Energy of an electrorheological solid calculated with inclusion of higher multipoles

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We have investigated the contributions of higher multipoles to the energy of an electrorheological solid. We find that, with the dipole and octupole moments taken into account, the fcc structure becomes almost degenerate in energy with the bct: Favoring of the latter is only by $\frac{1}{10}$ to $\frac{1}{4}$ of its dipole value. The thirty-two-pole effect is opposite to that of the octupole so that, when it is also added, the energy by which the bct structure is favored is restored to about $\frac{1}{2}$ to $\frac{4}{5}$ of its dipole value.

INTRODUCTION

An electrorheological (ER) fluid consists of a suspension of dielectric particles in a liquid of low dielectric constant.[1] Its viscosity increases dramatically in the presence of an applied electric field. When the applied field exceeds some critical value, the ER fluid turns into a solid, whose shear modulus increases as the field is further strengthened. In a recent paper,[2] Tao and Sun showed that, in the dipole approximation, the body-centered tetragonal (bct) structure (see Fig. 1) has the lowest energy among the fcc, sc, and bct structures, and separated chains. They concluded that the bct structure is the ground-state structure of an ER solid.

Because the separations between dielectric spheres are small, the higher multipoles are important. We therefore consider the electrostatic interaction between dielectric spheres up to the thirty-two-pole contribution, to see whether it affects the energy comparison among different structures.

GENERAL FORMULATION

We proceed by expressing the energy as a quadratic function of all multipole moments of a single sphere, assuming all spheres to be equivalently placed in the lattice. Apart from that, the present section applies to any lattice.

The energy per sphere is

$$U=\int\left[-\mathbf{P}\cdot[\mathbf{E}_{\rm ext}+\tfrac{1}{2}\mathbf{E}_{\rm other}+\tfrac{1}{2}\mathbf{E}_{\rm self}]+\frac{\mathbf{P}^2}{2\chi}\right]d^3x\ , \tag{1}$$

where $\mathbf{E}_{\rm ext}$ represents the applied field, $\mathbf{E}_{\rm other}$ represents the field produced by the induced charge of other spheres, $\mathbf{E}_{\rm self}$ represent the field produced by the surface charge of said sphere, and the $\mathbf{P}^2/2\chi$ term is the restoring force term.

Let $V(\mathbf{r})$ be the total potential at $\mathbf{r}$. Inside a sphere, we have $\nabla\cdot\mathbf{D}=0$, where $\mathbf{D}=-(1+4\pi\chi)\nabla V$, and therefore $\nabla^2V=0$. Hence, taking the origin at the center of the sphere, we can expand the potential with use of spherical harmonics:

$$V(\mathbf{r})=\sum_{l,m}V_{lm}Y_l^m(\theta,\phi)\left[\frac{r}{a}\right]^l\ , \tag{2}$$

where a is the radius of the sphere. Since V is real and $Y_l^{m*}=(-1)^mY_l^{-m}$, we have $V_{l,-m}=(-1)^mV_{lm}^*$. Because $\mathbf{P}=-\chi\nabla V$, we obtain

$$\int-\mathbf{P}\cdot\mathbf{E}_{\rm ext}d^3x=\left[\frac{4\pi}{3}\right]^{1/2}\chi a^2V_{10}E_{\rm ext}=-\mathbf{p}\cdot\mathbf{E}_{\rm ext}\ ,$$

where $\mathbf{p}$ is the net dipole moment of a sphere, and

$$\int\frac{\mathbf{P}^2}{2\chi}d^3x=\frac{\chi a}{2}\sum_{l,m}l|V_{lm}|^2\ . \tag{3}$$

To find the $\mathbf{p}\cdot\mathbf{E}_{\rm self}$ term, we write $\mathbf{E}_{\rm self}=-\nabla V_{\rm self}$, where

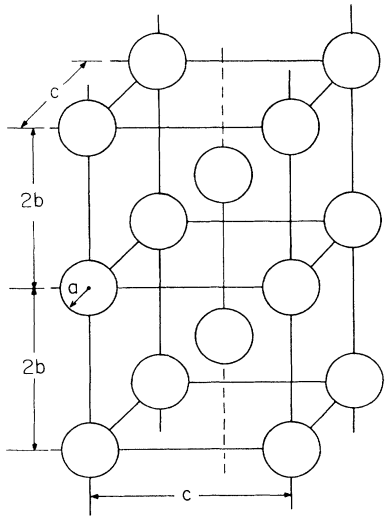

FIG. 1. Lattice structure for the generic tetragonal lattice considered in this paper. The bct structure corresponds to $a=b=1/\sqrt{6}c$; fcc, to $2a=c=\sqrt{2}b$.

