Structural transitions of an electrorheological and magnetorheological fluid

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An electrorheological and magnetorheological fluid has small spherical particles in a space where a uniform electric field is perpendicular to a uniform magnetic field. When the ratio between the electric field and magnetic field varies, structural transitions occur. If the electric (or magnetic) field is dominant, the ideal structure of the system is a body-centered tetragonal lattice with its fourfold rotational axis in the electric (or magnetic) field direction. When the electric field and magnetic field are compatible, under the dipolar approximation, the system may have a hexagonal close-packed (hcp) structure. However, because the energy difference between the hcp structure and face-centered cubic (fcc) lattice is small and compatible with the thermal energy at room temperature, the system may develop into a hcp-fcc mixed structure when the electric field and magnetic field are compatible. [S1063-651X(98)04305-0]

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Transitions between different crystallographic states are an important phenomenon in nature, because they involve intriguing physics and have many applications. Since the basic degrees of freedom in a solid are electronic and vibrational, we usually classify these transitions by whether they are driven primarily by electronic or vibrational instabilities. For example, the *cooperative John-Teller transitions* [1] are structural transitions of electronic states and the *displacive transition* [2] is caused by phonons.

In this paper, we study a system that will have structural transitions by a change of applied electric field and magnetic field. The system consists of fine spherical particles of radius a in micrometers, which are placed in a capacitor whose spacing $L \gg a$. In addition, there is a uniform magnetic field acting on the spheres. An N pole and an S pole separated by a distance $W \gg a$ produce a magnetic field perpendicular to the electric field. The particles are either in microgravity or in a liquid which provides a buoyancy to neutralize the gravity. Therefore, they are randomly distributed in space before the application of electric and magnetic fields. The media have both dielectric constants ϵ_f and magnetic permeability μ_f close to unity, while the particles have $\epsilon_p > \epsilon_f$ and $\mu_p \neq \mu_f$. Such a system acts as both electrorheological (ER) fluid [3,4] and magnetorheological (MR) fluid [5]. We take the electric field direction as the z direction and the magnetic field direction as the x direction.

One candidate for our system is a suspension of titanium-coated iron particles in silicon oil [6]. Other interesting candidates include a slurry of superconducting spheres coated with insulating film in a liquified gas. In a static electric field, superconducting spheres, though having insulating surface, have a high effective ϵ_p. Meanwhile the Meissner effect makes the superconducting spheres a diamagnetic substance with $\mu_p = 0$. The research on ER fluids and MR fluids has found a variety of particles that can be polarized by both electric field and magnetic field [3].

We first consider the case in which there is electric field only. As the electric field is applied, the particles obtain an induced dipole moment, $\vec{p} = \alpha a^3 \epsilon_f \vec{E}_l$ where $\alpha = (\epsilon_p - \epsilon_f)/(\epsilon_p + 2\epsilon_f)$ and $\vec{E}_l$ is the local effective field acting on the particles. $\vec{E}_l = \vec{E} + \Delta\vec{E}$, $\vec{E}$ is the applied electric field, and $\Delta\vec{E}$ is the induced dipolar field. Two dipoles at $\vec{r}_i$ and $\vec{r}_j$ have an interaction,

$$u_p(\vec{r}_{ij}) = [p^2 r_{ij}^2 - 3(\vec{p} \cdot \vec{r}_{ij})^2]/(\epsilon_f r_{ij}^5), \qquad (1)$$

where $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$. The hard-core interaction is added to the above dipolar interaction to prevent the particles from overlapping.

A quantity, $p^2/(\epsilon_f a^3 k_B T) = \nu/(a^3 k_B T)$, characterizes the ratio between the dipolar interaction and the thermal energy [7]. Here we use $\nu = p^2/\epsilon_f$ to simplify the notation. A simple estimation can show that in typical ER fluids the dipolar interaction is much stronger than the thermal energy when $a \geq 1$ μm. For example, for a system $E = 1$ kV/mm, $\alpha = 0.5$, $\epsilon_f = 2.2$, $a = 1$ μm, and $T = 300$ K, $p^2/(\epsilon_f a^3 k_B T) \sim 1.5 \times 10^4$. As pointed by Halsey and Toor, when the system forms a structure of single separated chains, the Landau-Peierls thermal fluctuation will play an important role in forcing the single chains to merge together because of the screening effect [8]. It is also expected that as the system forms thick columns, the role of thermal fluctuation will become minor. In this paper, since we will only study the close-packed structures under strong electric or magnetic fields, we will not discuss the effect of thermal fluctuations.

