

### Electric-field-induced phase transition in electrorheological fluids

R. Tao

*Department of Physics, Southern Illinois University, Carbondale, Illinois 62901*

(Received 28 August 1992)

We study an electrorheological fluid consisting of spherical dielectric particles in a liquid of low dielectric constant. At a fixed temperature, there are two critical electric fields  $E_{c2} < E_{c1}$ . When the applied field  $E < E_{c2}$ , the system is a fluid with no long-range order. When  $E_{c2} < E < E_{c1}$ , the particles form chains between two electrodes, but the distribution of these chains is random. This state is similar to an induced nematic liquid crystal. As  $E$  exceeds  $E_{c1}$ , the system is a solid whose ideal structure is a body-centered tetragonal lattice with  $\mathbf{a}_1 = \sqrt{6}a\hat{x}$ ,  $\mathbf{a}_2 = \sqrt{6}a\hat{y}$ , and  $\mathbf{a}_3 = 2a\hat{z}$ , where  $a$  is the radius of dielectric spheres and  $\hat{z}$  is the field direction.

PACS number(s): 82.70.Gg, 61.90.+d, 64.75.+g

An electrorheological (ER) fluid consists of a suspension of fine dielectric particles in a liquid of low dielectric constant [1–6]. Its apparent 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 reversible. Upon electric-field cutoff, the system immediately resumes its original liquid state. The time scale for the transition is of the order of milliseconds. This property makes ER fluids of potential use in industries and technologies, especially in the automotive and aerospace industries.

What role does the base liquid play in ER fluids? It has been found that a good ER fluid requires that the dielectric particles and the base liquid have almost the same density. Otherwise, the sedimentation effect weakens the ER effect considerably. Therefore, one main role of the base liquid is to provide a buoyant force to reduce the gravity and create an effective low-gravity environment. The physics of ER fluids is, therefore, related to the physics of electric-field-induced phase transition in a low-gravity environment.

This paper examines the phase transition in ER fluids. We consider an ER system that has small spherical dielectric particles of dielectric constant  $\epsilon_p$  in a liquid of dielectric constant  $\epsilon_f$ ,  $\epsilon_f < \epsilon_p$ . The whole system is confined between two parallel plates, upon which a voltage is applied to produce an electric field. The field directions is in the  $z$  direction. The two plates are at  $z = 0$  and  $z = L$ . We assume that the buoyancy neutralizes the gravity.

We have found that this system will experience two phase transitions as the applied electric field increases. At a fixed temperature, there are two critical electric fields  $E_{c2} < E_{c1}$ . When the electric field  $E < E_{c2}$ , the system is a fluid with no long-range order. When  $E_{c2} < E < E_{c1}$ , the system begins to form chains between two electrodes, but the distribution of these chains is random. This is a state similar to an induced nematic liquid crystal, because the chains have the orientation in the field direction [7]. As  $E$  exceeds  $E_{c1}$ , the system is a solid whose ideal structure is a body-centered tetragonal (bct) lattice with conventional Bravais vectors  $\mathbf{a}_1 = \sqrt{6}a\hat{x}$ ,

$\mathbf{a}_2 = \sqrt{6}a\hat{y}$ , and  $\mathbf{a}_3 = 2a\hat{z}$ , where  $a$  is the radius of dielectric spheres (Fig. 1).

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

$$v(1 - 3 \cos^2 \theta_{ij}) / r_{ij}^3 = -v \left[ 2 + \rho \frac{\partial}{\partial \rho} \right] r_{ij}^{-3}, \tag{1}$$

where  $v = (\mathbf{p})^2 / \epsilon_f$ ,  $\rho = [(x_i - x_j)^2 + (y_i - y_j)^2]^{1/2}$ ,  $r_{ij} = [\rho^2 + (z_i - z_j)^2]^{1/2}$ , and  $\theta_{ij}$  is the angle between the joint line of the two dipoles and the  $z$  direction. As dipoles cannot overlap, we also add a hard-core interaction to the above dipolar interaction.

