line vanishes because $\langle \boldsymbol{\mu}'_1 \cdot \boldsymbol{\mu}'_2 \rangle_{\omega_1 \omega_2} = 0$. Furthermore, the contribution from the kernel $\mathcal{D}_{12}$ vanishes in Eq. (50), after the average over the orientation of $\mathbf{R}_{12}$ because the factors $\langle e^{-\beta u_{12}(0)} \rangle_{\omega_1 \omega_2}$ and $\langle e^{-\beta u_{12}(0)} (\boldsymbol{\mu}'_1 \cdot \boldsymbol{\mu}'_2) \rangle_{\omega_1 \omega_2}$ only depend on the separation R_{12} . If we further neglect the contribution from kernel $\mathcal{D}_{121}$ and terms depending on $\mathcal{D}^2$, the second dielectric virial coefficient becomes simply

$$B = \frac{\beta}{9\epsilon_{\text{out}} a^6} \left\langle \int d\mathbf{R}_{12} (e^{-\beta u_{12}(0)} - 1) (\boldsymbol{\mu}'_1 \cdot \boldsymbol{\mu}'_2) \right\rangle_{\omega_1 \omega_2}. \quad (51)$$

Notice that $\boldsymbol{\mu}'$ differs from $\boldsymbol{\mu}$ by a numerical factor $3/(\epsilon_r + 2)$. Apart from this factor, the above approximation [Eq. (51)] has the same form as for non-polarizable dipolar particles.

3. Numerical calculation

We present numerical values of the first two dielectric virial coefficients to quantify the effect of polarization for neutral systems. The coefficients A_0 and B_0 evaluated from Eqs. (36) and (42) are plotted in Fig. 4 against the relative

FIG. 4. Dielectric virial coefficients A_0 and B_0 of a system of neutral particles with permittivity ϵ_{in} embedded in the dielectric medium with permittivity ϵ_{out} as a function of the ratio $\epsilon_r = \epsilon_{\text{in}}/\epsilon_{\text{out}}$.

dielectric permittivity $\epsilon_r = \epsilon_{\text{in}}/\epsilon_{\text{out}}$, in the range from 0 to 20. Both virial coefficients increase monotonically with ϵ_r , reaching finite limits as $\epsilon_r \rightarrow 0$ or $\epsilon_r \rightarrow \infty$ and passing zero at $\epsilon_r = 1$. The limit $\epsilon_r \rightarrow \infty$ corresponds to a system with conductive inclusions, exhibiting the maximum dielectric enhancement that can be achieved with inclusions of high permittivity particles. In this regime, the two coefficients approach $A_0 = 4\pi/3 \simeq 4.19$ and $B_0 = 56\pi^2/81 \simeq 6.82$, respectively. On the other hand, the limit $\epsilon_r \rightarrow 0$ represents a conductive system embedded with dielectric particles and the first two coefficients approach $A_0 = -2\pi/3 \simeq -2.09$ and $B_0 = -8\pi^2/81 \simeq -0.975$ (Appendix D), respectively. Numerical values for the coefficient B_0 at finite ϵ_r values are tabulated in Table I.

The effective medium permittivity can be estimated by using Eq. (3). The influence of polarization is assessed by comparing our theory with two other competing models, the M-G mixing rule and the Bruggeman empirical rule. The Bruggeman rule arises as a phenomenological modification of the M-G result³³

TABLE I. The second dielectric virial coefficient for polarizable neutral inclusions.

ϵ_r	B_0	ϵ_r	B_0	ϵ_r	B_0	ϵ_r	B_0
0.00	-0.9748	0.50	-0.0603	2.00	0.1129	12.0	3.3595
0.05	-0.7727	0.55	-0.0413	3.00	0.4566	13.0	3.5424
0.10	-0.6087	0.60	-0.0273	4.00	0.8847	14.0	3.7078
0.15	-0.4761	0.65	-0.0173	5.00	1.3132	15.0	3.8578
0.20	-0.3691	0.70	-0.0103	6.00	1.7111	16.0	3.9944
0.25	-0.2834	0.75	-5.6041×10^{-3}	7.00	2.0702	17.0	4.1194
0.30	-0.2150	0.80	-2.7131×10^{-3}	8.00	2.3905	18.0	4.2339
0.35	-0.1609	0.85	-1.0834×10^{-3}	9.00	2.6756	19.0	4.3394
0.40	-0.1185	0.90	-3.0414×10^{-4}	10.0	2.9295	20.0	4.4367
0.45	-0.0855	0.95	-3.6056×10^{-5}	11.0	3.1562	∞	6.8234

$$\frac{\epsilon_{BG}}{\epsilon_{out}} = \frac{b + \sqrt{8\epsilon_r + b^2}}{4}, \quad b = (2 - 3v) + (3v - 1)\epsilon_r, \quad (52)$$

where v is the volume fraction of the inclusion. An explicit expansion shows that the above two expressions have the same linear dependence on $\bar{\rho}$ as the dielectric virial expansion, but differences appear at the quadratic order.