It has been shown in a recent work [9] that the ground state of ER fluids is a body-centered tetragonal (bct) lattice, which has the field direction distinct from the other directions (Fig. 1). The bct lattice has only one fourfold rotational axis, which is parallel to the electric field in the present situation. The ground state energy is unchanged if the bct lattice rotates around the fourfold rotational axis.

The prediction about the bct lattice has been confirmed by laser diffraction experiment [10], Monte Carlo simulations, and computer simulations [11]. In a real ER system, there are higher order induced multipoles. Calculations carried out by Friedberg and Yu including contributions form higher mul-
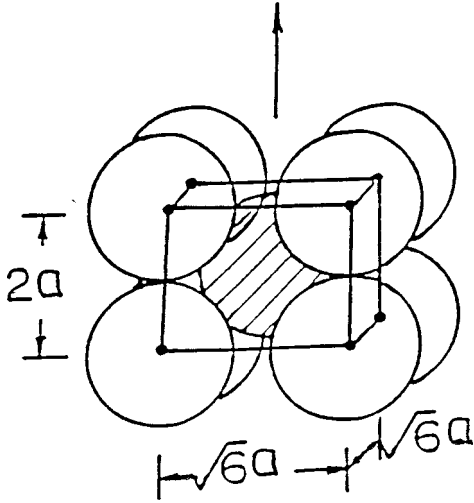
FIG. 1. The bct lattice has only one fourfold rotational axis. The three conventional Bravias lattice vectors are $\vec{a}_1 = \sqrt{6}a\hat{x}$, $\vec{a}_2 = \sqrt{6}a\hat{y}$, and $a_3 = 2a\hat{z}$.

tipoles also confirm the bct lattice obtained from the dipolar approximation [12]. Davis studied a system of touching metallic spheres, for which the dipolar approximation does not apply. He has concluded that the bct lattice is also favored by surface energy for this system, while the leading divergent bulk energy is degenerate for the bct lattice, face-centered cubic (fcc) lattice, and hexagonal close-packed (hcp) structure [13]. The theory proposed recently by Tam and his co-workers also finds the bct lattice as the ground state [14].

On the other hand, if the system is in a magnetic field only, it is a pure MR fluid. The spheres obtain an induced magnetic moment, $\vec{m} = \beta a^3 \mu_f \vec{H}_l$, where $\beta = (\mu_p - \mu_f)/(\mu_p + 2\mu_f)$ and $\vec{H}_l$ is the local effective magnetic field acting on the particles. Two magnetic dipoles at $\vec{r}_i$ and $\vec{r}_j$ have an interaction,

$$u_m(\vec{r} = [m^2 r_{ij}^2 - 3(\vec{m} \cdot \vec{r}_{ij})^2]/(\mu_f r_{ij}^5). \tag{2}$$

Similar to a pure ER fluid, a pure MR fluid also has a bct lattice as the ground state, but its fourfold rotational axis is in the magnetic field direction.

What is the ground state if both electric field and magnetic field are applied? This is the question to be investigated in our present paper. In the ideal case, as we considered here, the ground state is the state minimizing the electric and magnetic interactions. This ground state must have a crystalline structure.

We introduce a parameter

$$\xi = p\sqrt{\mu_f}/(m\sqrt{\epsilon_f}) = (H_l \beta \sqrt{\mu_f})/(E_l \alpha \sqrt{\epsilon_f}) \tag{3}$$

that measures the competition between the electric static interaction and the magnetic static interaction. We have found that as ξ changes, structural transitions occur. Under the dipolar approximation, when the electric field and magnetic field are compatible, we may have a hcp structure. However, the energy difference between the hcp structure and fcc lattice is very small and compatible with the thermal energy at room temperature. Therefore, the system may also develop into a hcp-fcc mixed structure when the electric field and

magnetic field are compatible. Such a hcp-fcc mixed structure, i.e., a mixture of random stacking of hexagonally close-packed layers and fcc packing is often found in crystallization of hard-sphere colloids [15–17].