The competition between the thermal energy and the dipolar interaction determines the state of our ER system. From Eq. (1), the dipolar interaction is proportional to  $E_l^2$ . In a low electric field, the thermal motion dominates and the system remains a fluid. When the dipolar interaction is dominated as the field increases, the dielec-

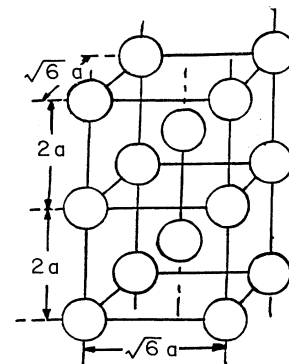


FIG. 1. Three-dimensional body-centered tetragonal (bct) structure, which can be regarded as a compound of chains of class A and chains of class B. The particles have radius  $a$  and are not shown to scale.

tric particles stop ignoring each other and begin to form structures between the two electrodes [3]. It is well known that a detailed study of phase transition needs to define order parameters that are nonvanishing only in the ordered state [9]. In an early work, we pointed out that the ideal structure of the induced ER solid is a bct lattice that can be regarded as a compound of chains of class *A* and class *B*, where a chain of class *A* has its dipoles at  $z_j = 2ja$ , ( $j = 1, 2, \dots$ ) and a chain of class *B* has its dipoles at  $z_j = (2j - 1)a$ , ( $j = 1, 2, \dots$ ) [3]. The applied electric field makes the space anisotropic. The dipolar force is also anisotropic, which leads to additional effects. The bct structure is the state benefited by the anisotropic interactions. This prediction has been verified by Monte Carlo simulations [5] and laser diffraction experiments [6]. In the experiments, the measured structure constants match the bct structure very well. In a real ER system, there are higher-order induced multipoles. A recent calculation by Friedberg and Yu, including contributions from higher multipoles, also confirms the bct lattice obtained from the dipolar approximation [8].

The reciprocal lattice of the above bct lattice has three primitive vectors  $\mathbf{b}_1 = 2\pi\hat{x}/\sqrt{6}a - \pi\hat{z}/a$ ,  $\mathbf{b}_2 = 2\pi\hat{y}/\sqrt{6}a - \pi\hat{z}/a$ , and  $\mathbf{b}_3 = 2\pi\hat{z}/a$ . The order parameters are then given by [9]

$$\rho_j = \sum_{i=1}^N \exp(i\mathbf{b}_j \cdot \mathbf{r}_i) / N, \quad (j = 1, 2, 3). \quad (2)$$

The order parameter  $\rho_3$  characterizes the formation of chains in the  $z$  direction because chains of both class *A* and class *B* have a coherent contribution to  $\rho_3$ . The other two parameters  $\rho_1$  and  $\rho_2$  characterize the structure in the  $x$ - $y$  plane. All the three order parameters are unity if the ER system is the ideal bct lattice. When the dielectric particles are randomly distributed,  $\rho_j$  ( $j = 1, 2, 3$ ) are all vanishing. We introduce a dimensionless quantity

$$\theta = kTd^3\epsilon_f / (\mathbf{p})^2, \quad (3)$$

which characterizes the competition between the dipolar interaction and the thermal energy. Here  $d = 2a$  is the diameter of the spherical particles.

To study the phase transition, we need the canonical ensemble average of  $\rho_j$ ,

$$\bar{\rho}_j = \sum (e^{-\beta U} \rho_j) / \sum (e^{-\beta U}), \quad (4)$$

where the summations are taken over all configurations of the ER system and  $\beta = 1/kT$ . The Coulomb energy of the system  $U$  is given by

$$U = -\frac{1}{2} \sum (\mathbf{E} + \Delta\mathbf{E}) \cdot \mathbf{p}, \quad (5)$$

where  $U_d = -1/2 \sum \Delta\mathbf{E} \cdot \mathbf{p}$  is the dipolar interaction energy. We note that  $U_d$  is the dipolar approximation, neglecting higher-order multipoles [10]. Since the applied external field is uniform, Eq. (4) can be written as

$$\bar{\rho}_j = \sum (e^{-\beta U_d} \rho_j) / \sum (e^{-\beta U_d}). \quad (6)$$

