Field-induced structure transformation in electrorheological solids

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We have computed the local electric field in a body-centered tetragonal (bct) lattice of point dipoles via the Ewald-Kornfeld formulation, in an attempt to examine the effects of a structure transformation on the local-field strength. For the ground state of an electrorheological solid of hard spheres, we identified a different structure transformation from the bct to the face-centered cubic (fcc) lattices by changing the uniaxial lattice constant c under the hard-sphere constraint. In contrast to the previous results, the local field exhibits a nonmonotonic transition from bct to fcc. As c increases from the bct ground state, the local field initially decreases rapidly towards the isotropic value at the body-centered cubic lattice, decreases further, reaching a minimum value and increases, passing through the isotropic value again at an intermediate lattice, reaches a maximum value and finally decreases to the fcc value. An experimental realization of the structure transformation is suggested. Moreover, the change in the local field can lead to a generalized Clausius-Mossotti equation for the bct lattices.

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I. INTRODUCTION

When a strong field is applied to a composite medium, the induced change of the medium can lead to spectacular behavior, both in electrical transport and in optical response [1]. If a strong electric field is applied to a suspension of particles where the particles have a large electric polarizability, the induced dipole moments of the particles can order the suspended particles into a body-centered tetragonal (bct) lattice [2]. This process is known as the electrorheological (ER) effect.

Recently, Tao and Jiang [3] proposed that a structure transformation from the bct ground state to some other lattices can occur when one simultaneously applies a magnetic field perpendicular to the electric field and the polarized particles possess magnetic dipole moments. Sheng and coworkers [4] verified the proposal experimentally and observed a structure transformation from the bct to face-centered cubic (fcc) lattices. Motivated by these studies, we propose an alternative structure transformation from the bct to the fcc structure, through the application of electric fields only.

The plan of the paper is as follows. We will adopt the point-dipole approximation [2] and calculate the dipole lattice sum via the Ewald-Kornfeld formulation in Sec. II. In Sec. III, we discuss the effects of a structure change on the local field when the lattice constants vary. If we change the uniaxial-lattice constant under the hard-sphere condition, a series of transformations occur among the bct ground state, body-centered cubic (bcc), intermediate and fcc lattices (see Fig. 1). The results will be compared with those of a tetragonal lattice. We also make a contact with macroscopic concept and derive the Clausius-Mossotti equation. In Sec. IV, we will compute the dipole interaction energy as a function of various lattices and discuss a possible structure transformation by the application of rotating electric fields. Discussion and conclusion on our results will be given.

II. FORMALISM

In this section, we apply the Ewald-Kornfeld formulation [5,6] to compute the local electric field for a bct lattice of point dipoles. The bct lattice can be regarded as a tetragonal lattice, plus a basis of two point dipoles, one of which is located at a corner and the other of which at the body center of the tetragonal unit cell. The tetragonal lattice has a lattice constant $c=q\xi$ along the z axis and lattice constants $a=b=\xi q^{-1/2}$ along the x and y axes. The volume of the tetragonal unit cell remains $V_c=\xi^3$ as q varies. In this way, the degree of anisotropy of the tetragonal lattice is measured by how q is deviated from unity and the uniaxial anisotropic axis is along the z axis.

So far, the lattice parameter ξ remains arbitrary. For hard spheres in an ER solid, however, the lattice parameter ξ can be determined from the relation: $2a^2+c^2=16R^2$, where R is the radius of the spheres. The hard-sphere condition requires $a\geqslant 2R$ and $c\geqslant 2R$. For the bct ground state, $a=b=\sqrt{6}R$ and $c=2R$, while for the fcc lattice, $a=b=2R$ and $c=\sqrt{8}R$ [2]. The bcc lattice is characterized by $a=b=c=\sqrt{16/3}R$. Each sphere has a point dipole embedded at its center.