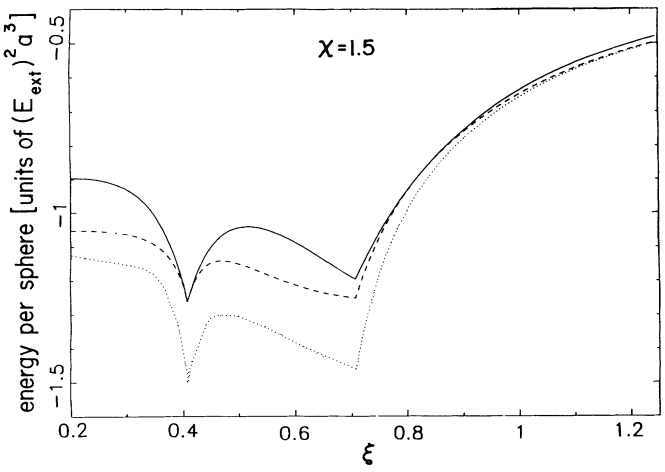

FIG. 2. Energy per sphere as a function of ξ, for $\chi=1.5$. The solid line corresponds to dipole approximation; the dashed line corresponds to dipole+octupole approximation; the dotted line corresponds to dipole+octupole+thirty-two-pole approximation. The end-point minimum near $\xi=0.41$ is for the bct structure; the one near $\xi=0.71$ is for the fcc structure.

TABLE I. Total energies in the bct and fcc structures in the dipole approximation (only $l=1$ considered) for various susceptibilities χ. The energies are given in units of $(E_{ext})^2 a^3$.

χ	U_{bct}	$U_{fcc}-U_{bct}$
0.4	−0.599 300	0.015 427
0.9	−0.994 563	0.041 779
1.5	−1.260 621	0.066 376
2.2	−1.445 130	0.086 560
3.5	−1.635 675	0.110 023
5.0	−1.753 023	0.125 769
∞	−2.105 485	0.178 847

$$V_{self}=\sum_{l,m} V_{self}^{lm} Y_l^m(\theta,\phi) f_l(r) , \tag{4}$$

where $f_l(r)=(r/a)^l$ for $r<a$ or $(a/r)^{l+1}$ for $r>a$. Since $\nabla^2 V=0$ inside the sphere, the source of V_{self} is entirely at $r=a$, where

$$\hat{\mathbf{r}}\cdot\nabla V_{self}^{in}-\hat{\mathbf{r}}\cdot\nabla V_{self}^{out}=4\pi\sigma=4\pi\mathbf{P}\cdot\hat{\mathbf{r}}=-4\pi\chi\hat{\mathbf{r}}\cdot\nabla V^{in} ; \tag{5}$$

whence

$$\frac{2l+1}{4\pi a} V_{self}^{lm}=-\chi\frac{l}{a}V_{lm} \tag{6}$$

and therefore

$$\tfrac{1}{2}\int -\mathbf{P}\cdot\mathbf{E}_{self} d^3x=\frac{\chi a}{2}\sum_{l,m}\frac{l 4\pi\chi l^2}{2l+1}|v_{lm}|^2 . \tag{7}$$

Note that we do not need to know the value of $V(\mathbf{r})$ outside the sphere.

We now turn to the term $\mathbf{P}\cdot\mathbf{E}_{other}$ in Eq. (1). Define $u=x+iy$ and $v=x-iy$. It is easy to derive the following formula:

$$Y_l^m(\theta,\phi)\frac{1}{r^{l+1}}=\begin{cases}(-1)^{l-m}2^m\left[\dfrac{2l+1}{4\pi}\dfrac{1}{(l-m)!(l+m)!}\right]^{1/2}\dfrac{\partial^m}{\partial v^m}\dfrac{\partial^{l-m}}{\partial z^{l-m}}\left[\dfrac{1}{r}\right], & m\geq 0 ,\\ (-1)^l 2^{|m|}\left[\dfrac{2l+1}{4\pi}\dfrac{1}{(l-m)!(l+m)!}\right]^{1/2}\dfrac{\partial^{|m|}}{\partial u^{|m|}}\dfrac{\partial^{l-|m|}}{\partial z^{l-|m|}}\left[\dfrac{1}{r}\right], & m\leq 0 .\end{cases} \tag{8}$$