Let us outline the calculation of electric dipolar interactions. The calculation of magnetic dipolar interactions is similar. If the dipole under consideration is at the origin, the dipolar energy per particle is given by

$$u = \frac{1}{2} \sum_j{}' [p^2 r_j^2 - 3(\vec{p} \cdot \vec{r}_j)^2]/(r_j^5 \epsilon_f), \tag{4}$$

where the summation $\sum_j'$ is over all dipoles, except the one at the origin. The symmetry of simple cubic (sc) lattice, body-centered cubic (bcc) lattice, and fcc lattice makes their dipolar energy independent of the dipole direction. For these structures, the electric and magnetic dipolar energy per particle can be expressed as $-2\pi c(p^2/\epsilon_f + m^2/\mu_f)/3$ where c is the particle density. Hence the close-packed sc lattice has the dipolar energy per particle

$$u_{sc} = -(\pi/12)(1+\xi^2)\nu/a^3 = -0.261799(1+\xi^2)\nu/a^3. \tag{5}$$

The close-packed bcc lattice has

$$u_{bcc} = -(\pi\sqrt{3}/16)(1+\xi^2)\nu/a^3 = -0.340087(1+\xi^2)\nu/a^3. \tag{6}$$

The close-packed fcc lattice has the dipolar energy lower than that of the sc and bcc lattices,

$$u_{fcc} = -[\pi/(6\sqrt{2})](1+\xi^2)\nu/a^3 = -0.370240(1+\xi^2)\nu/a^3. \tag{7}$$

The dipolar energy of the bct lattice and hcp structure depends on the field directions. As shown in Fig. 2, the hcp structure can be considered as a hexagonal lattice with a base of two particles: one particle at the origin and the other at $\frac{2}{3}\vec{b}_1 + \frac{1}{3}\vec{b}_2 + \frac{1}{2}\vec{c}$. We have $|\vec{b}_1| = |\vec{b}_2| = 2a$ and $|\vec{c}| = 4a\sqrt{2/3}$. The hcp structure has only one threefold rotational axis, the c axis.

Generally, if the dipole orientation is perpendicular to an n-fold rotational axis of the lattice, their interaction energy is invariant under a rotation around the n-fold rotational axis. This can be seen from Fig. 3 where a dipole is on an n-fold rotational axis and n dipoles are symmetrically around the axis. As the dipoles are pointing to a direction perpendicular to the rotational axis, the interaction between the dipole on the axis and n other remaining dipoles is given by

$$p^2[n/r^3 - (3\rho^2/r^5)] \sum_{j=0}^{n-1} \cos^2(\theta + 2\pi j/n)$$

$$= np^2[1 - 3\rho^2/(2r^2)]/r^3, \tag{8}$$

which is independent of angle θ_0. Therefore, if the hcp structure is infinitely large and its c axis is perpendicular to both electric field and magnetic field, then both electric and magnetic dipolar energy are invariant when the hcp structure rotates around the c axis.
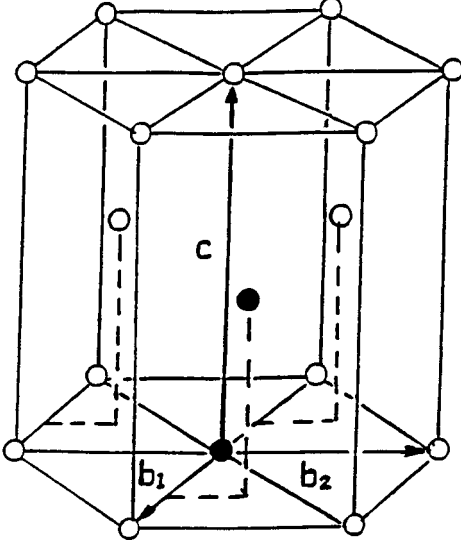
FIG. 2. The close-packed hcp structure can be considered as a hexagonal lattice with a base of two particles. A primitive cell has $|\vec{b}_1|=|\vec{b}_2|=2a$ and $|\vec{c}|=4a\sqrt{2/3}$. One particle of the base is at the origin and the other is at $\frac{2}{3}\vec{b}_1+\frac{1}{3}\vec{b}_2|\frac{1}{2}\vec{c}$. The c axis is a three-fold rotational axis. The particles have radius a and are not shown to the scale in the figure.