Figure 5(a) compares the predictions of the M-G mixing rule, the Bruggeman rule, and the virial expansion to the experimental data for a BaTiO₃-PVDF composite measured at 1 kHz.³⁴ The dispersion of BaTiO₃ nanoparticles is achieved by capping particles with surfactants. The frequency is high enough to ensure the elimination of the contribution from free charges (Fig. 3 of Ref. 35). The effective medium picture still applies because the size of the nanoparticles is orders of magnitudes smaller than the wavelength.^{36,37}

The comparison shows clearly that the M-G mixing rule captures the initial increment of the effective permittivity ϵ_m with inclusion concentration, as expected, but underestimates ϵ_m in the more concentrated regime. This behavior is also expected for composites with a sharp discontinuity of dielectric permittivity at the interface since the inter-particle interactions are neglected.⁴³ On the other hand, the Bruggeman formula is found to over-correct the effect of inter-particle interactions, in agreement with the trend observed in the literature.⁹ Although the truncation of the dielectric virial expansion to second order only adds a single term beyond the M-G mixing term, the theory captures the trend of the experimental data remarkably well in the range of concentration examined, for this system with a relative permittivity $\epsilon_r = 15.6$.

FIG. 5. Comparisons between experimental effective medium dielectric permittivities^{34,38–42} and predictions of the M-G mixing rule (red dashed), the Bruggeman rule (blue dotted), and the second-order virial expansion (black solid), for composites with neutral spherical inclusions. (a) Comparison with a random composite having relative permittivity $\epsilon_r = 15.6$.³⁴ (b) Comparison with samples spanning a range of ϵ_r values: $\epsilon_r = 6.7$ (■), 15.6 (●), 75 (○), 208 (△), and 5933 (○). Open markers: samples approaching the conducting limit.

Figure 5(b) exhibits a more exhaustive comparison between the predictions of the second-order virial expansion and a set of six experimental data.^{34,38–42} The data are all measured at frequencies between 1 and 10 kHz. The values of ϵ_r range between 6.7 and 5933, approaching effectively the limit of conducting inclusion. Data for the two samples with modest permittivities, $\epsilon_r = 6.7$ and 15.6, agree with the predictions of the virial expansion, up to a filling fraction of 50%. The remaining data with higher relative permittivities, $\epsilon_r = 75$, 208, 227, and 5933, exhibit no clear dependence on ϵ_r , implying that the conductor limit has been reached. Surprisingly, the limiting behavior displayed by the cluster of data points is still captured by the virial expansion with the two leading-order terms kept.

An alternative test of the theories is provided by measurements of the permittivity of porous materials, which are effectively “inverted” composites. One such comparison is displayed in Fig. 6, for porous SiO₂-air with $\epsilon_{in} = 1$ and $\epsilon_r = 0.238$. In contrast to composites, the permittivity of porous samples decreases weakly with porosity since ϵ_r is always less than unity and the dielectric discontinuity is small. The data show that this dependence is captured by any of the three theories tested. The difference among theories is negligible, suggesting that the dominant polarization effects for porous samples are captured by the M-G mixing rule. This observation is consistent with the fact that the second dielectric virial coefficient B_0 is small near $\epsilon_r = 1$, presented by Table I and Fig. 4.

We now consider the particles with permanent dipoles. The coefficient A , given by Eq. (36), is straightforward to evaluate. The coefficient B , given by Eq. (50), is simplified to Eq. (51), by including only contributions from the permanent dipoles. The integral in Eq. (51) involves averages over the molecular orientations ω_1 and ω_2 and the summation over inter-particle separation R_{12} . Since the integrand is independent of the orientation of R_{12} , after the averages over ω_1 and ω_2 , we obtain

$$B = \left(\frac{3}{\epsilon_r + 2} \right)^2 \frac{(4\pi)^2 \beta \mu^{*2}}{9\epsilon_{out} a^3} \times \left\langle \int_0^\infty dR_{12} R_{12}^2 \hat{\mu}_1 \cdot \hat{\mu}_2 (e^{-\beta u_{12}(0)} - 1) \right\rangle_{\omega_1 \omega_2}, \quad (53)$$

FIG. 6. Comparison between measured effective medium dielectric permittivity⁴⁴ and predictions of the M-G mixing rule (red dashed), the Bruggeman rule (blue dotted), and the second-order virial expansion (black solid) for SiO₂-Air with varying porosity. The relative permittivity: $\epsilon_r = 0.238$.

where $\beta\mu^{*2} \equiv \frac{\mu^2}{4\pi\epsilon_0 a^3 k_B T}$. This integral involves three independent parameters, ω_1 , ω_2 , and R_{12} . But the average over ω_1 can be dropped since, after the average over ω_2 , the result becomes independent of the orientation $\hat{\mu}_1$, which ultimately leaves us a three-dimensional integral, two dimensions in orientation ω_2 and one in distance R_{12} .

