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Effects of geometric anisotropy on local field distribution: Ewald–Kornfeld formulation

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Abstract

We have applied the Ewald–Kornfeld formulation to a tetragonal lattice of point dipoles, in an attempt to examine the effects of geometric anisotropy on the local field distribution. The various problems encountered in the computation of the conditionally convergent summation of the near field are addressed and the methods of overcoming them are discussed. The results show that the geometric anisotropy has a significant impact on the local field distribution. The change in the local field can lead to a generalized Clausius–Mossotti equation for the anisotropic case.

1. Introduction

When a strong field is applied to a macroscopically heterogeneous or composite medium, the induced change of the medium can lead to quite interesting behaviour, both in electrical transport and in optical response [1]. These phenomena are most pronounced in the case of periodic composites. In the case of a cubic lattice of dipoles, elementary (dipole lattice) arguments show that the correction to the Lorentz cavity field (due to all the dipoles inside the cavity) strictly vanishes [2].

However, when the lattice symmetry is lowered by an external means—e.g., under the influence of an external force/torque, the lattice is deformed, either lengthened in one direction and/or contracted in the other direction—the correction to the cavity field will not vanish. We call this phenomenon geometric anisotropy [3]. The lattice deformation can easily be realized by the electrorheological effect on a suspension of polarized particles, in which the particles aggregate into anisotropic structures. In this work, we will apply the Ewald–Kornfeld formulation [4, 5] to a tetragonal lattice of point dipoles, in an attempt to obtain a convergence of the infinite-lattice sum and hence examine the effects of geometric anisotropy on the local field distribution.

The plan of the paper is as follows. In the next section, we will consider a tetragonal lattice of point dipoles and apply the Ewald–Kornfeld formulation to calculate the local field. In section 3, we perform numerical calculation and the various problems encountered in the computation of the conditionally convergent summation of the near field will be addressed. In section 4, we discuss the relation between the present formulation and the established local

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field concepts. We will show that the change in the local field can lead to a generalized Clausius–Mossotti equation valid for the anisotropic case. A discussion of related problems will be given.

2. Formalism

Consider a tetragonal lattice with lattice constant qa along the z-axis and lattice constant $aq^{-1/2}$ along the x- and y-axes. In this way, the degree of anisotropy is measured by how q deviates from unity and the uniaxial anisotropic axis is along the z-axis. The lattice constants have been chosen such that the volume of the unit cell $V_c = a^3$ remains unchanged as q varies. The lattice vector is given by

$$\boldsymbol{R} = a(q^{-1/2}l\hat{\boldsymbol{x}} + q^{-1/2}m\hat{\boldsymbol{y}} + qn\hat{\boldsymbol{z}}) \tag{1}$$

where l, m, n are integers. There are N point dipoles $\boldsymbol{p}_i$ located at $\boldsymbol{r}_i$ in a unit cell. The local electric field $\boldsymbol{E}_i$ at a particular point dipole at $\boldsymbol{r}_i$ can be expressed as a sum of the electric fields of all dipoles at $\boldsymbol{r}_{\boldsymbol{R}j}$:

$$\boldsymbol{E}_i = \sum_j{}' \sum_{\boldsymbol{R}} \mathsf{T}_{i\boldsymbol{R}j} \cdot \boldsymbol{p}_j \tag{2}$$

where the prime denotes a restricted summation which excludes $j = i$ when $\boldsymbol{R} = 0$ and

$$\mathsf{T}_{ij} = -\boldsymbol{\nabla}_i \boldsymbol{\nabla}_j \frac{1}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \tag{3}$$

is the dipole interaction tensor. Equation (2) can be recast in the Ewald–Kornfeld form [4, 5]:

$$\begin{aligned}\boldsymbol{p}_i \cdot \boldsymbol{E}_i = {} & \sum_j{}' \sum_{\boldsymbol{R}} \left[-(\boldsymbol{p}_i \cdot \boldsymbol{p}_j)B(r_{i\boldsymbol{R}j}) + (\boldsymbol{p}_i \cdot \boldsymbol{r}_{i\boldsymbol{R}j})(\boldsymbol{p}_j \cdot \boldsymbol{r}_{i\boldsymbol{R}j})C(r_{i\boldsymbol{R}j})\right] \\ & - \frac{4\pi}{V_c} \sum_{\boldsymbol{G}\neq 0} \frac{1}{G^2} \exp\left(-\frac{G^2}{4\eta^2}\right)[(\boldsymbol{p}_i \cdot \boldsymbol{G}) \exp(\mathrm{i}\boldsymbol{G} \cdot \boldsymbol{r}_i) \sum_j (\boldsymbol{p}_j \cdot \boldsymbol{G}) \exp(-\mathrm{i}\boldsymbol{G} \cdot \boldsymbol{r}_j)] \\ & + \frac{4\eta^3 p_i^2}{3\sqrt{\pi}}\end{aligned} \tag{4}$$

