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Three-Dimensional Structure of Induced Electrorheological Solid

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The induced electrorheological solid has thick columns in the field direction (z axis), spreading between two electrodes. The ground state is proposed to be a body-centered tetragonal (bct) lattice with $\mathbf{a}_1=\sqrt{6}a\hat{\mathbf{x}}$, $\mathbf{a}_2=\sqrt{6}a\hat{\mathbf{y}}$, and $\mathbf{a}_3=2a\hat{\mathbf{z}}$, where a is the radius of dielectric spheres. This bct lattice can be regarded as a compound of chains of class A and B, where chains B are obtained from chains A by shifting a distance a in the z direction.

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There has been an enormous resurgence of interest in the field of electrorheological (ER) fluids during the last couple of years [1]. An ER fluid consists of a suspension of fine dielectric particles in a liquid of low dielectric constant [2–7]. Its viscosity increases dramatically in the presence of an applied electric field. If the electric field exceeds a critical value, the ER fluid turns into a solid whose yield stress increases as the field is further strengthened. The phenomenon is completely reversible and the time scale for the transition is of the order of millisecond. This property makes ER fluids attractive for many futuristic technologies [1].

In a recent work [3,4], we pointed out that the nature of ER fluids lies in electric-field-induced solidification. At a fixed temperature, there is a critical electric field E_c. As the applied electric field exceeds E_c, the phase transition occurs: ER fluids turn into a solid. However, the question about the structure of the induced ER solid is open, and has attracted great attention for its relationship to the properties of ER fluids. In a recent Letter [5], Halsey and Toor claimed that dielectric particles in ER fluids form columns, spreading between two electrodes. Each column has a width $\sim a(L/a)^{2/3}$, where a is radius of dielectric particle and L the distance between two parallel electrodes. As for the structure of columns, they are uncertain, but suggested a face-centered cubic (fcc) lattice.

In this Letter, we report a body-centered tetragonal (bct) structure which has an energy lower than that of the fcc lattice and other structures. We believe this is the ground state of the induced ER solid.

Consider a model which has been widely used in the study of ER fluids [5–7]. The model has spheric dielectric particles of dielectric constant ϵ_p suspended in a liquid of dielectric constant ϵ_f, $\epsilon_p>\epsilon_f$. The fluid is confined between two infinite parallel electrodes which are denoted as $z=0$ and $z=L$. When the electric field is applied, the spheres acquire dipole moments in the z direction, $\mathbf{p}=\alpha\epsilon_f a^3\mathbf{E}_{\text{loc}}$, where $\alpha=(\epsilon_p-\epsilon_f)/(\epsilon_p+2\epsilon_f)$ and $\mathbf{E}_{\text{loc}}$ is the local electric field. $\mathbf{E}_{\text{loc}}$ and $\mathbf{p}$ will be determined self-consistently later. The total Coulomb energy includes both the dipolar interaction and the interaction between dipoles and the external field. As will be shown, when the dipolar interaction energy is minimized, the total Coulomb energy is minimized. Therefore, we consider the dipolar interaction energy first. Two dipoles at $\mathbf{r}_i$ and $\mathbf{r}_j$ have an interaction

$$U(\mathbf{r}_{ij})=\nu(1-3\cos^2\theta_{ij})/r_{ij}^3=-\nu\left(2+\rho\frac{\partial}{\partial\rho}\right)\frac{1}{r_{ij}^3}, \quad (1)$$

where $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|=[\rho^2+(z_i-z_j)^2]^{1/2}$ is the distance between them, $\rho=[(x_i-x_j)^2+(y_i-y_j)^2]^{1/2}$, $0\le\theta_{ij}\le\pi/2$ the angle between their joint line with the z direction, and $\nu=\mathbf{p}^2/\epsilon_f$. Since two dipoles cannot overlap, we also add a hard-core interaction to the dipolar interaction. A dipole $\mathbf{p}$ inside the capacitor at (x,y,z) produces an infinite number of images which also interact with the dipole itself and other dipoles. All of its images have the same dipole moment $\mathbf{p}$ and are at $(x,y,-z)$ and $(x,y,2Lj\pm z)$ for $j=\pm1,\pm2,\ldots$. The interaction between a dipole with an image produced by another dipole has the same form as Eq. (1). However, the interaction of a dipole at $\mathbf{r}_i$ with one of its own images at $\mathbf{r}_j$ is given by $\frac{1}{2}U(\mathbf{r}_{ij})$. At a sufficiently strong electric field or low temperature, the electric field exceeds E_c and an ER fluid becomes a solid. This is because the Coulomb interaction becomes dominant, compared with the kinetic energy [3,4]. The induced solid structure must be the configuration which minimizes the Coulomb energy.