However, the dipole-dipole interaction is long-ranged, which slows down the convergence of the numerical quadrature. One way to handle this issue is to isolate the contribution from the slowly decaying tail,

$$\Delta B = \left(\frac{3}{\epsilon_r + 2} \right)^2 \frac{(4\pi)^2 \beta\mu^{*2}}{9\epsilon_{\text{out}} a^3} \times \left\langle \int_0^\infty dR_{12} R_{12}^2 \hat{\mu}_1 \cdot \hat{\mu}_2 \left(e^{-\beta u_{12}(0)} - e^{-\beta u_{12}^{\text{DD}}} \right) \right\rangle_{\omega_2}, \quad (54)$$

where $u_{12}^{\text{DD}} = \frac{\mu^2}{4\pi\epsilon_{\text{out}}} \hat{\mu}_1 \cdot \mathcal{D}_{12} \cdot \hat{\mu}_2$ is a dipole-dipole interaction. The difference between $u_{12}(0)$ and u_{12}^{DD} arises from the polarization contribution. The remaining integral ΔB converges rapidly and is readily treated numerically. The contribution from the long-ranged tail, denoted by B^{DD} , can be evaluated using the Taylor series of the integrand [Eq. (6) of Ref. 19].

The first virial coefficient for polarizable dipolar particles is plotted against the magnitude of the dipole moment in Fig. 7, for relative permittivities $\epsilon_r = 2$ and $\epsilon_r = 0.5$, respectively. The dashed curve applies for the reference system containing non-polarizable particles, with $\epsilon_r = 1$. The coefficient A increases monotonically with $\beta\mu^{*2}$ because of the contribution from permanent dipole moments. The contribution due to particle polarizability α is important when $\beta\mu^{*2} \lesssim 3$. As the dipole moments grow further, the main polarization effects come from the screening of dipoles by its own surface,²³ i.e., through the screening factor $3/(\epsilon_r + 2)$ in Eq. (53).

The second virial coefficient B includes contributions from the permanent dipole, the induced dipole, and their cross terms. By neglecting all but the contribution from the permanent dipoles, Eq. (51) is applicable in systems dominated by dipolar interactions. The polarization effects reveal themselves for these systems through (1) the presence of

FIG. 7. Dielectric virial coefficient A as the function of reduced dipolar energy $\beta\mu^{*2}$ for the system of polarizable dipolar particles where $\epsilon_r = 2.0$ and $\epsilon_r = 0.5$ with $\epsilon_r = 1$ as the reference.

the screening factor and (2) the polarization energy from the strings $\{1; 2; 1\}$ and $\{2; 1; 2\}$. The screening factor damps both B^{DD} and ΔB . The terms $\{1; 2; 1\}$ and $\{2; 1; 2\}$, although depending on the angle between dipole moment and the inter-particle separation, are always attractive when $\epsilon_r > 1$ and are repulsive otherwise. Therefore, depending on whether the particle's permittivity exceeds that of the host, the polarization correction to the second virial coefficient can be positive, when $\epsilon_r > 1$, or negative, when $\epsilon_r < 1$. These observations are confirmed by the calculations displayed in Fig. 8, showing the importance of polarization on dielectric screening.

C. The higher-order virial coefficient

The third and higher-order virial coefficients, in principle, can be derived similarly, but emerge in more complicated expressions involving multiple surface integrals and high-dimensional quadratures. For instance, the third-order virial coefficient contains two spatial and three orientational integrations. We only provide the expression for the third virial coefficient of the particles lacking permanent dipoles, which is simpler because the coupling between permanent dipoles

FIG. 8. The second virial coefficients and their components, B^{DD} [Eq. (6) of Ref. 19] and ΔB [Eq. (54)] for (a) $\epsilon_{\text{in}} = 2.0$, $\epsilon_{\text{out}} = 1.0$ and (b) $\epsilon_{\text{in}} = 1.0$, $\epsilon_{\text{out}} = 2.0$. The corresponding orientation dependences of the inter-particle polarization energy [Eq. (41)] at $R_{12} = 4a$ are shown in the right column.

and induced charges is absent and because there is no need for orientational average.

The one-body and two-body potentials have been provided while discussing the first and the second virial coefficients. The three-body potential can be written as $u_{123} = \alpha^2 \mathbf{E}_0 \cdot \mathcal{T} \cdot \mathbf{E}_0$, where $\mathcal{T} = \mathcal{T}(\mathbf{R}_{12}, \mathbf{R}_{13})$ is the configuration-dependent interaction kernel, analogous to $\mathcal{D}$, which arises from strings of the form $\{1; 2; 3\}$, $\{1; 21; 3\}$, $\{1; 32; 3\}$, etc. and their permutations.