where $r_{i\boldsymbol{R}j} = |\boldsymbol{r}_i - \boldsymbol{r}_{\boldsymbol{R}j}|$, η is an adjustable parameter and $\boldsymbol{G}$ is a reciprocal-lattice vector:

$$\boldsymbol{G} = \frac{2\pi}{a}(q^{1/2}u\hat{\boldsymbol{x}} + q^{1/2}v\hat{\boldsymbol{y}} + q^{-1}w\hat{\boldsymbol{z}}). \tag{5}$$

The coefficients B and C are given by

$$B(r) = \frac{\operatorname{erfc}(\eta r)}{r^3} + \frac{2\eta}{\sqrt{\pi} r^2} \exp(-\eta^2 r^2) \tag{6}$$

$$C(r) = \frac{3\operatorname{erfc}(\eta r)}{r^5} + \left(\frac{4\eta^3}{\sqrt{\pi} r^2} + \frac{6\eta}{\sqrt{\pi} r^4}\right) \exp(-\eta^2 r^2) \tag{7}$$

where $\operatorname{erfc}(r)$ is the complementary error function. Thus the dipole lattice sum of equation (2) becomes a summation over the real-lattice vector $\boldsymbol{R}$ as well as the reciprocal-lattice vector $\boldsymbol{G}$. Here we have considered an infinite lattice. For finite lattices, one must be careful about the effects of different boundary conditions [6]. We should remark that although a tetragonal lattice is considered, equation (4) is applicable to arbitrary Bravais lattices. The adjustable parameter η is chosen such that both the summations in the real and reciprocal lattices converge most rapidly. In what follows, we will limit ourselves to one dipole per unit cell, and the Ewald–Kornfeld summation (equation (4)) can be carried out. We will consider two cases depending on whether the dipole moment is parallel or perpendicular to the uniaxial anisotropic axis. In both cases, we will compute the local field as a function of the degree of anisotropy q.

3. Numerical results

Consider the longitudinal-field case: $\boldsymbol{p} = p\hat{\boldsymbol{z}}$, i.e., the dipole moments being along the uniaxial anisotropic axis. The local field $\boldsymbol{E}$ at the lattice point $\boldsymbol{R} = 0$ reduces to

$$E_z = p\sum_{\boldsymbol{R}\neq 0}[-B(R) + n^2q^2C(R)] - \frac{4\pi p}{V_c}\sum_{G\neq 0}\frac{G_z^2}{G^2}\exp\left(\frac{-G^2}{4\eta^2}\right) + \frac{4p\eta^3}{3\sqrt{\pi}} \qquad (8)$$

and $E_x = E_y = 0$. The local field will be computed by summing over all integer indices, $(l, m, n) \neq (0, 0, 0)$ for the summation in the real lattice and $(u, v, w) \neq (0, 0, 0)$ for that in the reciprocal lattice. Because of the exponential factors, we may impose an upper limit on the indices, i.e. we consider all indices ranging from $-L$ to L, where L is a positive integer. For $q \neq 1$, the regions of summation will be rectangular rather than cubic in both the real and reciprocal lattices. The computation has been repeated for various degrees of anisotropy with q ranging from 0.5 to 2.0. A plateau value for E_z is found for each q within a certain range of η-values, indicating that convergence of the local field has indeed been achieved with the upper limit $L = 4$.

For a larger anisotropy, however, there have been two problems associated with the computation of the conditionally convergent summation:

(1) The range of η that gives the plateau value shrinks as q increases. Even no plateau value could be observed, say, for $q = 0.1$. In this case, the summation may still converge but possibly for a much larger L and the computation time may be prohibitive.
(2) The local field can be used to evaluate the depolarization factor ϕ, defined by $\boldsymbol{E}_{\text{far}} = 4\pi\phi\boldsymbol{P} = \boldsymbol{E}_{\text{local}} - \boldsymbol{E}_{\text{near}}$, where $\boldsymbol{P} = \boldsymbol{p}/V_c$ is the total dipole moment per unit volume. The near field is the $\eta \to 0$ limiting value of the short-range part of the summation. We find that if a direct summation over the near field is performed, ϕ fluctuates seriously with the increase of L, which is unacceptable.

