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Ground state of an electrorheological fluid

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The ground state of an electrorheological fluid is examined for high dielectric contrast ($\epsilon_p/\epsilon_f \to \infty$). In contrast to the result of Tao and Sun [Phys. Rev. Lett. **67**, 398 (1991)] for the dipole limit, three structures are found to be degenerate: face-centered cubic, hexagonal close packed, and body-centered tetragonal. However, particle column surface energy favors the body-centered tetragonal structure, which has a lower surface energy per particle at the critical volume fraction of particles.

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Tao and Sun [1,2] have predicted that the ground state of an electrorheological (ER) fluid is a body-centered tetragonal (bct) lattice. Recent experiments appear to confirm this prediction [3]. Since the theory is based upon a dipole approximation and is applied to particles that are touching, where such an approximation may not be valid, it is of interest to reexamine the ground state from a different perspective. Letting ϵ_p and ϵ_f be the dielectric constants of the particles and fluid, respectively, we expect the dipole approximation to break down when $\beta=(\epsilon_p-\epsilon_f)/(\epsilon_p+2\epsilon_f)$ is near unity. (The analysis of Tao and Sun is valid for small β; however $\beta \approx 1$ may be more realistic for many ER fluids of interest.) Thus in this paper we consider the limiting case where $\epsilon_p/\epsilon_f \to \infty$, since the failure of the dipole limit should be largest in this limit.

The most convenient method to determine the ground state is to consider the effective dielectric constant for the composite fluid, ϵ_{eff}. The lattice structure with the largest $(\epsilon_{\text{eff}}-\epsilon_f)/\phi_c$, where ϕ_c is the volume fraction of particles at touching for a given lattice, should be the equilibrium structure. Batchelor and O'Brien [4] have shown how to calculate the dielectric constant under these conditions. Here we assume that conductivity effects can be neglected, that is, the applied electric field is at high enough frequency that $\sigma/\omega \ll \epsilon$ for each phase. (Typically, $f > 10^2$ Hz, see Ref. [5].) Let us consider Fig. 1, where the small gap between two adjacent particles (taken to be spheres of radius R) is depicted. The upper sphere is at potential Φ_1 and the lower at Φ_0 with the difference given by

$$\Phi_1-\Phi_0=-E_0 d\,, \tag{1}$$

where E_0 is the applied field and d is the vertical separation of the sphere centers. The electrostatic energy in the gap is given by (minimum gap is $w \ll R$)

$$U=\tfrac{1}{2}\epsilon_f\int_0^R 2\pi\rho\, d\rho\frac{(\Phi_1-\Phi_0)^2}{w+\rho^2/R}\,, \tag{2}$$

where we have taken the cutoff to be R. Equation (2) can be evaluated easily:

$$U=\tfrac{1}{2}\epsilon_f\pi(\Phi_1-\Phi_0)^2 R\ln(R/w)\,. \tag{3}$$

To find the effective dielectric constant, we must equate the energy in a unit volume to the gap energy times the number of gaps, i.e.,

$$\tfrac{1}{2}\epsilon_{\text{eff}}E_0^2=\frac{n}{v_0}U\,, \tag{4}$$

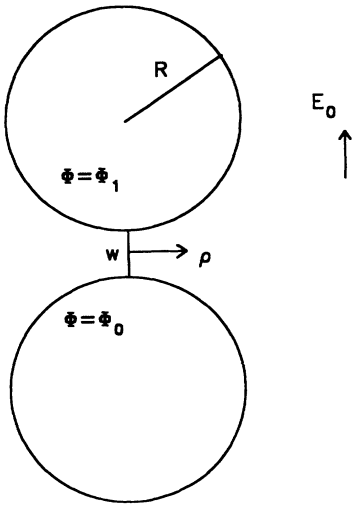

FIG. 1. Gap region between two spherical particles of radius R. The minimum gap is $w \ll R$. The spheres are at potentials Φ_1 and Φ_0, whose difference is determined by the applied electric field.

TABLE I. Value of K_1 [for ϵ_{eff}, see Eq. (5)], critical volume fraction (ϕ_c), and ratio K_1/ϕ_c.

Lattice	K_1	ϕ_c	Ratio
Simple cubic	$\pi/2$	$\pi/6$	3
Face-centered cubic	$\sqrt{2}\pi$	$\pi/3\sqrt{2}$	6
Body-centered cubic	$\sqrt{3}\pi/2$	$\sqrt{3}\pi/8$	4
Body-centered tetragonal	$4\pi/3$	$2\pi/9$	6
Hexagonal close packed	$\sqrt{2}\pi$	$\pi/3\sqrt{2}$	6
Diamond	$\sqrt{3}\pi/8$	$\sqrt{3}\pi/16$	2
Single chain d, vertical spacing L, lateral spacing	$\pi d^2/2L^2$	$\pi d^2/6L^2$	3
2D hexagonal d, lattice constant L, lateral spacing	$\sqrt{3}\pi d/L$	$2\pi d/3\sqrt{3}L$	9/2

TABLE II. Surface energy per unit area e_s in units of $\frac{1}{2}\epsilon_f E_0^2 R \ln(R/w)$ for several faces and lattices.