Using this notation, Eq. (14) for the third-order cluster integral can be written as

$$b_3 = \frac{1}{6\lambda^6} \int d\mathbf{R}_{12} d\mathbf{R}_{13} e^{3\alpha E_0^2/2} \left[e^{-\alpha^2 \mathbf{E}_0 \cdot (\mathcal{T} + \mathcal{D}_{12} + \mathcal{D}_{13} + \mathcal{D}_{23}) \cdot \mathbf{E}_0} - e^{-\alpha^2 \mathbf{E}_0 \cdot \mathcal{D}_{12} \cdot \mathbf{E}_0} - e^{-\alpha^2 \mathbf{E}_0 \cdot \mathcal{D}_{13} \cdot \mathbf{E}_0} - e^{-\alpha^2 \mathbf{E}_0 \cdot \mathcal{D}_{23} \cdot \mathbf{E}_0} + 2 \right]. \quad (55)$$

The two-body interaction kernels $\mathcal{D}_{12}$, $\mathcal{D}_{13}$, and $\mathcal{D}_{23}$ are evaluated for separations $\mathbf{R}_{12}$, $\mathbf{R}_{13}$, and $\mathbf{R}_{23}$, respectively. The three-body interaction kernel $\mathcal{T}$ depends on both $\mathbf{R}_{12}$ and $\mathbf{R}_{13}$. All these kernels are expressed in units of polarizability. It is apparent that b_3 vanishes in the limit $\mathbf{E}_0 \rightarrow \mathbf{0}$. Recalling that b_2 vanishes in the same limit, the following expression is deduced, from Eq. (8), for the third-order virial coefficient:

$$C_0 = \frac{k_B T \lambda^6}{3\epsilon_{\text{out}} a^9} \lim_{\mathbf{E}_0 \rightarrow \mathbf{0}} \frac{\nabla_{\mathbf{E}_0} b_3}{\mathbf{E}_0} = -\frac{\alpha^2}{9\epsilon_{\text{out}} a^9} \int d\mathbf{R}_{12} d\mathbf{R}_{13} \hat{\mathbf{E}}_0 \cdot \mathcal{T} \cdot \hat{\mathbf{E}}_0. \quad (56)$$

This coefficient is the third-order virial correction to the M-G mixing rule, which scales as $(\epsilon_r - 1)^3$ because both α and $\mathcal{T}$ scale as $(\epsilon_r - 1)$.

V. SUMMARY

A systematic framework is developed for analyzing the dielectric properties of composites containing polarizable dipolar particles. The particles are treated as dielectric objects with internal permittivity differing from the host. With the aid of the Clausius-Mossotti relation, the effective medium dielectric permittivity is cast as a virial series, whose coefficients depend on particle's shape, particle's dipole, and mismatches of the permittivity at the interface. The theory generalizes previous work for non-polarizable dipolar fluids.^{19,20}

The virial expansion is particularly useful when the energy can be expanded as a sum of terms involving a small number of particles, i.e., clusters. Non-polarizable dipolar fluids are suitable for such an expansion because they only contain two-body dipole-dipole interactions. The energy in polarizable systems is intrinsically of many-bodied nature since every dielectric interface can be polarized, can polarize a second one, and can interact with a third one via the induced charges on the second, etc. The decomposition of the total energy for these systems relies on the multiple-scattering formalism that we developed recently.^{22,23} Solving Poisson's equation within this formalism iteratively gives rise to an expansion of the total energy in terms of one-body, two-body, three-body, etc. interactions. All terms involved are uniquely determined by the relative positions of particles in clusters. The polarization effects are replaced with

a set of surface integrals performed over the induced surface charges. For spherical particles, we showed that these surface integrals can be exactly converted into line integrals,²³ which greatly simplifies their application.

The previous multiple-scattering formalism assumes the absence of external fields. Studying dielectric properties requires a generalization that includes the effects of external fields on interfacial polarization. Section III shows that, in the case of spherical particles, these effects can be accounted for by inserting an induced dipole at the particle center. Consequently, the theory for polarizable dipolar fluids²³ developed previously can be directly applied to derive the dielectric virial expansion.

Explicit expressions are derived for the first, the second, and the third dielectric virial coefficients, with polarization corrections. The expression for the first dielectric virial coefficient is identical to the polarizability of polar molecules.¹¹ The leading-order correction for the second dielectric virial coefficient results from the two-body polarization term, e.g., $\{1; 2; 1\}$. The correction to the third dielectric virial coefficient includes the contributions from three-body polarization terms, e.g., $\{1; 2; 3\}$.

The virial series simplifies significantly when the permanent dipole moments are set to vanish, which is appropriate for studying dielectric composites. In such a case, we show that the first virial coefficient reproduces the M-G mixing rule.⁶ The second and the third virial terms allow for systematic improvements upon the M-G expression, which is necessary for studying concentrated composites. The expression for the effective dielectric permittivity ϵ_m including contributions from the second virial term is given by

$$\frac{\epsilon_m - \epsilon_{\text{out}}}{\epsilon_m + 2\epsilon_{\text{out}}} = \left(\frac{4\pi}{3} \right) \frac{\epsilon_r - 1}{\epsilon_r + 2} \tilde{\rho} + B_0(\epsilon_r) \tilde{\rho}^2, \quad (57)$$

where the values of coefficient B_0 for a range of ϵ_r have been tabulated in Table I. The coefficient B_0 is positive for $\epsilon_r > 1$, implying that the second-order virial term adds a positive correction to the M-G mixing rule when applied to composites. It is negative for $\epsilon_r < 1$, but the magnitude is small typically, implying that the M-G mixing rule captures the main polarization contribution to the medium permittivity for porous materials.