In order to overcome these problems, the region of summation has been taken to be inside a sphere of radius Ja in the real lattice, and one of radius $2\pi J/a$ in the reciprocal lattice, where J is a positive integer. All of the contribution from the dipoles outside the sphere will be discarded. In this way, those dipoles that contribute significantly to the local field but were not considered in the rectangular box are included in the summation. As a result, the computation time can be shortened as a much smaller value of J can be used for convergence. The summation is repeated with increasing J for convergence. We find that the summation does indeed converge to a plateau value within a wide range of η even for large anisotropy.

The second problem is also overcome by summation over a sphere. Although there are still some fluctuations of the ϕ-value, the amplitude of fluctuation is greatly reduced. We find that ϕ converges to 0.33 at $J = 8$. Physically, this reminds us that ϕ is exactly equal to $1/3$, independent of the degree of anisotropy. This implies that the far field is always equal to $4\pi\boldsymbol{P}/3$, as from far away, the lattice structure is irrelevant. What concerned us was just the total dipole moment per unit volume. The fluctuation around $\phi = 1/3$ is attributed to the slow convergence and rapid fluctuation of the near field, rather than the local field which converges more rapidly. This analysis thus provides us with an accurate means of finding the near field by subtracting the far field, i.e., $4\pi\boldsymbol{P}/3$, from the local field.

For the transverse-field case in which the dipole moments are perpendicular to the uniaxial anisotropic axis, equation (8) can still be applied to evaluate the local field by modifying G_z to G_x while taking the gradient along the direction of the dipole, say the x-axis, and obtaining the expression for the local field.

The results of the local field strength (normalized to $4\pi P/3$) against $\log_{10} q$ for the longitudinal- and transverse-field cases are plotted in figure 1(a) and figure 1(b) respectively. For comparison, the near field is also plotted in the same figure. The near field vanishes at $q = 1$, in accord with the previous result. As q decreases, the local field for the longitudinal-field case increases rapidly while that for the transverse-field case decreases rapidly. In both cases, when q deviates from unity, the effect of geometric anisotropy has a pronounced impact on the local field strengths.