The lattice vector of the tetragonal lattice is given by

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

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

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

where "prime" denotes a restricted summation that excludes $j=i$ when $\mathbf{R}=\mathbf{0}$ and

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

is the dipole interaction tensor. Equation (2) can be recast in the Ewald-Kornfeld form [5,6]:

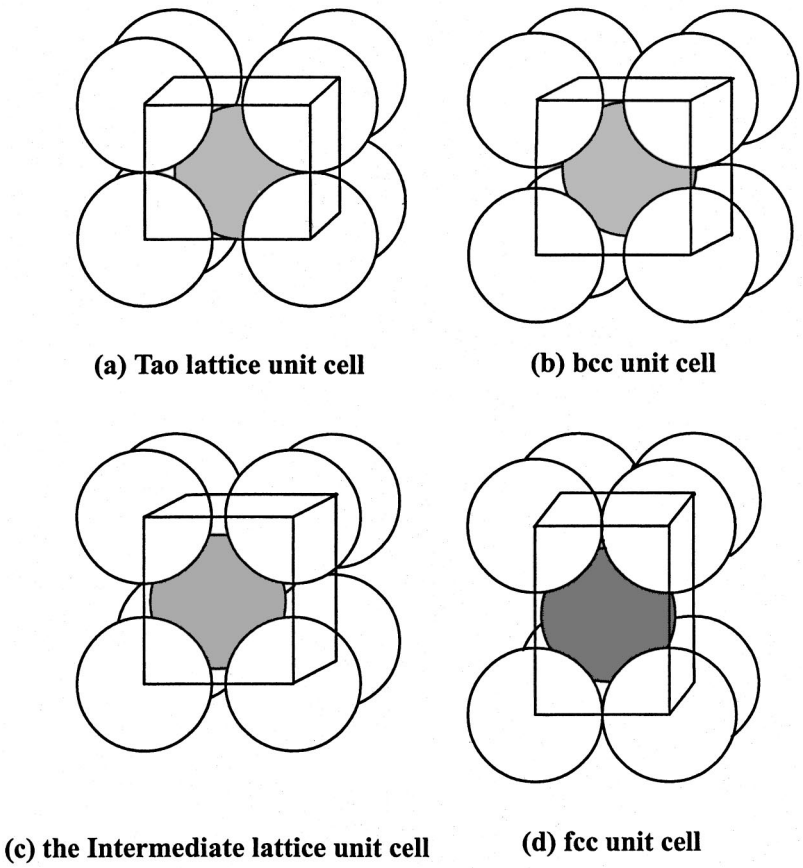

FIG. 1. A sequence of unit cells of bct lattices during structure transformation: (a) Tao's bct lattice, (b) bcc lattice, (c) intermediate lattice, and (d) fcc lattice.

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

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

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

The B and C coefficients are given by

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

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

where $\mathrm{erfc}(r)$ is the complementary error function. Thus the dipole lattice sum of Eq. (2) becomes a summation over the real-lattice vector $\mathbf{R}$ as well as the reciprocal-lattice vector $\mathbf{G}$. Here we have considered an infinite lattice. For finite lattices, one must be careful about the effects of different boundary conditions [7].

We should remark that although a tetragonal lattice is considered, Eq. (4) is applicable to arbitrary Bravais lattices. The adjustable parameter η is chosen so that both the summations in the real and reciprocal lattices converge most rapidly. In what follows, we will limit ourselves to the bct cell with two dipoles per tetragonal cell, and the Ewald-Kornfeld summation [Eq. (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.

III. EFFECTS OF STRUCTURE TRANSFORMATION ON THE LOCAL FIELD

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

$$E_z=p\sum_{j=1}^{2}{}'\sum_{\mathbf{R}}\left[-B(R_j)+z_j^2q^2C(R_j)\right]-\frac{4\pi p}{V_c}\sum_{\mathbf{G}\neq 0}S(\mathbf{G})\frac{G_z^2}{G^2}\exp\left(\frac{-G^2}{4\eta^2}\right)+\frac{4p\eta^3}{3\sqrt{\pi}},\tag{8}$$