The comparisons in Fig. 5 to experimentally measured permittivities for composites, with spherical neutral inclusions and with a range of ϵ_r values, show that Eq. (57) improves the M-G mixing rule notably. The dependence of the effective medium permittivity on inclusion concentration is nearly quantitatively described by the second-order virial expansion, even for composites with conducting inclusions. On the other hand, Fig. 6 shows that the M-G mixing rule can reliably predict the permittivity for porous materials with typical ϵ_r values. These agreements are indeed remarkable, given that no fitting parameter is used.

These comparisons have been applied to random composites, for which care is taken to ensure particle dispersion. The virial expansion developed in this work, however, is applicable for a statistical dispersion with well-defined interaction Hamiltonian, e.g., for systems with significant van der Waals interactions between particles. These interactions affect the

spatial distribution of particulate inclusions. Their affect on the dielectric permittivity is explained by inserting the appropriate Boltzmann weight to Eq. (42) for B_0 ,

$$B_0 = -\frac{\alpha^2}{3\epsilon_{\text{out}}\alpha^6} \int d\mathbf{R}_{12} \hat{\mathbf{E}}_0 \cdot \mathcal{D} \cdot \hat{\mathbf{E}}_0 e^{-\beta U^{(2)}(\mathbf{R}_{12})}, \quad (58)$$

where $U^{(2)}(\mathbf{R}_{12})$ is the two-body interaction potential in the absence of an external field.

The values of B_0 tabulated in Table I and used in the comparisons are approximate. Only the lowest order polarization term between two particles, i.e., $\{1; 2; 1\}$, is included in Eq. (42). The higher-order polarization contribution, such as terms of nature $\{1; 21; 2\}$, have been dropped. Nonetheless, the agreements between prediction and experimental data suggest that these contributions are likely negligible. More extensive numerical work would be needed to verify this point and, along the same line, to explore the effects of the third-order virial term.

In summary, this work provides a coherent framework for investigating the effects of interfacial polarization on static dielectric screening in composite materials or molecular fluids. The predicted effective permittivity is fully specified by the relative permittivity $\epsilon_r = \epsilon_{\text{in}}/\epsilon_{\text{out}}$ and the inclusion volume fraction $\rho\alpha^3$, as demonstrated in Fig. 5 for the case of neutral inclusions. The explicit dependence on particle size drops since it is the only length scale in monodisperse samples. In polydisperse composites, the leading or the M-G term remains additive, and its contribution is determined by the overall particle volume fraction. However, the second-order virial contribution would be sensitive to the distribution of particle sizes. This dependence, as well as the predicted dependence of the permanent dipole of particles, remains to be tested experimentally. Such tests would prove invaluable for assessing the accuracy of the higher-order virial terms. Finally, we note the theory can be naturally generalized to composites

containing anisotropic and heterogeneous inclusions, which will be presented in the future.

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APPENDIX A: ORIENTATIONAL AVERAGE OF A SUM OF DIPOLES

We show below how the average of the sum of dipoles, i.e., Eq. (9), is evaluated for non-polarizable particles. The exponential factor depending on the field $\mathbf{E}_0$ is invariant with respect to rotations along the $\mathbf{E}_0$ axis. Henceforth the average of $\sum_{i=1}^m \boldsymbol{\mu}_i$ is taken as invariant with respect to rotations along the $\mathbf{E}_0$ axis since the result is only applied for vectors pointing along the direction $\mathbf{E}_0$, which we denote by $\hat{\mathbf{n}}$. Thus, the average can be conveniently written as

$$\beta \left\langle \left(\hat{\mathbf{n}} \cdot \sum_{i=1}^m \boldsymbol{\mu}_i \right) e^{\beta \mathbf{E}_0 \cdot (\sum_{i=1}^m \boldsymbol{\mu}_i)} \mathcal{K} \right\rangle_{\{\omega_i\}} \hat{\mathbf{n}}. \quad (A1)$$

The dielectric virial coefficients are equal to the ratio between the above expression and $\mathbf{E}_0 = E_0 \hat{\mathbf{n}}$, evaluated in the limit $E_0 \rightarrow 0$. The result simplifies upon insertion of the Taylor expansion for the Boltzmann factor, which leads to the expression

$$\lim_{E_0 \rightarrow 0} \beta \left\langle \left(\hat{\mathbf{n}} \cdot \sum_{i=1}^m \boldsymbol{\mu}_i \right) \left(1 + \beta \mathbf{E}_0 \cdot \sum_{i=1}^m \boldsymbol{\mu}_i + \frac{1}{2} \left(\beta \mathbf{E}_0 \cdot \sum_{i=1}^m \boldsymbol{\mu}_i \right)^2 + \cdots \right) \mathcal{K} \right\rangle_{\{\omega_i\}} \frac{1}{E_0} = \beta^2 \hat{\mathbf{n}} \cdot \sum_{i=1}^m \sum_{j=1}^m \langle \boldsymbol{\mu}_i \boldsymbol{\mu}_j \mathcal{K} \rangle_{\{\omega_i\}} \cdot \hat{\mathbf{n}}. \quad (A2)$$

The higher-order terms vanish in the limit $E_0 \rightarrow 0$. The linear term vanishes by rotational symmetry. Averaging over the other orientations for fixed values of the dipoles $\boldsymbol{\mu}_i$ leaves a scalar, say c , independent of the orientation of the $\boldsymbol{\mu}_i$. Further averaging $c\boldsymbol{\mu}_i$ over the orientations implies that $\boldsymbol{\mu}_i$ vanishes. The final expression, Eq. (A2), can be understood as the magnitude of the dipole-dipole fluctuation, a standard behavior for the linear-response of an equilibrium system. For an anisotropic fluid, the expectation value of the dyads contributes to the tensorial dielectric permittivity.