In the experiments and molecular-dynamics simulations, it has been found that upon application of an electric field, the dielectric particles in ER fluids first form chains between two plates [2–7]. Chains then aggregate to form columns. The formation of chains is easy to understand because the dipolar energy has its minimum when two dipoles join together and align in the field direction. The interaction between chains is the subject of our study.

A chain, i.e., a line of particles between the two plates, combining with its images becomes an infinite chain. We will discuss some differences between a physical infinite chain and a finite chain with its images. For the moment, we consider the structure consisting of physical infinite chains. Without loss of generality, we consider a chain having particles at $\mathbf{r}_j=2aj\hat{\mathbf{z}}$ ($j=0,\pm1,\pm2,\ldots$). The self-energy of the chain is given by

$$\sum_{i<j} U(\mathbf{r}_i-\mathbf{r}_j)=\tfrac{1}{2}\sum_{i\neq j} U(\mathbf{r}_i-\mathbf{r}_j)\,. \qquad (2)$$

As $\mathbf{r}_i-\mathbf{r}_j=2a(i-j)\hat{\mathbf{z}}$, the self-energy per particle in an infinite chain, u_0, is

$$u_0=-\frac{v}{4a^3}\sum_{s=1}^{\infty}\frac{1}{s^3}=-0.300514\frac{v}{a^3}\,. \qquad (3)$$

Consider the interaction between this chain and a dipole $\mathbf{p}$ at $\mathbf{r}=\boldsymbol{\rho}+z\hat{\mathbf{z}}$,

$$U_i(\rho,z)=-v\left(2+\rho\frac{\partial}{\partial\rho}\right)\sum_{j=-\infty}^{\infty}\frac{1}{[\rho^2+(z-2ja)^2]^{3/2}}\,. \qquad (4)$$

Let

$$f(\rho,z)=\sum_{j=-\infty}^{\infty}\frac{1}{[\rho^2+(z-2ja)^2]^{3/2}}\,.$$

Since the periodicity, $f(\rho,z)=f(\rho,z+2a)$, we can expand f into the form

$$f(\rho,z)=\sum_{s=-\infty}^{\infty}f_s(\rho)e^{-is\pi z/a}\,.$$

Then we have

$$f_s(\rho)=\frac{1}{2a}\int_0^{2a}\sum_{j=-\infty}^{\infty}\frac{dz\,e^{is\pi z/a}}{[\rho^2+(z-2ja)^2]^{3/2}} =\frac{\pi s}{a^2\rho}K_1\left(\frac{s\pi\rho}{a}\right), \qquad (5)$$

where $K_1(x)$ is a modified Bessel function. We have

$$f(\rho,z)=\frac{1}{a\rho^2}+\sum_{s=1}^{\infty}\frac{2\pi s}{a^2\rho}K_1\left(\frac{s\pi\rho}{a}\right)\cos\left(\frac{s\pi z}{a}\right). \qquad (6)$$

The formula $dxK_1(x)/dx=-xK_0(x)$ enables us to write Eq. (4) as

$$U_i(\rho,z)=\frac{v}{a^3}\sum_{s=1}^{\infty}2\pi^2s^2K_0\left(\frac{s\pi\rho}{a}\right)\cos\left(\frac{s\pi z}{a}\right). \qquad (7)$$

The property of K_0 makes Eq. (7) converge exponentially. Because of the hard-core interaction, the minimum value for ρ is $\sqrt{3}a$ at $z=(2j+1)a$. Then $s\pi\rho/a>\pi\sqrt{3}s\geq 5.4413$. The asymptotic behavior of $K_0(x)\to(\pi/2x)^{1/2}e^{-x}$ (for $x\gg 1$) gives the leading term of Eq. (7), $U_i(\rho,z)\approx(v/a^3)\pi^2(2a/\rho)^{1/2}e^{-\pi\rho/a}\cos(\pi z/a)$. The next correction is small. For example, at $\rho=\sqrt{3}a$ and $z=a$, the correction is only about 1%.

From $F_\rho=-\partial U_i/\partial\rho$, we note that the interaction U_i is attractive when $(2j+\frac{1}{2})a<z<(2j+\frac{3}{2})a$; otherwise, it is repulsive. $F_z=-\partial U_i/\partial z$ always pulls the dipole to a position of $z=(2j+1)a$. Therefore, the interaction pulls the dipole to $\rho=\sqrt{3}a$ and $z=(2j+1)a$, where U_i is minimized to $-0.04442565v/a^3$.