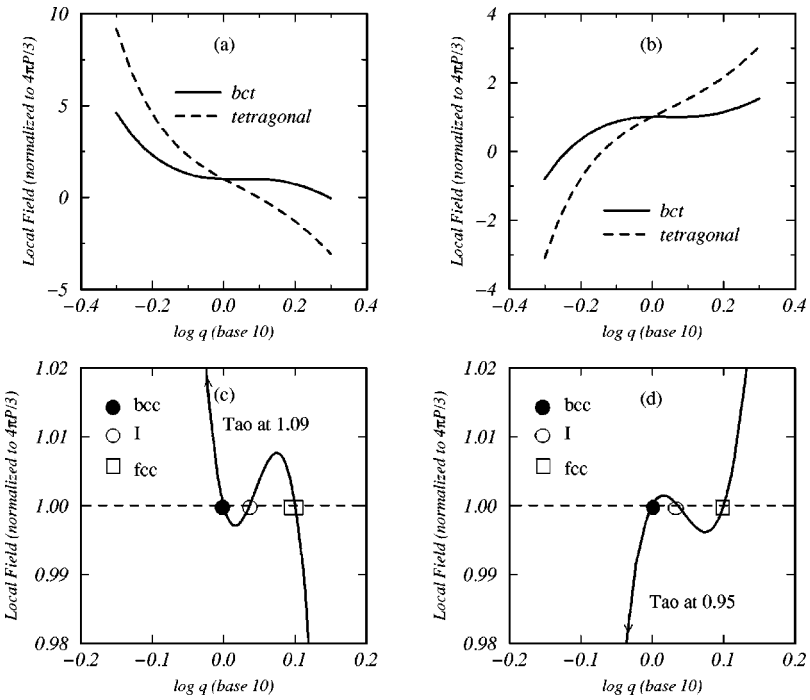

FIG. 2. (a) The local-field factor plotted against $\log_{10}q$ for dipole moments along the uniaxial anisotropic axis. (b) Similar to (a), but for dipole moments perpendicular to the uniaxial anisotropic axis. (c) and (d): Magnified versions of (a) and (b), respectively, to show the different lattices during structure transformation.

and $E_x=E_y=0$. In the equation, z_j and R_j are respectively given by

$$z_j=n-\frac{j-1}{2}, \quad R_j=\left|\mathbf{R}-\frac{j-1}{2}(a\hat{\mathbf{x}}+a\hat{\mathbf{y}}+c\hat{\mathbf{z}})\right|,$$

and $S(\mathbf{G})=1+\exp[i(u+v+w)/\pi]$ is the structure factor. The local field will be computed by summing over all integer indices $(j,l,m,n)\neq(1,0,0,0)$ 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 to the indices, i.e., all indices ranging from $-L$ to L, where L is a positive integer. For $q\neq1$, 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: $1<\eta<10^{0.6}$. For instance, the calculations with $\eta=10^{0.5}$ yield numerical results already accurate up to 16 significant figures, indicating that convergence of the local field has indeed been achieved with the upper limit $L=4$. For larger anisotropy (either $q\ll1$ or $q\gg1$), a spherical region of summation can help the convergence [8].

For the transverse-field case in which the dipole moments are perpendicular to the uniaxial anisotropic axis, Eq. (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 obtain the expression of 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 Figs. 2(a) and 2(b) respectively. For comparison, the corresponding results for a tetragonal lattice [8] (i.e., in the absence of the body centers) are also plotted on the same figure. 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 anisotropy has a pronounced effect on the local-field strengths.

Unlike the tetragonal case, the local field of the bct lattice does not vary much near $q=1$. When we magnify the scales in Figs. 2(c) and 2(d), we observe a nonmonotonic behavior as q increases: as c increases from bct, the local field initially decreases rapidly towards the isotropic value at bcc, decreases further, reaching a minimum value and increases, passing through the isotropic value again at an intermediate lattice, reaches a maximum value and finally decreases to the fcc value. The isotropic value of the intermediate lattice is attributed to the symmetry of the dipole interaction tensor.

Our present theory is of microscopic origin, in the sense that we have computed the lattice summation by the Ewald-Kornfeld formulation. We have not invoked any macroscopic concepts like the Lorentz cavity field [9–11] in the calculations. However, to corroborate with these established concepts can lead to a modification of the Clausius-Mossotti equation.