To calculate the dipolar interaction, we introduce a function

$$f(x, y) = \sum_{j=-\infty}^{\infty} [x^2 + (y - 2jL)^2]^{-3/2}. \quad (7)$$

The interaction between a dipole inside the capacitor at  $(x, y, z)$  with its infinite number of images at  $(x, y, 2Lj \pm z)$ , ( $j = \pm 1, \pm 2, \dots$ ), is given by

$$u_s(z) = -v\zeta(3)/(4L^3) - v f(0, 2z), \quad (8)$$

where the constant  $\zeta(3) = \sum_{n=1}^{\infty} 1/n^3 = 1.2020569\dots$ . The interaction of a dipole at  $(x, y, z)$  with another dipole and its infinite number of images at  $(x', y', 2Lj \pm z')$ , ( $j = 0, \pm 1, \pm 2, \dots$ ) is given by

$$u_i(\rho, z, z') = -v \left[ 2 + \rho \frac{\partial}{\partial \rho} \right] [f(\rho, z - z') + f(\rho, z + z')], \quad (9)$$

where  $\rho = [(x - x')^2 + (y - y')^2]^{1/2}$ . Because of the periodicity,  $f(x, y) = f(x, y + 2L)$ , we can expand  $f$  into the form  $f(x, y) = \sum_{s=-\infty}^{\infty} f_s(x) e^{-is\pi y/L}$  with

$$f_s(x) = \int_0^{2L} dy e^{is\pi y/L} f(x, y) / (2L) \\ = \pi s K_1(s\pi x/L) / (L^2 x), \quad (10)$$

where  $K_1(x)$  is a modified Bessel function. Equation (7) now reads as

$$f(x, y) = 1/(Lx^2) + \sum_{s=1}^{\infty} 2\pi s K_1(s\pi x/L) \\ \times \cos(s\pi y/L) / (L^2 x). \quad (11)$$

The formula  $d[xK_1(x)]/dx = -xK_0(x)$  enables us to write  $u_i$  in Eq. (9) as

$$u_i(\rho, z, z') = v \sum_{s=1}^{\infty} 4\pi^2 s^2 K_0(s\pi\rho/L) \cos(s\pi z/L) \\ \times \cos(s\pi z'/L) / L^3. \quad (12)$$

Since  $K_0$  is divergent at  $\rho = 0$ , for the case of  $\rho = 0$ , we use

$$u_i(0, z, z') = -2v[f(0, z - z') + f(0, z + z')]. \quad (13)$$

The total dipolar interaction energy of the system is now given by

$$U_d = \sum_j u_s(z_j) + \frac{1}{2} \sum_{j \neq k} u_i(\rho_{jk}, z_j, z_k). \quad (14)$$

To calculate  $\bar{\rho}_j$  in Eq. (6), we apply the Metropolis algorithm [11]. Our simulations take  $N = 178$  dielectric particles inside a capacitor with spacing  $L = 28a$ . In the  $x$  and  $y$  directions, the system has  $360a \times 360a$  and a periodic boundary condition. We start at  $\theta = 0$ , then increase  $\theta$  slowly. The state of  $\theta = 0$  represents an extremely strong electric field that has the ideal bct lattice structure. For each  $\theta$ , the simulations repeat  $1000N = 178000$  Monte Carlo steps. In each step, we pick a particle in the configuration to make a trial move to a position randomly distributed in the space, then calculate the change of dipolar interaction of the system due to the random move  $\delta U_d$ . If  $\delta U_d \leq 0$ , we accept the new configuration. If  $\delta U_d > 0$ , the probability to accept the new configuration is  $\exp(-\delta U_d/kT)$ . When the new configuration is accepted, we calculate the new  $\rho_j$

( $j=1,2,3$ ) for statistical average. If the new configuration is rejected, the previous configuration is retained and the previous values of  $\rho_j$  are counted again in statistical average. Then, the next random trial will be either on the newly accepted configuration or the retained previous configuration. After  $1000N$  Monte Carlo steps are completed for one  $\theta$ , we calculate the average values of  $\rho_j$ . Then, we increase  $\theta$  by 0.01 and repeat the above procedure. The starting configuration at  $\theta+0.01$  is the final configuration at  $\theta$ . To make sure that our average obtained on the Metropolis sampling is the true canonical ensemble average, we examine the results after  $200N$ ,  $400N$ ,  $600N$ ,  $800N$ , and  $1000N$  Monte Carlo steps and see how they are stabilized. This examination convinces us that the Metropolis sampling is effective.