When the fluid is isotropic, the tensor is proportional to the Kronecker- δ . The contractions with the “test” field $\hat{\mathbf{E}}$, which has arbitrary orientations, select the value of the

diagonal entries, which are equal, and, therefore, equal to 1/3 times the *trace* of the permittivity tensor. Consequently, Eq. (A2) reduces to

$$\begin{aligned} & \frac{\beta^2}{3} \left\langle \left(\sum_{i=1}^m \boldsymbol{\mu}_i \cdot \sum_{j=1}^m \boldsymbol{\mu}_j \right) \mathcal{K} \right\rangle_{\{\omega_i\}} \\ &= \frac{m\beta^2}{3} \langle [\mu^2 + (m-1)\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2] \mathcal{K} \rangle_{\{\omega_i\}}. \end{aligned} \quad (A3)$$

The two terms in the square brackets are contributions from the self-product and cross-product, respectively. The first term can be understood as the Debye polarization generalized to

interacting particles. The second term can be understood as the contraction $\hat{\mathbf{n}} \cdot \langle \boldsymbol{\mu}_1 \boldsymbol{\mu}_2 \mathcal{K} \rangle_{\{\omega_i\}} \cdot \hat{\mathbf{n}}$. The expectation $\langle \boldsymbol{\mu}_2 \mathcal{K} \rangle_{\{\omega_i | i \neq 1\}}$ yields a vector whose direction parallels vector $\boldsymbol{\mu}_1$ and whose magnitude does not depend on the direction of $\boldsymbol{\mu}_1$. Therefore, we have $\hat{\mathbf{n}} \cdot \langle \boldsymbol{\mu}_1 \boldsymbol{\mu}_2 \mathcal{K} \rangle_{\{\omega_i\}} \cdot \hat{\mathbf{n}} = \hat{\mathbf{n}} \cdot \langle \hat{\boldsymbol{\mu}}_1 \hat{\boldsymbol{\mu}}_1 \rangle_{\omega_1} \cdot \hat{\mathbf{n}} \langle \boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 \mathcal{K} \rangle_{\{\omega_i\}} = \langle \boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 \mathcal{K} \rangle_{\{\omega_i\}} / 3$.

APPENDIX B: THE THIRD VIRIAL COEFFICIENT

The third-order term follows the same lines of analysis for the first and the second virial coefficients, and thus we have

$$b_3 = \frac{1}{6} \langle e^{\beta(\boldsymbol{\mu}_1 + \boldsymbol{\mu}_2 + \boldsymbol{\mu}_3) \cdot \mathbf{E}_0} \times (\mathcal{I}_{123} - \mathcal{I}_{12} - \mathcal{I}_{23} - \mathcal{I}_{31} + 2) \rangle_{\omega_1 \omega_2 \omega_3}, \quad (\text{B1})$$

$$\mathcal{I}_{123} \equiv \frac{1}{(\lambda^3)^2} \int d\mathbf{R}_{12} d\mathbf{R}_{13} e_{12} e_{23} e_{31} e_{123}, \quad (\text{B2})$$

$$\mathcal{I}_{ij} \equiv \frac{1}{(\lambda^3)^2} \int d\mathbf{R}_{12} d\mathbf{R}_{13} e_{ij}. \quad (\text{B3})$$

The factors $\mathcal{I}_{123}$, $\mathcal{I}_{12}$, etc. play a role analogous to that of $\mathcal{I}_{12}$. It is useful to note that these configuration averages are uniquely specified by the relative orientation of the dipoles $\boldsymbol{\mu}_1$, $\boldsymbol{\mu}_2$, and $\boldsymbol{\mu}_3$ and are invariant with respect to arbitrary spatial rotation.

$$\frac{\beta^2}{3} \langle \boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 (\mathcal{I}_{123} - \mathcal{I}_{12} - \mathcal{I}_{13} \mathcal{I}_{12} - \mathcal{I}_{23} \mathcal{I}_{12}) \rangle_{\omega_1 \omega_2 \omega_3} = \frac{\beta^2}{3} \langle \boldsymbol{\mu}_2 \cdot \boldsymbol{\mu}_3 (\mathcal{I}_{123} - \mathcal{I}_{23} - \mathcal{I}_{12} \mathcal{I}_{23} - \mathcal{I}_{31} \mathcal{I}_{23}) \rangle_{\omega_1 \omega_2 \omega_3}. \quad (\text{B7})$$