More precisely, we use the result of the local field to evaluate the effective polarizability α_{eff} of the dipole lattice. 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 α is the polarizability of an isolated dipole and $\beta=E/P$ is the local-field factor. We will use β_z and β_{xy} to denote the local-field factors parallel and perpendicular to the uniaxial anisotropic axis. Note that $\beta_z=\beta_{xy}=4\pi/3$ when $q=1$. Let $P=p/V_c$, the above equation becomes a self-consistent equation. Solving yields

$$p=\left(\frac{\alpha}{1-\alpha\beta/V_c}\right)E_0\equiv\alpha_{\rm eff}E_0\,. \tag{9}$$

The effective dielectric constant $\epsilon_{\rm eff}$ is given by $1+4\pi\alpha_{\rm eff}/V_c$. Thus,

$$\frac{\epsilon_{\rm eff}-1}{\beta'\epsilon_{\rm eff}+(3-\beta')}=\frac{4\pi\alpha}{3V_c'}, \tag{10}$$

where $\beta'=3\beta/4\pi$ and $V_c'=V_c/2$. For the bcc lattice, $\beta'=1$, $\epsilon_{\rm eff}$ satisfies the well-known Clausius-Mossotti equation. Thus Eq. (10) represents a generalization of the Clausius-Mossotti equation to the bct lattices.

IV. STRUCTURE TRANSFORMATION VIA ROTATING ELECTRIC FIELDS

The results of the local-field strength as well as the generalized Clausius-Mossotti equation allow us to compute the dipole interaction energy per particle in the ER solid, similar to calculations of Tao and Sun [2]. If an uniaxial field $\mathbf{E}=\hat{\mathbf{z}}E_z$ is applied, the dipole interaction energy per particle is given by $u=-\mathbf{p}\cdot\mathbf{E}/2\epsilon_2$, where ϵ_2 is the dielectric constant of the host medium. Since $E_z=\beta_z(2p/V_c)$ and $p=\alpha E_z$, we obtain

$$u=-\frac{\beta_z}{(V_c/a^3)} \tag{11}$$

in units of $p^2/\epsilon_2 a^3$. As q increases from the bct ground state to the fcc structures, the volume of the unit cell increases initially, reaching a maximum at the bcc structure, then decreases to the fcc structure. As the local-electric-field strength remains almost constant in the range $1<q<1.5$, the increase in the magnitude of the dipole energy per particle is attributed to the decrease in the volume of the unit cell. Concomitantly, as shown in Fig. 3, the energy per particle initially increases from the bct ground state, reaching a maximum near the bcc structure and then decreases all the way towards the fcc structure. The transformation involves climbing up an energy barrier beyond which the fcc structure becomes stable, which is in contrast with the smooth and monotonic transition proposed in previous work [3,4].

Next we apply a rotating electric field $E_{xy}=rE_z$ in the plane perpendicular to the uniaxial electric field, where $r=E_{xy}/E_z$ is the ratio of the rotating to axial field strength. The instantaneous electric fields are $E_x=E_{xy}\cos(\omega t+\phi)$ and $E_y=E_{xy}\sin(\omega t+\phi)$, where ω is the angular velocity of the rotating field and ϕ is an arbitrary phase angle. In this case, the dipole interaction energy per particle is modified to

$$u=-\frac{\beta_z+r^2\beta_{xy}}{(1+r^2)(V_c/a^3)} \tag{12}$$

in units of $p^2/\epsilon_2 a^3$. As shown in Fig. 3, when we increase the ratio r, the bct ground-state energy increases while the fcc energy remains unchanged, but there is still an energy barrier between the bct and fcc states for small r. When $r>2.6$, the energy barrier disappears and the fcc structure is the most stable. Physically one has to break the chains to make the structure transformation possible when the strength of the rotating electric field is sufficiently large.