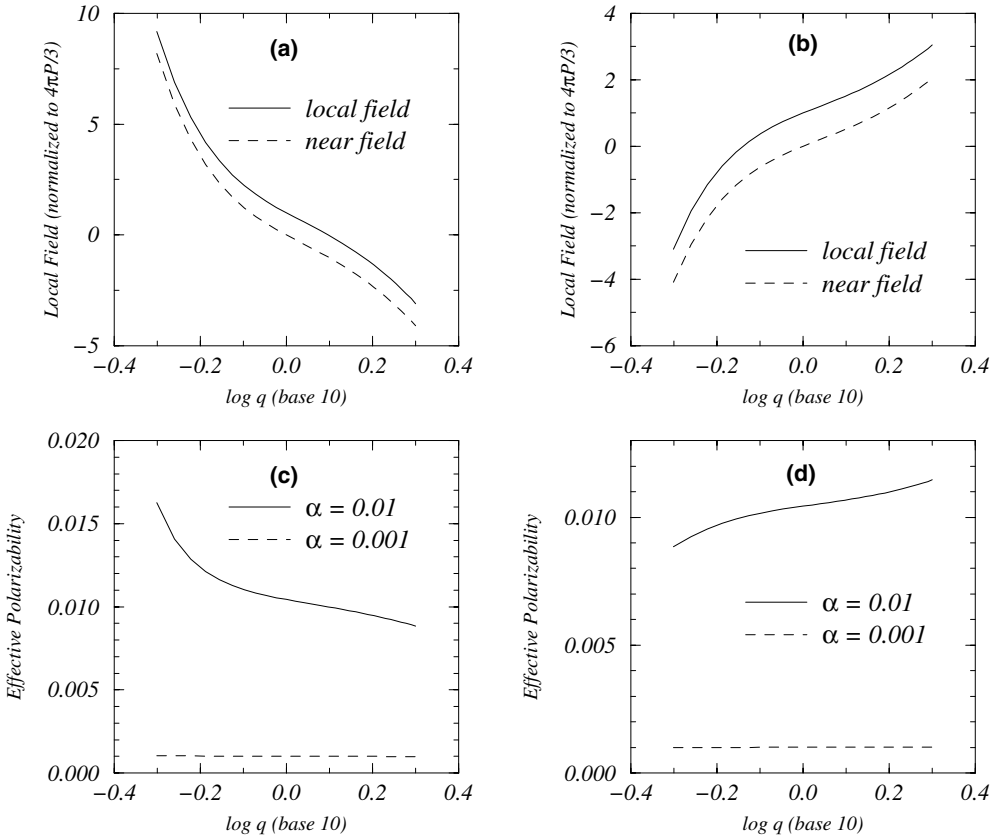

Figure 1. (a) The normalized local field strength plotted against $\log_{10} q$ for dipole moments along the uniaxial anisotropic axis. When q deviates from unity, the effect of geometric anisotropy has a strong impact on the local field strengths. (b) Similar to (a), but for dipole moments perpendicular to the uniaxial anisotropic axis. (c) The effective polarizability plotted against $\log_{10} q$ for dipole moments along the uniaxial anisotropic axis. When q deviates from unity, the effect of geometric anisotropy has a similar impact on the effective polarizability. (d) Similar to (c), but for dipole moments perpendicular to the uniaxial anisotropic axis.

4. Contact with macroscopic concepts

4.1. The generalized Clausius–Mossotti equation

Our present theory is of microscopic origin, in the sense that we have computed the lattice summation using the Ewald–Kornfeld formulation. We have not invoked any macroscopic concepts like the Lorentz cavity field [7–9] in the calculations. However, incorporation of

these established concepts can lead to a modification of the Clausius–Mossotti equation valid for the anisotropic case.

More precisely, we use the result for the local field to evaluate the effective polarizability α_{eff} of the dipole lattice, which is given by

$$\alpha_{\text{eff}} = \frac{\alpha}{1 - \alpha\beta/V_c} \tag{9}$$

where α is the polarizability of an isolated dipole, and $\beta = E/P$ is the local field factor. Note that $\beta = 4\pi/3$ when $q = 1$. To see this, observe that the total field acting on a dipole is the sum of the applied field E_0 and the local field due to all other dipoles; hence

$$p = \alpha(E_0 + \beta P)$$

where E_0 is the applied electric field. Let $P = p/V_c$; the above equation becomes a self-consistent equation. Solving yields

$$p = \left(\frac{\alpha}{1 - \alpha\beta/V_c}\right) E_0.$$

The effective dielectric constant ϵ_{eff} is given by $1 + 4\pi\alpha_{\text{eff}}/V_c$. For a cubic lattice, $\beta = 4\pi/3$, ϵ_{eff} satisfies the well-known Clausius–Mossotti equation:

$$\frac{\epsilon_{\text{eff}} - 1}{\epsilon_{\text{eff}} + 2} = \frac{4\pi\alpha}{3V_c}. \tag{10}$$

Thus equation (9) represents a generalization of the Clausius–Mossotti equation to the anisotropic lattice.

The result for the effective polarizability is plotted against $\log_{10} q$ in figure 1(c) for the longitudinal-field case while in figure 1(d) it is plotted for the transverse-field case with $\alpha = 0.001, 0.01$ and $V_c = 1$. For a small $\alpha = 0.001$, the effective polarizability is almost independent of q. However, for a larger $\alpha = 0.01$, the effective polarizability exhibits similar behaviour to the local field. As q decreases, α_{eff} for the longitudinal-field case increases rapidly while that for the transverse-field case decreases rapidly. Again, when q deviates from unity, the effect of geometric anisotropy has a strong impact on the effective polarizability.

4.2. The Onsager reaction field

A problem with the Lorentz theory is in regard to its generalization to polar media with permanent dipole moments μ. A simple replacement of the polarizability α by $\alpha + \mu^2/k_B T$ in the Clausius–Mossotti relation leads to a divergent dielectric constant, a phenomenon known as the polarization catastrophe. In 1936, Onsager [10] resolved this problem by introducing a reaction field: while the Lorentz local field at the origin is due to all dipole moments of the lattice in the absence of the dipole moment at the origin, the reaction field at the origin arises from the additional polarization of the surrounding dipole moments due to the dipole moment $\boldsymbol{p}_0$ at the origin.