When there is second infinite chain around, the dipolar interaction energy per particle, u, is $u_0+\frac{1}{2}U_i(\rho,z)$ because all dipoles in the second chain have coordinates $(\rho,z+2aj)$ $(j=0,\pm 1,\pm 2,\ldots)$. The factor $\frac{1}{2}$ comes from the fact that the interaction energy is shared by both dipoles. If these chains are far apart $(\rho\to\infty)$, $u=u_0$. When $\rho=2a$ and $z=0$, the two chains are repulsive, and $u=-0.291405v/a^3$ is high. The minimum of u, $-0.3227268v/a^3$, is obtained when the second chain has coordinates $\rho=\sqrt{3}a$ and $z=a$.

We define infinite chains with their dipoles at $z_j=2ja$ $(j=0,\pm 1,\pm 2,\ldots)$ as chains of class A and infinite chains with $z_j=(2j+1)a$ as chains of class B. To benefit the dipolar interaction, the ER solid must have chains of both classes A and B. Two chains of the same class are repulsive, and otherwise they are attractive, namely,

$$U_{AA}(\rho)=U_{BB}(\rho)=\frac{v}{a^3}\sum_{s=1}^{\infty}2\pi^2s^2K_0\left(\frac{s\pi\rho}{a}\right)$$

and

$$U_{AB}(\rho)=\frac{v}{a^3}\sum_{s=1}^{\infty}2\pi^2s^2K_0\left(\frac{s\pi\rho}{a}\right)\cos(s\pi)\,.$$

These interactions are short ranged and bear some similarity to the Yukawa potential. The problem of structure of ER fluids is equivalent to finding the ground state for a two-dimensional system which has two classes of parti-

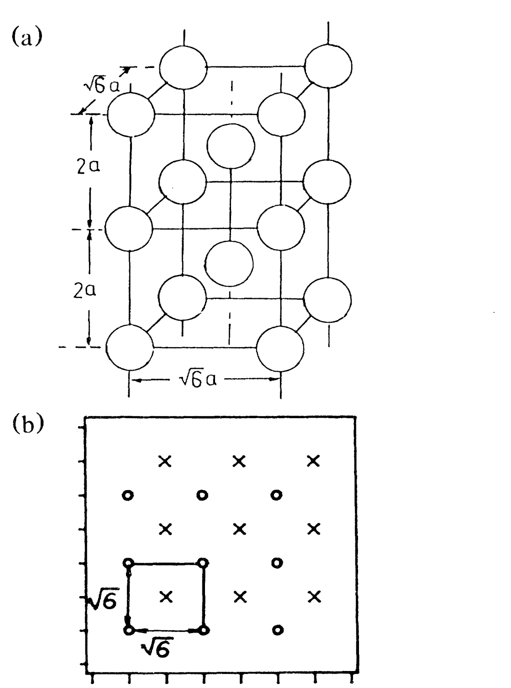

FIG. 1. (a) Three-dimensional body-centered tetragonal (bct) structure (the particles have radius a and are not shown to scale). (b) The bct structure is represented by a two-dimensional crystal in which ○ represent the A chains and × represent B chains. The unit is a.

cles, A and B, via the above interactions. The distance between two chains of different class is $\rho \geq \sqrt{3}a$, but the distance between two chains of the same class is $\rho \geq 2a$.

To minimize the potential energy, the ground state must have a structure such that an A (or B) chain has as many B (or A) chains around at the minimum distance $\sqrt{3}a$ as possible and is as far away from other A (or B) chains as possible. Our bct lattice with $\mathbf{a}_1 = \sqrt{6}a\hat{\mathbf{x}}$, $\mathbf{a}_2 = \sqrt{6}a\hat{\mathbf{y}}$, and $\mathbf{a}_3 = 2a\hat{\mathbf{z}}$ [Fig. 1(a)] is such a structure. It can be described by a two-dimensional crystal, as in Fig. 1(b). In this bct structure, an A (or B) chain has four B (or A) chains as its nearest neighbors at $\rho = \sqrt{3}a$, and four next-nearest-neighbor A (or B) chains at $\rho = \sqrt{6}a$. The dipolar interaction energy per particle is $u = -0.381\,268 v/a^3$.