If the fourfold rotational axis in the bct lattice is parallel to the z axis, we can expand Eq. (4) into the following form:

$$u=\frac{1}{2}\sum_j{}' \ [p_x^2(r_j^2-3x_j^2)+p_y^2(r_j^2-3y_j^2)$$
$$+p_z^2(r_j^2-3z_j^2)]/(\epsilon_f r_j^5),\qquad(9)$$

where $\vec{p}=p_x\hat{x}+p_y\hat{y}+p_z\hat{z}$; $\hat{x}$, $\hat{y}$, and $\hat{z}$ are unit vectors along the Cartesian axes. The cross terms are vanishing in the expansion of Eq. (4). It is clear that the calculation of dipolar energies can be decomposed into evaluation of the following three quantities,

$$\sum_j{}' \ (r_j^2-3x_j^2)/r_j^5, \quad \sum_j{}' \ (r_j^2-3y_j^2)/r_j^5,$$

$$\sum_j{}' \ (r_j^2-3z_j^2)/r_j^5,\qquad(10)$$
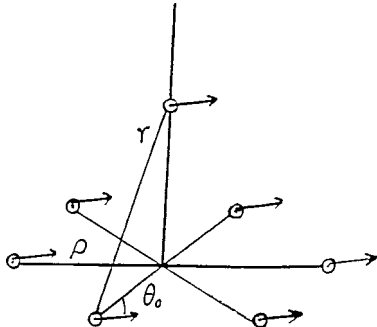

FIG. 3. As electric (magnetic) dipoles are in the direction perpendicular to the n-fold rotational axis, the electric (magnetic) dipolar energy is invariant under a rotation around the axis.

which are themselves directly related to the dipolar energies when the dipoles have a direction parallel to one of the Cartesian axes. For the above bct lattice, from Eq. (8), $\Sigma'_j(r_j^2-3x_j^2)/r_j^5=\Sigma'_j(r_j^2-3y_j^2)/r_j^5$.

Now we only need to calculate two quantities for the bct lattice: (1) the dipolar energy when the orientation of dipoles is parallel to the main rotational axis of the structure, (2) the dipolar energy when the orientation of dipoles is parallel to a lattice axis but perpendicular to the main rotational axis.

Since the evaluation of the above two quantities employs the same method, we just outline the calculation of the first one here [9]. Assume that the dipole at consideration is at the origin and the dipoles are pointing in the z direction. Regularly arranged dipoles on the z axis at positions $z_j=b_j$ ($j=\pm1,\pm2,\ldots$) have the dipolar interaction with the dipole at the origin.

$$u_s(x)=-4\nu\zeta(3)/b^3,\qquad(11)$$

where the constant $\zeta(3)=\Sigma_{n=1}^\infty 1/n^3=1.202\,0569\ldots$. On a lattice axis parallel to the z axis, the dipoles are also regularly separated by distance b. We denote their positions as $\vec{p}+\hat{z}(jb+z_0)$ ($j=1,\pm1,\pm2,\ldots$) where $\vec{p}$ is a vector perpendicular to the z axis and z_0 is a constant. The dipole at the origin experiences the following interactions from all dipoles on the above lattice axis,

$$u_i(\rho,z_0)=-\nu(2+\rho\partial/\partial\rho)f(\rho,z_0),\qquad(12)$$

where the function $f(\rho,z)$ is defined as

$$f(\rho,z)=\sum_{j=-\infty}^\infty [\rho^2+(z-jb)^2]^{-3/2}.\qquad(13)$$

Because of the periodicity, $f(\rho,z)=f(\rho,z+b)$, we can expand f into the form $f(\rho,z)=\Sigma_{s=-\infty}^\infty f_s(\rho)e^{-i2s\pi z/b}$ with

$$f_s(\rho)=\int_0^b dz e^{i2s\pi z/b}f(\rho,z)/b=4\pi sK_1(2\pi s\rho/b)/(b^2\rho),$$
$$(14)$$

where $K_1(\rho)$ is a modified Bessel function. Equation (13) now reads

$$f(\rho,z)=2/(b\rho^2)+\sum_{s=1}^\infty 8\pi sK_1(2s\pi\rho/b)$$
$$\times\cos(2\pi sz/b)/(b^2\rho).\qquad(15)$$