The absolute values of  $\bar{\rho}_j$  are plotted in Fig. 2. It is clear that  $|\bar{\rho}_1|$  and  $|\bar{\rho}_2|$  have almost identical behavior, while  $|\bar{\rho}_3|$  is noticeably different. At  $\theta=0$ , all the three order parameters equal to unity. As  $\theta$  increases,  $|\bar{\rho}_j|$  ( $j=1,2,3$ ) remains unity for a while. Then, near  $\theta=0.16$ ,  $|\bar{\rho}_1|$  and  $|\bar{\rho}_2|$  drop quickly, while  $|\bar{\rho}_3|$  does not drop quickly until  $\theta$  reaches 0.22. Afterwards,  $|\bar{\rho}_1|$  and  $|\bar{\rho}_2|$  tend to zero much faster than  $|\bar{\rho}_3|$ . There are two important quantities,  $\theta_1=0.28$  and  $\theta_2=0.67$ , as marked in Fig. 2. When  $\theta$  reaches  $\theta_1$ ,  $|\bar{\rho}_1|$  and  $|\bar{\rho}_2|$  are essentially vanishing and their fluctuation after  $\theta>\theta_1$  is due to the finite-size effect. However,  $|\bar{\rho}_3|$  does not vanish until  $\theta$  reaches  $\theta_2$ . As  $\theta>\theta_2$ ,  $|\bar{\rho}_3|$  is essentially vanishing and fluctuating due to the finite-size effect.

The above results indicate three regions of  $\theta$ . For  $0\leq\theta<\theta_1$ , all three  $|\bar{\rho}_j|$  are nonvanishing; the ER system is a solid whose ideal structure is the bct lattice. When  $\theta_1<\theta<\theta_2$ ,  $|\bar{\rho}_1|=|\bar{\rho}_2|=0$ , while  $|\bar{\rho}_3|>0$ . Since  $\rho_3$  characterizes the formation of chains in the  $z$  direction, the ER system in this state has chains in the field direction, but the distribution of these chains is random, no ordering in the  $x$  and  $y$  directions. It is clear that this state is similar to an induced nematic liquid crystal, because the chains have orientation in the  $z$  direction. As  $\theta>\theta_2$ ,

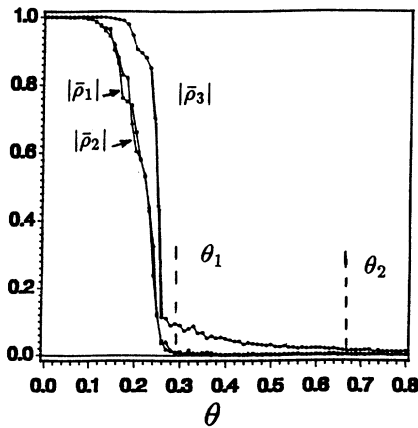


FIG. 2. Change of  $|\bar{\rho}_1|$ ,  $|\bar{\rho}_2|$ , and  $|\bar{\rho}_3|$  vs  $\theta$ . The curves of  $|\bar{\rho}_1|$  and  $|\bar{\rho}_2|$  are almost identical, while  $|\bar{\rho}_3|$  decreases much slower than  $|\bar{\rho}_1|$  and  $|\bar{\rho}_2|$  as  $\theta$  increases.

$\bar{\rho}_1=\bar{\rho}_2=\bar{\rho}_3=0$ , the ER system is a fluid with no ordering at all.