Thus, for $r>a$, Eq. (4) becomes

$$V_{self}(\mathbf{r})=\sum_{\substack{l,m\\(0\leq m\leq l)}} A_{lm}\left[\frac{\partial^m}{\partial v^m}+(-1)^m\frac{\partial^m}{\partial u^m}\right]\frac{\partial^{l-m}}{\partial z^{l-m}}\left[\frac{1}{r}\right], \tag{9}$$

where

$$A_{lm}=(1-\tfrac{1}{2}\delta_{m,0})(-a)^{l+1}(-2)^m l\chi\left[\frac{4\pi}{2l+1}\frac{1}{(l-m)!(l+m)!}\right]^{1/2} V_{lm} .$$

Now

$$-\tfrac{1}{2}\int \mathbf{P}\cdot\mathbf{E}_{other} d\mathbf{r}=\tfrac{1}{2}\int\rho(\mathbf{r})V_{other}(\mathbf{r})d\mathbf{r}=\sum_h{}'\tfrac{1}{2}\int\rho(\mathbf{r})V_{self}(\mathbf{r}-\mathbf{R}_h)d\mathbf{r} ,$$

where the $\sum'_h$ means sum over all the lattice points except the origin. For each sphere h, let $U_h=X_h+iY_h$, $V_h=X_h=iY_h$; then we have from Eq. (9)

$$\begin{aligned}\tfrac{1}{2}\int\rho(\mathbf{r})V_{other}(\mathbf{r})d\mathbf{r}&=\tfrac{1}{2}\sum_h{}'\int\sum_{\substack{l,m\\(0\leq m\leq l)}} A_{lm}\left[\frac{\partial^m}{\partial v^m}+(-1)^m\frac{\partial^m}{\partial u^m}\right]\frac{\partial^{l-m}}{\partial z^{l-m}}\left[\frac{1}{|\mathbf{r}-\mathbf{R}_h|}\right]\rho(\mathbf{r})d\mathbf{r}\\ &=-\tfrac{1}{2}\sum_h{}'\sum_{\substack{l,m\\(0\leq m\leq l)}}(-1)^l A_{lm}\left[\frac{\partial^m}{\partial V_h^m}+(-1)^m\frac{\partial^m}{\partial U_h^m}\right]\frac{\partial^{l-m}}{\partial Z_h^{l-m}}\int\left[\frac{1}{|\mathbf{r}-\mathbf{R}_h|}\right]\rho(\mathbf{r})d\mathbf{r}\\ &=-\tfrac{1}{2}\sum_h{}'\sum_{\substack{l,m\\(0\leq m\leq l)}}(-1)^l A_{lm}\left[\frac{\partial^m}{\partial V_h^m}+(-1)^m\frac{\partial^m}{\partial U_h^m}\right]\frac{\partial^{l-m}}{\partial Z_h^{l-m}}V_{self}(\mathbf{R}_h) ,\end{aligned} \tag{10}$$

TABLE II. Same as in Table I, but with octupole moments included (all $l \leq 3$). The V_{30}/V_{10} ratios are also given.

χ	U_{bct}	$U_{\text{fcc}} - U_{\text{bct}}$	V_{30}/V_{10} (bct)	V_{30}/V_{10} (fcc)
0.4	−0.599 318	0.004 969	0.002 833	−0.462 218
0.9	−0.994 635	0.008 851	0.004 182	−0.053 790
1.5	−1.260 758	0.010 179	0.004 934	−0.056 766
2.2	−1.445 326	0.012 268	0.005 396	−0.058 305
3.5	−1.635 947	0.013 973	0.005 832	−0.059 592
5.0	−1.753 350	0.014 721	0.006 081	−0.060 267
∞	−2.106 008	0.016 599	0.006 754	−0.061 903