Here we have changed the index convention such that $\mathbf{R}_1$ is the reference point. To further simplify the result, we note that

$$\mathcal{I}_{12} \mathcal{I}_{23} = \frac{1}{(\lambda^3)^2} \int d\mathbf{R}_{12} d\mathbf{R}_{13} (e_{12} e_{23} - e_{12} - e_{23} + 1). \quad (\text{B8})$$

The contributions from “ $-e_{12} + 1$ ” vanish after the average $\langle \boldsymbol{\mu}_2 \cdot \boldsymbol{\mu}_3 \dots \rangle_{\omega_1 \omega_2 \omega_3}$. A similar analysis applies to $\mathcal{I}_{31} \mathcal{I}_{23}$. Then expanding the expressions for $\mathcal{I}_{123}$ and $\mathcal{I}_{23}$ yields

$$\frac{\beta^2}{3(\lambda^3)^2} \langle (\boldsymbol{\mu}_2 \cdot \boldsymbol{\mu}_3) \int d\mathbf{R}_{12} d\mathbf{R}_{13} e_{23} \times (e_{12} e_{31} e_{123} - e_{12} - e_{31} + 1) \rangle_{\omega_1 \omega_2 \omega_3}. \quad (\text{B9})$$

Finally, the third virial coefficient can be written as

$$C = \frac{4\pi}{9} \beta \langle (\boldsymbol{\mu}_2 \cdot \boldsymbol{\mu}_3) \int d\mathbf{R}_{12} d\mathbf{R}_{13} e_{23} \times (e_{12} e_{31} e_{123} - e_{12} - e_{31} + 1) \rangle_{\omega_1 \omega_2 \omega_3}. \quad (\text{B10})$$

When the three-body interaction vanishes, we have $e_{123} = 1$, and the last expression becomes identical to that derived previously for non-polarizable dipolar particles.²⁰ The above analysis also shows that, as expected, the three-body interaction is relevant for the third and higher-order virial coefficients.

The zero-field limit of b_3 is $\frac{1}{6} \langle \mathcal{I}_{123} - \mathcal{I}_{12} - \mathcal{I}_{23} - \mathcal{I}_{31} + 2 \rangle_{\omega_1 \omega_2 \omega_3}$ and its gradient can be evaluated using Eq. (10),

$$\lim_{E_0 \rightarrow 0} \nabla_{E_0} b_3 / E_0 = \frac{\beta^2}{6} \langle [\mu^2 + 2\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2] \times (\mathcal{I}_{123} - \mathcal{I}_{12} - \mathcal{I}_{23} - \mathcal{I}_{31} + 2) \rangle_{\omega_1 \omega_2 \omega_3}. \quad (\text{B4})$$

The contributions to the third virial coefficient apart from terms depending on $\nabla_{E_0} b_3$ can be simplified as follows:

$$\begin{aligned} \lim_{E_0 \rightarrow 0} \left([-4b_2 \nabla_{E_0} b_2 + (8b_2^2 - 3b_3) \nabla_{E_0} b_1] / E_0 \right) \\ = -\frac{2\beta^2}{3} \langle \mathcal{I}_{12} \rangle_{\omega_2} \langle \boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 \mathcal{I}_{12} \rangle_{\omega_1 \omega_2} \\ - \frac{\beta^2 \mu^2}{6} \langle \mathcal{I}_{123} - \mathcal{I}_{12} - \mathcal{I}_{23} - \mathcal{I}_{31} + 2 \rangle_{\omega_1 \omega_2 \omega_3}. \end{aligned} \quad (\text{B5})$$

Combining the above two terms leads to

$$\begin{aligned} \frac{\beta^2}{3} [\langle \boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 (\mathcal{I}_{123} - \mathcal{I}_{12} - \mathcal{I}_{23} - \mathcal{I}_{31} + 2) \rangle_{\omega_1 \omega_2 \omega_3} \\ - 2 \langle \mathcal{I}_{12} \rangle_{\omega_2} \langle \boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 \mathcal{I}_{12} \rangle_{\omega_1 \omega_2}]. \end{aligned} \quad (\text{B6})$$

Here the terms $\langle \boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 \mathcal{I}_{23} \rangle_{\omega_1 \omega_2 \omega_3}$, $\langle \boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 \mathcal{I}_{31} \rangle_{\omega_1 \omega_2 \omega_3}$, and $\langle \boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 \rangle_{\omega_1 \omega_2 \omega_3}$ vanish because $\langle \boldsymbol{\mu}_1 \rangle_{\omega_1}$ and $\langle \boldsymbol{\mu}_2 \rangle_{\omega_2}$ vanish. Further noting that $\langle \mathcal{I}_{12} \rangle_{\omega_2} = \langle \mathcal{I}_{13} \rangle_{\omega_3} = \langle \mathcal{I}_{23} \rangle_{\omega_3}$ are constant independent of the actual index used, we can re-write the above as