In the present case, the Onsager reaction field at the origin is given by

$$\boldsymbol{R}_0 = \alpha \sum_{R \neq 0} \mathbf{T}_{0R} : \mathbf{T}_{R0} \cdot \boldsymbol{p}_0 \tag{11}$$

where α is the bare polarizability and $\mathbf{T}$ is the dipole interaction tensor:

$$\mathbf{T}_{0R} = \boldsymbol{\nabla}_R \boldsymbol{\nabla}_R \frac{1}{R} = \mathbf{T}_{R0}. \tag{12}$$

Unlike the summation of the local field, the infinite sum (equation (11)) for the Onsager reaction field is indeed absolutely convergent. No Ewald–Kornfeld formulation is needed because the

product **T**:**T** is positive definite. For a simple cubic lattice of dipole moments, on summing over nearest neighbours, the result is

$$R_0 = 12\alpha p_0 / V_c^2$$

which is already close to the infinite-lattice limit $R_0 \approx 16.8\alpha p_0 / V_c^2$. It is instructive to extend the consideration to anisotropic lattices. The reaction field is conveniently expressed as $R_0 = \lambda\alpha p_0 / V_c^2$, where λ is the reaction-field factor. Again, the summation over a sphere has helped the convergence. We perform the direct summation in the real lattice to obtain the reaction-field factor for q ranging from 0.5 to 2.0. In figures 2(a) and 2(b), we plot λ versus $\log_{10} q$ for the longitudinal- and transverse-field cases respectively. There is a minimum λ around $q = 1$ (but not exactly at $q = 1$) in both cases and λ increases rapidly when q deviates from unity. As is evident from figure 2, the effect of geometry anisotropy has a strong impact on the reaction-field strength.

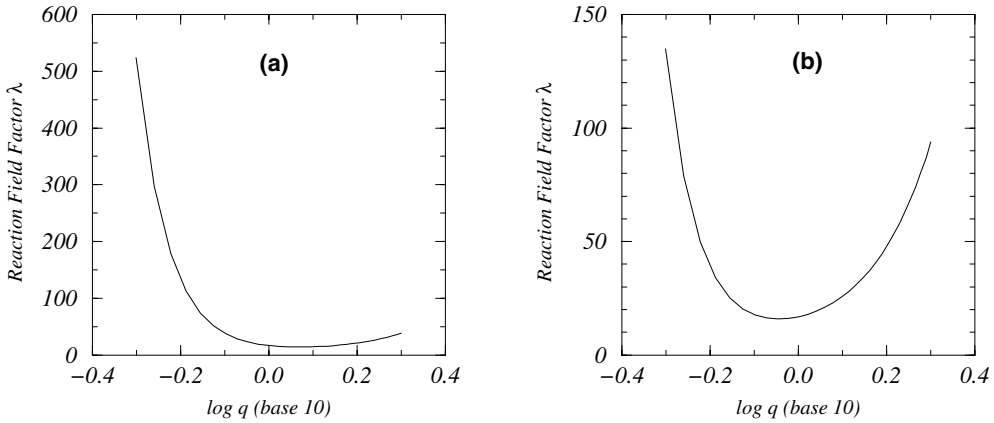

Figure 2. (a) The reaction-field factor plotted against $\log_{10} q$ for dipole moments along the uniaxial anisotropic axis. When q deviates from unity, the effect of geometric anisotropy has a strong impact on the reaction-field strengths. (b) Similar to (a), but for dipole moments perpendicular to the uniaxial anisotropic axis.

5. Discussion and conclusions

Here a few comments on the results are in order. We should remark that the present work employs the electrostatic (dipole) approximation. While such an approximation is simpler to implement and suffices in many cases, for optical properties of composites of metallic particles embedded in a dielectric host medium, one must go beyond the electrostatic approximation [11].

It is possible to extend the present theory to statistical geometric anisotropy [12], e.g., that being induced by the electrorheological effects [3]. We may also extend the formulation to a randomly dilute lattice of dipoles to mimic mixed magnetic and nonmagnetic ions.

Although we have employed a lattice structure in the present work, our formalism can readily be applied to an assembly of randomly placed dipoles by considering a more complex basis in a unit cell. Such an extension will be useful for the study of dielectric liquids under an intense electric field.

In conclusion, we have applied the Ewald–Kornfeld formulation to a tetragonal lattice of point dipoles to examine the effects of geometric anisotropy on the local field distribution. The

various problems encountered in the computation of the conditionally convergent summation are addressed and the methods of overcoming them are discussed. We suggest that the large value of the derivative of the local field with respect to the degree of anisotropy suggests potential applications as artificial piezoelectric materials, as one can change the degree of anisotropy easily in a suspension.

Acknowledgments

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