and therefore

$$-\tfrac{1}{2}\int \mathbf{P}\cdot\mathbf{E}_{\text{other}}\,d\mathbf{r} = \tfrac{1}{2} \sum_{\substack{l,m \\ (0\leq m\leq l)}} \sum_{\substack{l',m' \\ (0\leq m'\leq l')}} (-1)^l A_{lm}\, A_{l'm'} F_{lm,l'm'}\ , \tag{11}$$

where

$$F_{lm,l'm'} = \sum_h{}' \left[\frac{\partial^m}{\partial V_h^m} + (-1)^m \frac{\partial^m}{\partial U_h^m} \right] \frac{\partial^{l-m}}{\partial Z_h^{l-m}} \left[\frac{\partial^{m'}}{\partial V_h^{m'}} + (-1)^{m'} \frac{\partial^{m'}}{\partial U_h^{m'}} \right] \frac{\partial^{l'-m'}}{\partial Z_h^{l'-m'}} \left[\frac{1}{R_h} \right] .$$

[Note that $(-1)^l F_{lm,l'm'} + (-1)^{l'} F_{l'm',lm} = 0$ if $l - l'$ is odd. This decoupling between moments of opposite parity is a consequence of assuming all spheres to have identical charge distributions.]

Finally from (1), the energy per sphere is now

$$U = S_{10} V_{10} + \tfrac{1}{2} \sum_{\substack{l,m \\ (0\leq m\leq l)}} \sum_{\substack{l',m' \\ (0\leq m'\leq l')}} G_{lm,l'm'} V_{lm} V_{l'm'}\ , \tag{12}$$

where

$$S_{10} = \left[\frac{4\pi}{3} \right]^{1/2} \chi a^2 E_{\text{ext}}\ ,$$

$$G_{lm,l'm'} = \delta_{ll'}\delta_{mm'}\chi a l \left[1 + \frac{4\pi\chi l}{2l+1} \right] + (-1)^{l'} a^{l+l'+2} (-2)^{m+m'} \chi^2 \frac{(1-1/2\delta_{m,0})(1-1/2\delta_{m',0}) 4\pi l l' F_{lm,l'm'}}{\sqrt{(2l+1)(2l'+1)(l-m)!\,(l+m)!\,(l'+m')!\,(l'-m')!}}\ .$$

TABLE III. Same as in Table II, with all $l = 5$ moments also included. Additional ratios are given in lower rows.

χ	U_{bct}	$U_{\text{fcc}} - U_{\text{bct}}$	V_{30}/V_{10} (bct)	V_{30}/V_{10} (fcc)
0.4	−0.636 016	0.007 977	0.003 701	−0.053 224
0.9	−1.129 040	0.022 274	0.003 422	−0.064 585
1.5	−1.507 692	0.038 412	0.002 465	−0.069 425
2.2	−1.797 211	0.053 882	0.001 571	−0.072 024
3.5	−2.123 158	0.074 577	0.000 505	−0.074 251
5.0	−2.339 264	0.090 216	−0.000 206	−0.075 440
∞	−3.071 912	0.154 538	−0.002 526	−0.078 383

χ	V_{50}/V_{10} (bct)	V_{50}/V_{10} (fcc)	V_{54}/V_{10} (bct)	V_{54}/V_{10} (fcc)
0.4	0.053 495	−0.040 110	−0.037 293	−0.038 926
0.9	0.064 151	−0.051 021	−0.048 641	−0.046 311
1.5	0.068 370	−0.055 828	−0.054 030	−0.049 291
2.2	0.070 519	−0.058 444	−0.057 105	−0.050 849
3.5	0.072 277	−0.060 701	−0.059 862	−0.052 160
5.0	0.073 178	−0.061 913	−0.061 388	−0.052 850
∞	0.075 272	−0.064 931	−0.065 361	−0.054 532

After minimizing with respect to all the V_{lm} we get

$$\sum_{\substack{l',m' \\ (0\le m'\le l')}} G_{lm,l'm'}V_{l'm'} = -S_{10}\delta_{lm,10} .$$

Defining the matrix $\underline{G}$ whose element at the (l,m)th row and (l',m')th column is $G_{lm,l'm'}$, we get

$$V_{lm} = -S_{10}(\underline{G}^{-1})_{lm,10} , \tag{13}$$
$$U = \tfrac{1}{2}S_{10}v_{10} .$$

APPLICATION AND RESULTS

Following Ref. 2 we consider the family of lattices shown in Fig. 1 and define the lattice spacing on the xy plane to be c, along the $\hat{\mathbf{z}}$ direction to be $2b$. Define the parameters $\xi \equiv b/c$ and $\alpha \equiv a/b$. Because of the fourfold rotational symmetry in the xy plane, m in Y_l^m can be a multiple of four only. Because the applied field is along the z direction, the potential is odd in z, so that $l-m$ can only be odd. We have therefore $V_{1,0}$, $V_{3,0}$, $V_{5,0}$, $V_{5,4}$, $V_{5,-4}$, ...