APPENDIX C: POLARIZATION IN A UNIFORM FIELD BY MULTIPLE-SCATTERING

We show below that the problem of describing the polarization of one sphere by a uniform electric field $\mathbf{E}_0$ can be solved within the multiple-scattering formalism by considering the effects of a point source placed at infinity. Reference 22 demonstrates that after multiple interfacial scattering, the field produced inside a sphere from a point charge q at $\mathbf{R}$ is given by

$$\phi(\mathbf{r}) = \frac{q}{4\pi\epsilon_{\text{out}}} \frac{1 - \epsilon_r}{1 + \epsilon_r} \left(\delta_{f,1} - g \int_0^1 df f^{g-1} \right) \frac{1}{|\mathbf{r} - \mathbf{R}|}. \quad (\text{C1})$$

Combining the contribution from the induced electric field, $-\nabla\phi(\mathbf{r}; q_1)$, and the source field yields

$$\begin{aligned} \mathbf{E}(\mathbf{r}) = -\frac{q}{4\pi\epsilon_{\text{out}}} \frac{1 - \epsilon_r}{1 + \epsilon_r} \left(\delta_{f,1} - g \int_0^1 df f^{g-1} \right) \\ \times \frac{f\mathbf{R} - f^2\mathbf{r}}{|\mathbf{r} - \mathbf{R}|^3} + \frac{q(\mathbf{r} - \mathbf{R})}{4\pi\epsilon_{\text{out}}|\mathbf{r} - \mathbf{R}|^3}. \end{aligned} \quad (\text{C2})$$

Taking the limits $R \rightarrow \infty$ and $q = 4\pi\epsilon_{\text{out}}E_0R^2$ provides a calculation for a system with a uniform electric field $\mathbf{E}_0$ along the $-\hat{\mathbf{R}}$ direction. The total field $\mathbf{E}(\mathbf{r})$ in Eq. (21) is found to

reduce to the expected form

$$\mathbf{E}(\mathbf{r}) = \frac{3}{\epsilon_r + 2} \mathbf{E}_0. \quad (\text{C3})$$

Similar results apply to the case of $\mathbf{r}$ lying outside the particle.

APPENDIX D: THE LIMITING BEHAVIOR OF THE SECOND DIELECTRIC VIRIAL COEFFICIENT

The second virial coefficient approaches the finite values at both limits $\epsilon_r \rightarrow 0$ and $\epsilon_r \rightarrow \infty$. For the case where $\epsilon_r \rightarrow \infty$, substituting Eq. (51) of Ref. 23 (note there is a redundant t^2 term in Ref. 23) into Eq. (42) gives the following expression for the second virial coefficient of neutral particles:

$$B_0 = -\frac{\alpha^2}{3\epsilon_{\text{out}}a^6} (2\times) \int d\mathbf{R}_{12} \frac{-1}{8\pi\epsilon_{\text{out}}} \frac{t^3}{R_{12}^3} \times \frac{1 + (\hat{\mathbf{E}}_0 \cdot \hat{\mathbf{R}}_{12})^2 (3 - 3t^2 + t^4)}{(1 - t^2)^3}. \quad (\text{D1})$$

The term t is defined by the ratio a/R_{12} . The polarizability α reduces to $4\pi a^3$ at the conductor limit, i.e., $\epsilon_r \rightarrow \infty$. The factor $(2\times)$ includes the contributions from strings $\{1; 2; 1\}$ and $\{2; 1; 2\}$. After the average over the orientation of $\mathbf{R}_{12}$, the term $(\hat{\mathbf{E}}_0 \cdot \hat{\mathbf{R}}_{12})^2$ reduces to $4\pi/3$. Thus we obtain, while setting the lower bound of R_{12} to $2a$ in order to prevent particles from overlapping,

$$B_0 = \frac{(4\pi)^2}{3} \int_{2a}^{\infty} dR_{12} R_{12}^2 \frac{t^3}{R_{12}^3} \frac{1 + (3 - 3t^2 + t^4)/3}{(1 - t^2)^3} = \left(\frac{4\pi}{3}\right)^2 \int_0^{1/2} dt \frac{3t^2 + t^2(3 - 3t^2 + t^4)}{(1 - t^2)^3}. \quad (\text{D2})$$

Noting that the terms $t^2(3 - 3t^2 + t^4)$ can be factored as $(t^2 - 1)^3 + 1$, we may further write

$$B_0 = \left(\frac{4\pi}{3}\right)^2 \int_0^{1/2} dt \left(\frac{3t^2 + 1}{(1 - t^2)^3} - 1 \right) = \frac{56}{81} \pi^2 \simeq 6.82. \quad (\text{D3})$$

Similarly, for the “inverse” conductor limit where $\epsilon_r \rightarrow 0$, Eq. (42) can be reduced to the following expression by noticing that $\alpha \rightarrow -2\pi a^3$, $\epsilon \rightarrow 1$, and $g \rightarrow 1$:

$$B_0 = -\frac{(2\pi)^2}{3} (2\times) 2\pi \int dR_{12} d\theta R_{12}^2 \sin \theta \frac{a}{8\pi R_{12}^4} \times \left(\frac{t^2 + \cos^2 \theta}{(1 - t^2)^3} - \frac{(2 + t^2) + (2 - t^2) \cos 2\theta}{4(1 - t^2)^2} \right) = -\frac{8\pi^2}{81} \simeq -0.975. \quad (\text{D4})$$

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