The formula $d[xK_1(x)]/dx=-xK_0(x)$ enables us to write u_i in Eq. (12) as

$$u_i(\rho,z_0)=\nu\sum_{s=1}^\infty 16\pi^2s^2K_0(2s\pi\rho/b)\cos(2s\pi z_0/b)/b^3.$$
$$(16)$$

The property of K_0 makes Eq. (16) converge very fast. The dipolar interaction energy per particle is given by
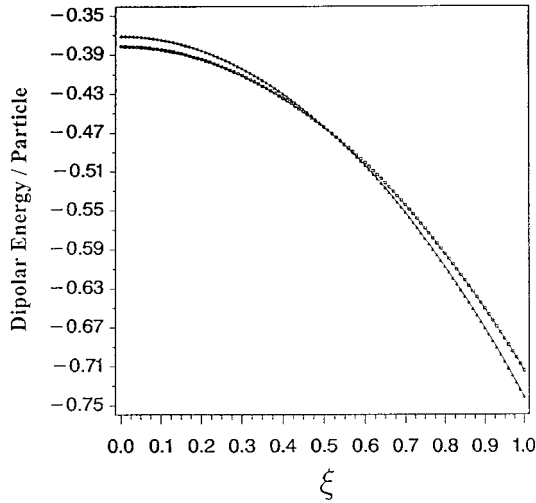
$$u=u_s/2+\sum_k{}' \ u_i(\rho_k,z_0)/2,\qquad(17)$$

FIG. 4. The dipolar energy per particle u_{bct1} and u_{hcp} in the region $0<\xi<1$. The energy units is $p^2/(\epsilon_f a^3)$. When $0<\xi<0.530\,405$, the bct lattice has a lower energy. When $0.530\,405<\xi$, the hcp structure has a lower energy. For $\xi>1$, the competition between u_{bct2} and u_{hcp} is similar, except that the magnetic field instead of electric field is dominant.

where the summation Σ'_k is over all lattice axes in the z direction, except the one passing through the origin. It is clear that this method can be employed to calculate magnetic dipolar interactions too.

When the fourfold rotational axis of the bct lattice is parallel to the electric field, the above method enables us to find the electric and magnetic dipolar energy per particle

$$u_{\text{bct1}}=-(0.381\,268+0.332\,967\xi^2)\,v/a^3. \qquad (18)$$

When the bct lattice has its fourfold rotational axis in the magnetic direction, the dipolar energy per particle is given by

$$u_{\text{bct2}}=-(0.332\,967+0.381\,268\xi^2)\,v/a^3. \qquad (19)$$

When the c axis of the hcp structure is perpendicular to both the electric field direction and magnetic direction, i.e., along the y direction, the dipolar energy per particle of the hcp structure is given by

$$u_{\text{hcp}}=-0.370\,663(1+\xi^2)\,v/a^3. \qquad (20)$$

This hcp structure has layers parallel to the x-z plane. In each layer particles form a close-packed hexagonal lattice. Using the above method, we can easily verify that the hcp structures with the c axis along the y direction has the energy lower than other hcp structures which have their c axis pointing in other directions.