A special problem arises in calculating $F_{10,10}$, i.e., the $\sum_h'(\partial/\partial Z_h)^2(1/R_h)$ term in Eq. (11), because the summand $P_2(\cos\theta)/R_h^3$ does not give uniform convergence. The correct way of doing this summation is first to sum all lattice points within a region of some geometrical shape which encloses the origin, then to replace the points outside that region by a continuum and to integrate instead of summing. The integral reduces to a surface term so that

$$F_{10,10} = \lim_{\infty} \left[\sum_{\text{inside}} + \int \text{surface} \right] .$$

For fast convergence we use Madelung's method with modern improvements. We first rewrite $F_{10,10}$ as

$$\sum_h' \frac{-1}{3} \left[X_h \frac{\partial}{\partial X_h} + Y_h \frac{\partial}{\partial Y_h} + Z_h \frac{\partial}{\partial Z_h} \right] \left[\frac{\partial}{\partial Z_h} \right]^2 \left[\frac{1}{R_h} \right] \tag{14}$$

by Euler's theorem on homogeneous functions, and treat three terms separately: for the first term ($X_h\partial/\partial X_h$ term), we sum over Y_h, Z_h for a given X_h and then sum over nonzero X_h, etc.[3,4] The sum within each plane is made rapidly convergent by Fourier decomposition. The inside region is then an infinite slab of large finite thickness. The resulting surface contribution is zero for the first two terms, and $(4\pi/3)np^2$ for the third, where $n = \alpha^3\xi^2/a^3$ is the density of spheres and $p = \sqrt{(4\pi/3)}\chi a^2 V_{10}$ is the dipole moment per sphere. For all other $F_{lm,l'm'}$ we sum directly over successive spherical shells, as the series is uniformly convergent. The shape of the lattice is determined by ξ. After computing the $f_{lm,l'm'}$ for a given ξ, we scale each by the appropriate power of α and determine the energy by Eq. (13). Requiring no overlap between neighboring spheres (hard sphere) puts a constraint on α:

$$0 < \alpha \le \min\left[1, \frac{1}{2\xi}, \frac{1}{2}\left[1+\frac{1}{2\xi^2}\right]^{1/2}\right] \equiv \alpha_{\max} .$$

The three constraints pertain, respectively, to the nearest neighbors $(0,0,2b)$, $(c,0,0)$, and $(c/2,c/2,b)$. The bct and fcc structures are defined by $1 = \frac{1}{2}\sqrt{1+1/2\xi^2}$ and by $1/2\xi = \frac{1}{2}\sqrt{1+1/2\xi^2}$, respectively. We have minimized this energy, using only V_{10} (dipole approximation), using V_{10} and V_{30} (dipole-octupole approximation), and using all $l \le 5$ multipoles (dipole–octupole–thirty-two-pole approximation). In all three cases the system is as dense as possible, i.e., $\alpha = \alpha_{\max}$. We find the bct and fcc structures both give end-point minima (see Fig. 2). In every case $U_{\text{bct}} < U_{\text{fcc}}$. Detailed numerical results are given in Tables I–III.

It may be noted that in the bct structure the octupole moment is anomalously small (compare column 3 and 4 of Table II). The reason is a fortuitous near-cancellation among the nearest neighbors, $2+8P_4(\frac{1}{2}) = -\frac{5}{16}$. This accounts for the near agreement in column 1 between Tables I and II. From the results up to thirty-two-poles, we expect the effect of higher multipole moments will be oscillatorily convergent. The higher multipole contributions are evidently not negligible, but it seems likely that the bct structure is the true ground state of an ER solid for all χ.[5]

ACKNOWLEDGMENT

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