The canonical ensemble average of the dipolar interaction per particle  $\bar{U}_d/N$  is plotted in Fig. 3. Though our system is small,  $\bar{U}_d/N$  clearly shows a jump as  $\theta$  crosses  $\theta_1$ , indicating the first-order phase transition from the nematic liquid-crystal state to the solid state. Since  $\bar{U}_d/N$  is smooth at  $\theta_2$  with no jump, the phase transition from the fluid state to the liquid-crystal state is of the second order. At  $\theta=0$ ,  $\bar{U}_d/N=-2.71188p^2/(\epsilon_f d^3)$ , which is slightly higher than  $-3.050144p^2/(\epsilon_f d^3)$ , the value for the infinite bct lattice. This deviation is due to the finite-size effect, since a system of 178 particles plus their images is a finite bct lattice with defects and surfaces [3]. We also note that a face-centered-cubic lattice of the same small size has dipolar energy  $-2.65465p^2/(\epsilon_f d^3)$  per particle, still higher than that of the bct lattice.

Let us estimate the latent heat for the first-order phase transition. We define a parameter  $\eta=-2\bar{U}_d d^3 \epsilon_f / (Np^2)$ . Then the average dipole field is given by  $\Delta E=\eta p / (\epsilon_f d^3)$ . Our results indicate that the dipole field and hence  $\eta$  is sensitive to the distribution of dielectric particles [3,10]. Using the Lorentz self-consistent method, we have the average  $\mathbf{E}_l=\mathbf{E}/(1-\alpha\eta/8)$ , the quantity  $\nu=p^2/\epsilon_f=\alpha^2 a^3 E^2 \epsilon_f / (1-\alpha\eta/8)^2$ , and the average Coulomb energy per particle  $\bar{U}/N=-\frac{1}{2}\alpha a^3 \epsilon_f E^2 / (1-\alpha\eta/8)^2$ . If  $\eta$  decreases from  $\eta'_1$  to  $\eta_1$  when  $\theta$  passes  $\theta_1$ , the latent heat per unit volume is given by

$$3\phi\alpha\epsilon_f E^2 [(1-\alpha\eta'_1/8)^{-2} - (1-\alpha\eta_1/8)^{-2}] / (8\pi), \quad (15)$$

where  $\phi=4\pi a^3 n/3$  is the volume fraction of the particles in the system. This latent heat is very small for a typical ER fluid. As a rough estimation, we take  $\eta_1\approx 0$  and  $\eta'_1\approx 6$ ,  $\phi=0.4$ ,  $E=10$  kV/cm,  $\epsilon_f=2.2$  (for petroleum oil),  $\alpha=0.5$ , the latent heat is only about 180 erg/cm<sup>3</sup>.

We can consider inducing the phase transitions in the ER fluid by two different approaches: (i) At a fixed temperature, increase the applied electric field; and (ii) at a

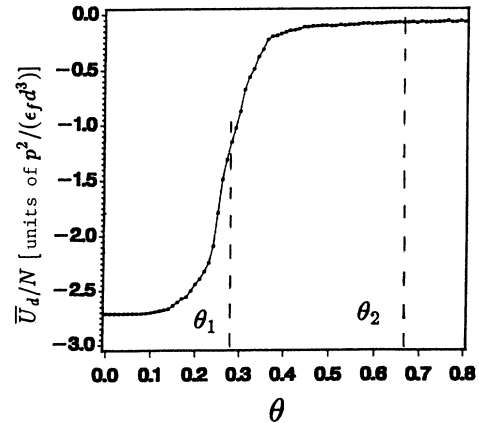


FIG. 3. Change of  $\bar{U}_d/N$  vs  $\theta$ . When  $\theta$  crosses  $\theta_1$ ,  $\bar{U}_d/N$  has a jump. There is no jump at  $\theta_2$ .

constant applied electric field, lower the temperature of the ER system. When the ER fluid has a fixed temperature, two critical electric fields are given by

$$E_{ci} = (1 - \alpha\eta_i/8)[8kT/(\alpha^2\epsilon_f a^3\theta_i)]^{1/2}, \quad (i=1,2), \quad (16)$$

where  $\eta_2$  is the value of  $\eta$  at  $\theta_2$ . When  $E < E_{c2}$ , the ER system is in a liquid state. As  $E_{c2} < E < E_{c1}$ , the ER system is similar to the induced nematic liquid crystal. As  $E_{c1} < E$ , the ER system is in the solid state.