From Eqs. (5), (6), (7), (18), (19), and (20), we see that the energy of sc and bcc lattices are too high. The fcc lattice and the hcp structure have their dipolar energies close, but u_{hcp} is always lower than u_{fcc}. Under the dipolar approximation, the competition thus is really between the two bct lattices and the hcp structure. Figure 4 plots the competition between u_{bct1} and u_{hcp} in the region $0<\xi<1$. The situation of $\xi>1$ is similar to $\xi<1$, except that the magnetic field is dominant and the competition is between the hcp structure
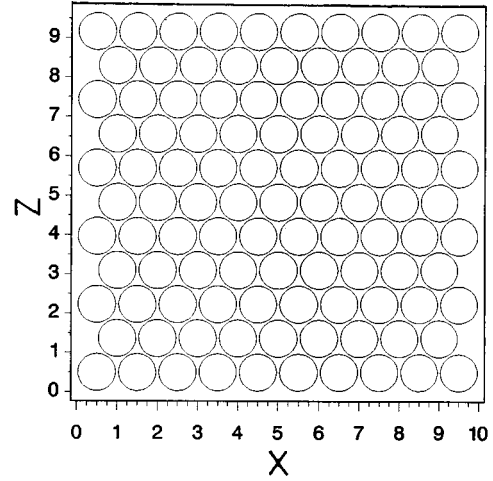

FIG. 5. The close-packed hcp structure has layers parallel to both the electric field and magnetic field. In each layer, dipoles form a hexagonal lattice. One of the axes is parallel to the magnetic field.

and bct lattice with its fourfold rotational axis parallel to the magnetic field. From Fig. 4, when $0<\xi<0.530\,405$, the bct lattice with its fourfold rotational axis in the electric field direction has the lowest energy. When $0.530\,405<\xi<1/0.530\,405=1.885\,35$, the system changes into the hcp structure with its c axis perpendicular to both electric field and magnetic field. When $\xi>1.885\,35$, the bct lattice with its fourfold rational axis along the magnetic field direction is preferred.

Our above calculation assumes that the system is infinite. As mentioned above, the hcp structure has layers, two-dimensional close-packed hexagonal lattice, parallel to the x-z plane. The dipolar energy is invariant if the hcp structure rotates around the y axis (c axis). In most experiments, instead of permanent magnets, magnetic coils are used. Then, magnetic dipoles have no images. Under such a circumstance, the system is infinite in the electric field direction because of infinite images of electric dipoles, but finite in the magnetic field direction. Now the dipolar energy is not invariant when the hcp structure rotates around the c axis. Some simple calculation can show that the lowest energy is obtained when the hcp structure has one lattice axis parallel to the magnetic field direction. One layer parallel to the x-z place of this hcp structure is plotted in Fig. 5.

There is one remark we would like to make at the conclusion of our paper. Limiting ourselves in the dipolar approximation, we conclude that as the relative strength of the magnetic dipolar interaction to the electric dipolar interaction increases, there are two structural transitions: from the bct lattice with its fourfold axis in the electric field direction to the hcp structure with its c axis perpendicular to both electric field and magnetic field, then to the bct lattice with its fourfold axis in the magnetic field direction. However, in close-packed structures, higher multipoles have a non-negligible contribution. It is naturally expected that this contribution may produce a shift in the critical values of ξ for the structure transitions. As shown by Friedberg and Yu [12] and others [14], the contribution from higher multipoles does not change the conclusion derived under the dipolar approximation. In the case of dominant electric field or magnetic field,

we will certainly have the bct lattice structure even if the contribution of higher multipoles is included. Since the dipolar energy difference between the hcp structure and fcc lattice is quite small, there is a chance that the contribution of higher multipoles may change the competition between the fcc lattice and the hcp structure. However, it is important to note that from Eq. (7) and Eq. (20), the energy difference between hcp and fcc is very small, only about $4.23 \times 10^{-4}(1+\xi^2)\nu/a^3$ per particle. The correction from higher multipoles will not increase the magnitude of this difference. This energy difference is very close to the thermal energy $k_B T$ at room temperature. Therefore, more likely, we will find a solid structure which is a mixture of fcc and hcp. Such a fcc-hcp mixed structure, i.e., a mixture of random stacking of hexagonally close-packed layers and fcc packing is often found in crystallization of hard-sphere colloids in gravity space and microgravity space [15–17].

If the experiment is performed at cryogenic temperature, the thermal energy is extremely weak. Then we need to consider contributions from higher multipoles that may make a difference in the competition between the hcp structure and fcc lattice. However, the correction from higher multipoles normally only reduces the magnitude of difference from the dipolar approximation. Therefore, the experiment to distinguish fcc and hcp structure will be difficult and requires extremely low temperature.

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