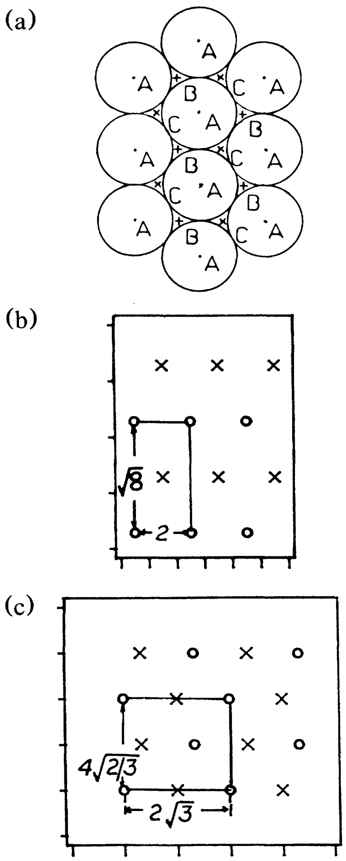

FIG. 2. (a) A close-packed layer of spheres with centers marked A. The second layer of spheres can be placed on top of this, above and parallel to the plane with centers at points B. When the third layer goes in over points C, the sequence is $ABCABC\ldots$, and the structure is face-centered cubic (fcc). When the third layer goes in over A, the sequence is $ABAB\ldots$, the structure is hexagonal close-packed (hcp). (b) The fcc structure is represented by a two-dimensional crystal in which ○ represent the A chains and × represent B chains. The unit is a. (c) The hcp structure is represented by a two-dimensional crystal in which ○ represent the A chains and × represent B chains. The unit is a.

We have compared our bct structure with other structures. The close packing has two structures [Fig. 2(a)]. The $ABCABC\ldots$ series is a fcc lattice which is equivalent to the two-dimensional crystal in Fig. 2(b). It has Bravais lattice vectors $\mathbf{a}_1 = 2a\hat{\mathbf{x}}$ and $\mathbf{a}_2 = 2\sqrt{2}a\hat{\mathbf{y}}$ and a basis with one A chain at a corner and one B chain at the center. Though an A (or B) chain also has four B chains at $\rho = \sqrt{3}a$, it has two next-nearest A (or B) chains at $\rho = 2a$. As a result, u is higher, $-0.370\,240\,2 v/a^3$ for fcc.

The $ABAB\ldots$ series is a hexagonal close-packed (hcp) structure which is described by the two-dimensional crystal in Fig. 2(c), with Bravais vectors $\mathbf{a}_1 = 2\sqrt{3}a\hat{\mathbf{x}}$ and $\mathbf{a}_2 = 4\sqrt{2/3}a\hat{\mathbf{y}}$. The basis has two A chains at (0,0) and $(4a/\sqrt{3}, 2a\sqrt{2/3})$ and two B chains at $(\sqrt{3}a, 0)$ and $(a/\sqrt{3}, 2a\sqrt{2/3})$. Similar to fcc, around an A (or B) chain, hcp has two next-nearest A (or B) chains at $\rho = 2a$. Thus, u is higher, $-0.370\,028\,9 v/a^3$.

We have also compared the bct structure with some other structures which are not formed by chains of A and B. For example, a three-dimensional cubic lattice with lattice spacing $2a$ can be regarded as a structure formed by chains of A only. Using Lorentz's method, we have the dipolar interaction energy per particle

$$\tfrac{1}{2}(-4\pi \mathbf{p} n/3\epsilon_f)\cdot \mathbf{p} = -(\pi/12)v/a^3 = -0.261\,799 v/a^3 ,$$

where $n = 1/(2a)^3$ is the particle density. All the above results are summarized in Table I which shows that the bct structure has the lowest energy.

Now consider $\mathbf{E}_{\text{loc}}$. $\mathbf{E}_{\text{loc}} = \mathbf{E} + \Delta\mathbf{E}$, where $\mathbf{E}$ is the external field and $\Delta\mathbf{E}$ is the field produced by the dipoles. $\Delta\mathbf{E}$ is proportional to $\mathbf{p}$ [8,9]. We introduce β such that $\Delta\mathbf{E} = \beta\mathbf{p}/a^3\epsilon_f$. The dipolar interaction energy per particle is $u = -\frac{1}{2}\mathbf{p}\cdot\Delta\mathbf{E}$. Then we have $\beta = -2ua^3\epsilon_f/(\mathbf{p})^2$ and $\mathbf{p} = \alpha\epsilon_f a^3(\mathbf{E} + \beta\mathbf{p}/a^3\epsilon_f)$. Hence

$$\mathbf{p} = \alpha\epsilon_f a^3\mathbf{E}/(1-\alpha\beta) . \tag{8}$$

The total Coulomb interaction energy per particle, including dipolar interaction and interaction between dipoles and the external field $\mathbf{E}$, is given by [8,9]

$$u_t = -\tfrac{1}{2}\mathbf{p}\cdot\mathbf{E} = -\frac{\alpha\epsilon_f a^3(\mathbf{E})^2}{2(1-\alpha\beta)} . \tag{9}$$

The lowest dipolar energy of u corresponds to the largest positive β which also gives the lowest u_t.