Lattice	e_s	$2e_s/\phi_c$
fcc (100)	$\pi/2$	$3\sqrt{2}$
fcc (110)	$\sqrt{2}\pi/2$	6
bct (100)	$\pi/\sqrt{6}$	$3\sqrt{6}/2$
bct (110)	$\pi/2\sqrt{3}$	$3\sqrt{3}/2$
hcp (1000)	$\sqrt{2}\pi/\sqrt{3}$	$4\sqrt{3}$

where n is the number of particles in a unit cell, v_0. (This must be generalized in an obvious way for structures with two or more different types of gaps.) Hence, for a simple cubic lattice where $n=1$ and $v_0=d^3$, we have (taking $d=2R$)

$$\epsilon_{\text{eff}}=\epsilon_f K_1 \ln(R/w),\quad K_1=\pi/2 . \tag{5}$$

The effective dielectric constant for all lattices can be expressed in the form equation (5) with K_1 depending upon the structure. We list K_1 for various lattices in Table I (simple cubic, face-centered cubic, and body-centered cubic were determined in Ref. [4]; also see Ref. [6] for further discussion). The bct lattice is of particular interest and is analyzed here. The lattice vectors are $\mathbf{a}_1=\sqrt{6}a\hat{\mathbf{x}}$, $\mathbf{a}_2=\sqrt{6}a\hat{\mathbf{y}}$, and $\mathbf{a}_3=2a\hat{\mathbf{z}}$ [1,2] with $R\rightarrow a$ at touching. There are two types of gaps: the first is between vertically adjacent spheres where the potential difference is $\Phi_1-\Phi_0=-2E_0a$ and the second is between particles displaced along the body diagonal where the potential difference is half as much, $\Phi_1'-\Phi_0'=-E_0a$. There is one gap of the first type per particle [energy U, which is given by Eq. (3)] and four of the second type (energy $U'=U/4$). Hence,

$$\frac{\epsilon_{\text{eff}}}{2}E_0^2=\frac{1}{12a^3}(U+4U') . \tag{6}$$

Making use of Eq. (3), we find the resulting effective dielectric constant to be given by Eq. (5) with

$$K_1=4\pi/3 . \tag{7}$$

The remaining entries in Table I can be found by similar arguments.

The free energy per particle is the negative of the electrostatic energy per particle. The latter is proportional to K_1/ϕ_c [only terms which diverge as $\ln(R/w)$ are retained]. Thus, the larger this ratio, the lower the free energy. We see that three structures have the same ratio, namely, face-centered cubic (fcc), body-centered tetragonal, and hexagonal close packed (hcp). There might be other structures that are degenerate with these three, but none have been found so far.

The implication of these findings is that for high contrast ratio (large ϵ_p/ϵ_f), structures such as fcc and hcp may form instead of or along with bct. Two effects, one of which is beyond the scope of the present study, may be important in determining the structure. The first is the dynamics of structure formation [7]. Simulations of particle ordering have only been reported for dipole interactions [8,9] or for two-dimensional (2D) (monolayer) films [10], so they shed no light on this question. At this point, possible modifications of the dynamics of structure formation are unknown. The other factor is the surface energy, which can be calculated (Table II) following the procedure of Toor and Halsey [11]. For a column of radius R_c, the energy per particle is

$$E_{\text{part}}=\frac{\epsilon_f}{2}E_0^2\ln(R/w)\left[\frac{K_1}{\phi_c}-\frac{2e_sR}{\phi_cR_c}\right] . \tag{8}$$

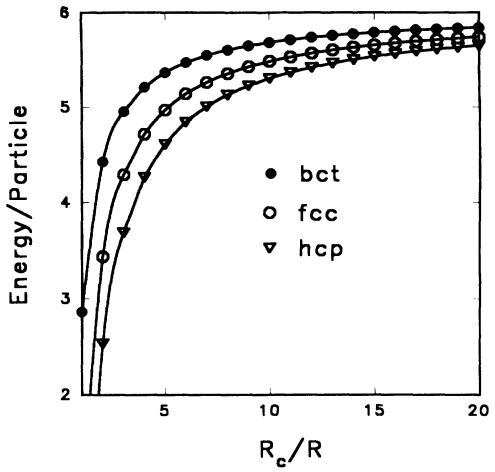

FIG. 2. Electrostatic energy per particle in a column of radius R_c for various lattices with each having a surface energy representative of low-index faces. The unit of energy is $\epsilon_f \ln(R/w)E_0^2/2$.

This relationship is plotted in Fig. 2 for fcc, hcp, and bct lattices, each with a surface energy representative of low index faces [an average of (100) and (110) for fcc and bct, (1000) for hcp]. It appears that at all column radii R_c, the bct lattice is preferred since the electrostatic energy per particle is the highest for this lattice (recall the free energy is the negative of the electrostatic energy). Unless dynamical considerations (or perhaps entropic effects which could be investigated with Monte Carlo simulations [2]) somehow favor fcc or hcp, one must conclude that the ground state is bct in the high contrast ratio limit as well as in the dipole limit. For intermediate contrast, there is no reason to suspect the ground state is other than bct.

The observation of the ground-state structure may be subtle. The simulations of Melrose [12] indicate that for E_0 larger than the solidification field particles aggregate into a gel-like structure in three dimensions (within the dipole approximation).

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