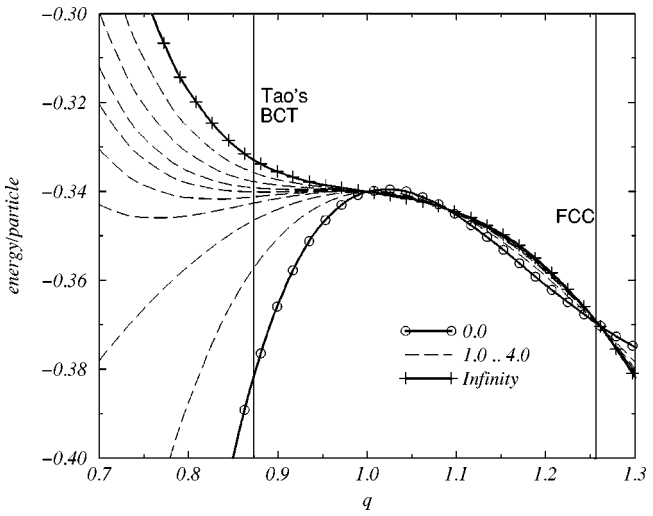

FIG. 3. The dipole interaction energy per particle plotted against q for different ratio $r=E_{xy}/E_z$ of the rotating to axial field strength. For hard spheres, the accessible regions are within the vertical lines depicted by Tao's bct and fcc. Along Tao's bct line and from bottom to top, $r=$ 0.0, 1.0, 1.6, 2.0, 2.2, 2.4, 2.6, 3.0, 4.0, and ∞. It is evident that the fcc structure is the most stable for large r.

From the energy consideration, we suggest that the structure transformation be realized in experiments by applying a rotating electric field in the plane perpendicular to the uniaxial electric field. In this field configuration, both the time average value of the induced dipole moment and that of the rotating electric field vanish in the plane. However, the instantaneous dipole moment will induce an overall attractive force between the particles in the plane perpendicular to the uniaxial field. This is very different from the previous transformation proposed by Tao and Jiang [3] and experimentally verified by Sheng and coworkers [4] by using crossed electric and magnetic fields on microparticles that possess permanent magnetic dipole moments. In our case, the field configuration is all electrical; no magnetic field and/or magnetic materials need to be used. Alternatively, we may apply the same rotating electric field configuration to a magnetorheological fluid to achieve the structure transformation.

V. DISCUSSION AND CONCLUSION

Here a few comments on our results are in order. As mentioned in Ref. [3], the energy difference between the fcc and hexagonal close-packed (hcp) structures is very small, and is comparable to the thermal energy, there is a competition between these structures. Therefore, we will likely find an fcc-hcp mixed structure. However, it appears that our field configuration helps a fourfold symmetry in the plane of the rotating field and the fcc structures may be more favorable. Nevertheless, we are awaiting experimental evidence on the proposed structure transformation.

Our calculations have been performed up to the point-dipole approximation, which is in the same spirit as done by Tao and Sun [2]. A dipole-induced-dipole (DID) model, which takes into account the mutual polarization effect between touching particles, can drastically improve the accuracy towards the fully multipolar calculations [12]. Since the DID contribution becomes important for small reduced separation $\sigma = d/2R < 1.1$ [12], we can simplify the calculations by limiting ourselves to touching spheres only. We may omit the nontouching spheres (unless the spheres get very close so that $\sigma = d/2R < 1.1$). Each sphere is in contact with eight neighboring spheres in the bct lattices and 12 neighboring spheres in the fcc lattice and the number of DID images dipoles is therefore finite. The generalization thus includes the original point dipoles as well as all the DID images dipoles at well-defined positions in the unit cell and the general formula [Eq. (4)] can indeed be used. The incorporation of the more accurate DID model into the Ewald-Kornfeld formulation is underway. However, we believe that the point-dipole results remain qualitatively correct.

In conclusion, we have applied the Ewald-Kornfeld formulation to a bct lattice of point dipoles to examine the effects of structure transformation on the local field distribution. We have found that the local field exhibits a nonmonotonic transition from bct to fcc. Moreover, we showed that the change in the local field can lead to a generalized Clausius-Mossotti equation for the bct lattices.

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