TABLE I. Dipolar interaction energy per particle for various structures.

Structure	u (units of $p^2/a^3\epsilon_f$)
bct lattice	−0.381 268
fcc lattice	−0.370 240 2
hcp structure	−0.370 028 9
Separated chains	−0.300 514
Cubic lattice	−0.261 799

The Lorentz method writes $\Delta\mathbf{E}=4\pi\mathbf{p}n/3\epsilon_f+\Delta\mathbf{E}_i$, where n is the particle density, and $\Delta\mathbf{E}_i$ is the contribution from dipoles near the position under investigation. For a cubic lattice, $\Delta\mathbf{E}_i=0$ and $n=1/(2a)^3$; hence $\beta=\pi/6$. In our bct structure, $n=1/(6a^3)$, and $\Delta\mathbf{E}_i$ is not vanishing: $\Delta\mathbf{E}_i=0.0643643\mathbf{p}/a^3\epsilon_f$ and $\beta=0.762496$.

Finally, consider the difference between infinite physical chains and chains with infinite images. We assume that $L=2la$, l an integer. The presence of two electrodes has no effect on chains B, but prevents chains A from having dipoles at $z=0$ and $z=L$. Then a chain A and its images are equivalent to infinite chains with missing dipoles at $z=Lj$ ($j=0,\pm1,\pm2,\ldots$). In the bct structure, we can treat them as defects of dipoles at $-\mathbf{p}$ at $n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3(2la)\hat{\mathbf{z}}$ (n_1, n_2, and n_3 are integers). Similar to the derivation of Eq. (7), we replace a by $L/2$ in Eq. (7) and obtain the interaction of these defects with a dipole $\mathbf{p}$ at (x,y,z),

$$\Delta U=-\frac{8v}{L^3}\sum_{n_1,n_2}\sum_{s=1}^{\infty}2\pi^2s^2K_0\left(\frac{2\pi s\rho_{n_1,n_2}}{L}\right)\cos\left(\frac{2\pi sz}{L}\right), \tag{10}$$

where $\rho_{n_1,n_2}=[(x-n_1\sqrt{6}a)^2+(y-n_2\sqrt{6}a)^2]^{1/2}$. If the cross section of the column has a radius $R\gg a$, we can replace $\sum_{n_1,n_2}$ by an integration $(1/6a^2)\int_0^R 2\pi\rho\,d\rho$. Then

$$\Delta U=\frac{2v\pi}{3La^2}+\frac{4v\pi}{3La^2}\sum_{s=1}^{\infty}\frac{2\pi sR}{L}K_1\left(\frac{2\pi sR}{L}\right)\cos\left(\frac{2\pi sz}{L}\right), \tag{11}$$

where we use $\int_0^R d\rho\,\rho K_0(b\rho)=1/b^2-K_1(bR)R/b$ and $\sum_{s=1}^{\infty}\cos(2\pi sz/L)=-\frac{1}{2}$. For chain B, $z=(2j-1)a$ ($j=1,\ldots,l$), $\sum_{j=1}^{l}\cos[\pi s(2j-1)/l]=0$. For chain A, $z=2ja$ ($j=1,\ldots,l-1$), $\sum_{j=1}^{l-1}\cos(2\pi js/l)=-1$. The average correction to the dipolar interaction per particle is then

$$\frac{1}{2}\overline{\Delta U}=\frac{v\pi}{3La^2}-\frac{2v\pi}{3(2l-1)La^2}\sum_{s=1}^{\infty}\frac{2\pi sR}{L}K_1\left(\frac{2\pi sR}{L}\right). \tag{12}$$

The leading correction term $(\pi a/3L)v/a^3$ decreases as a/L. Compare the bct structure with a structure of separated B chains at a finite L. When $u_{\mathrm{bct}}+\overline{\Delta U}/2<u_{\mathrm{chains}}$, the bct structure prevails. An estimation $L/a>\pi/3(0.381262\text{-}0.300514)=12.968$ is required if only the leading term is used. Therefore, when $L\gg 13a$, the induced ER solid has the bct structure, in spite of the defects. As $L\leq 12a$, the structure of separated chains prevails. We have confirmed this result in our Monte Carlo simulation for $L=10a$. Since in most experiments a is of the order of a micrometer while L has a size of cm, and so $L\gg 13a$, the ER solid has the bct structure.

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