When the ER fluid is under a constant electric field, we have two critical temperatures,

$$T_{ci} = \alpha^2\epsilon_f a^3 E^2 \theta_i (1 - \alpha\eta_i/8)^{-2}/(8k), \quad (i=1,2), \quad (17)$$

if  $\epsilon_f$  and  $\epsilon_p$  have little change in the temperature range under our consideration. When  $T > T_{c2}$ , the ER system is a liquid. When  $T_{c2} > T > T_{c1}$ , the ER system is similar to the nematic crystal state. When  $T < T_{c1}$ , the ER system is the solid bct lattice.

$E_{c1}$  and  $E_{c2}$  estimated from Eq. (16) are in a good range for experiments. For example, they are about 653 and 422 V/cm, respectively, for alumina particles of  $a = 1 \mu\text{m}$  in air at  $T = 300 \text{ K}$  in the microgravity space. However, the above values are for the ideal case where the buoyancy

neutralizes the gravity completely. Most ER fluids presently available have the dielectric particles heavier than the base liquid. Therefore, to overcome the sedimentation effect, for example, we stir the ER fluids in experiments to create a strong liquid flow, which forces the particles to spread around. The required critical electric fields are, therefore, higher than the value estimated by Eq. (16), because the solidification now needs to overcome much higher kinetic energy of the particles.

Our Monte Carlo simulation was performed on an IBM 3090/Vectorized supercomputer. A system of 178 particles in the simulations is small in comparison to the real system. However, to tackle a much larger system on our present computer is almost formidable. On the other hand, though our system is small, the many-body effect is clear in the results. Therefore, there is no reason to doubt the conclusions derived from our simulations.

This research is supported by the Office of Naval Research Grant. No. N00014-90-J-4041, Illinois Department of Energy and Natural Resources Grant No. SC-6, and grants from the Materials Technology Center and Office of Research Development and Administration of Southern Illinois University at Carbondale.

- 
- [1] For example, see *Electrorheological Fluids*, edited by R. Tao (World Scientific, Singapore, 1992); P. M. Adriani and A. P. Gast, *Faraday Discuss. Chem. Soc.* **90**, 1 (1990); W. M. Winslow, *J. Appl. Phys.* **20**, 1137 (1949); D. J. Klingenberg, F. van Swol, and C. F. Zukoski, *J. Chem. Phys.* **91**, 7888 (1989).
- [2] R. Tao, J. T. Woestman, and N. K. Jaggi, *Appl. Phys. Lett.* **55**, 1844 (1989).
- [3] R. Tao and J. M. Sun, *Phys. Rev. Lett.* **67**, 398 (1991).
- [4] T. C. Halsey and W. Toor, *Phys. Rev. Lett.* **65**, 2820 (1990).
- [5] R. Tao and J. M. Sun, *Phys. Rev. A* **44**, R6181 (1991).
- [6] T. J. Chen, R. N. Zitter, and R. Tao, *Phys. Rev. Lett.* **68**, 2555 (1992).
- [7] For example, see, P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974), pp. 7–56.
- [8] R. Friedberg and Y. Yu, *Phys. Rev. B* **46**, 6582 (1992).
- [9] For example, see, P. W. Anderson, *Basic Notions of Condensed Matter Physics* (Benjamin/Cummings, London, 1984), pp. 8–69.
- [10] P. Sheng and Z. Chen, *Phys. Rev. Lett.* **60**, 227 (1988); *Phys. Rev. B* **43**, 5735 (1991).
- [11] N. Metropolis, A. Rosenbluth, M. Rosenbluth, A. Teller, and E. Teller, *J. Chem. Phys.* **21**, 1087 (1953); S. Kirkpatrick, C. D. Gelatt, and M. P. Vecchi, *Science* **220**, 671 (1983); S. Kirkpatrick, *J. Stat. Phys.* **34**, 975 (1984).