

Surface and bulk energies of dipolar lattices

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We calculate the field due to lines and planes of dipoles, and use this to calculate the bulk and surface energies of various dipolar-lattice structures. The calculation technique is simpler than traditional Ewald methods, and is well suited to surface-energy calculations. We find strongly anisotropic surface energies for the lattices; the more closely packed lattices have negative surface energies for directions approximately parallel to the dipolar axis. These results should be applicable to ferro- and electrorheological fluids.

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I. INTRODUCTION

Dipolar interactions arise in many fields of physics, where they give rise to subtle effects, arising from the long-range and anisotropic nature of dipolar fields [1–3]. The field of a dipole drops off with distance r as r^{-3} . The field E , due to an extended array of dipoles of size R , is then naively given by

$$E \sim \int^R r^2 dr / r^3 \sim \ln R, \quad (1.1)$$

diverging logarithmically with system size. Because of this poor convergence, one must be very careful when evaluating the local field at a point within an array of dipoles. The field due to surfaces must be taken into account; the shape of a sample affects the local field. For a finite sample, dipole sums are marginally convergent, and a set of techniques have been developed to evaluate these sums, falling under the general rubric of “Ewald summations” [4,5]. Essentially, this approach involves breaking a sum up into two pieces, one which converges rapidly in ordinary space and one which converges rapidly in Fourier space.

The question of the bulk and surface energy of dipolar lattices arises in the study of electrorheological fluids. These are colloidal suspensions of polarizable particles in a less-polarizable, nonconducting fluid. Upon application of a strong electric field, the suspended particles are polarized, and form columnar structures aligned with the field. A common approximation used is to treat the particles as point dipoles, neglecting higher-order multipole moments. Tao and Sun argued that the ground-state structure of the condensed phase, in a purely dipolar approximation at zero temperature, is a body-centered tetragonal (bct) lattice, with particles close packed along the field direction [6]. Throughout this paper we will also make the point-dipole approximation.

Thus bulk fields determine the high-field or low-temperature structure of systems of polarizable particles (or of the analogous suspensions of ferromagnetic particles [2]). Surface energies arise in theories of structure formation in such suspensions; structure formation is im-

portant in determining their kinetic and dynamical properties [7].

In Secs. II and III we describe a technique in which we first calculate the field due to a one-dimensional periodic structure (a line of dipoles) or a two-dimensional periodic array (a plane of dipoles) [8]. The field due to each of these structures is finite; in fact, the calculation is exponentially convergent. In Sec. IV we calculate the field within various lattice structures by summing over lines and planes, while carefully taking into account the effect of surface charges. This approach is simpler than the normal approach to Ewald summations, and is particularly well suited to calculating surface energies, which we do in Sec. V.

II. FIELD DUE TO A LINE

We wish to calculate the field due to an infinite line of dipoles, with the dipole axis aligned with the line [9]. Let the dipoles be placed along the z axis at positions $z_n = nc$, with $n \in \mathbb{Z}$. We will use coordinates (ρ, z) , where ρ is a two-dimensional vector in the x - y plane. Since we are interested in the energy of interaction with dipoles perfectly aligned along the z axis, we only need the z component of the field; in the rest of this paper, we will use E to mean $E \cdot \hat{z}$.

Of course, we can ask ourselves how serious is this restriction. For ferromagnetic particles, a magnetic field aligns the dipoles, but does not appreciably change their magnitude. Thus in this case our assumption that all dipole moments are equal and aligned is valid. For electrorheological fluids, the dipoles are induced by the field. Thus, in principle, these moments can vary from position to position, and transverse fields might be relevant. For the lattice-energy computations, this effect is irrelevant, as we confine ourselves to Bravais lattices only. However, for the surface-energy computations, we are effectively restricting ourselves to effects of the lowest order in the polarizability of the particles—when particle-particle interactions are included, both dipole magnitudes and directions might vary near a surface.

Consider the function

$$\eta(\rho, z) = \sum_n \{ 1 / [(z - z_n)^2 + \rho^2]^{1/2} \} .$$

We can write this as

$$\eta(\rho, z) = (1/\rho) \sum_n [1 / (1 + \phi_n^2)^{1/2}]$$

where $\phi_n = (z - nc)/\rho$ and without loss of generality we set $0 < z < c$. Then

$$\eta(\rho, z) = \int d\phi \frac{1}{(1 + \phi^2)^{1/2}} \sum_{n=-\infty}^{\infty} \delta[\phi - (1/\rho)(nc - z)] . \quad (2.1)$$

We can use the Poisson-sum formula,

$$\begin{aligned} \sum_n \delta[(\phi + z/\rho) - nc/\rho] \\ = (\rho/c) \sum_{m=-\infty}^{\infty} \exp[2\pi im(\rho/c)(\phi + z/\rho)] , \end{aligned}$$

and the fact that $1/(1 + \phi^2)^{1/2}$ is even to get

$$\eta(\rho, z) = \frac{1}{c} \sum_{m=0}^{\infty} A_m \cos \left[2\pi m \frac{z}{c} \right] , \quad (2.2)$$

where

$$A_m = \int_{-\infty}^{+\infty} d\phi \frac{1}{(1 + \phi^2)^{1/2}} \cos(2\pi im\rho/c) \equiv I(k_m \rho) , \quad (2.3)$$

and $k_m = 2\pi m/c$. This is a standard representation for the modified Bessel function of the first kind [10]. $I(k_m \rho) = 2K_0(k_m \rho)$. The $m=0$ term has a logarithmic singularity, which, however, has no influence on the final result.

Now note that

$$\frac{d^2}{dz^2} \frac{d}{r} = \frac{d}{r^3} (3 \cos^2 \theta - 1) \quad (2.4)$$

is the field at a point (r, θ) due to a dipole of strength d located at the origin (in Gaussian units); thus, we can obtain the desired field as the second derivative with respect to z of η ;

$$E(\rho, z) = -\frac{2d}{c} \sum_{m=1}^{\infty} k_m^2 \cos(k_m z) K_0(k_m \rho) . \quad (2.5)$$

The modified Bessel function $K_0(x)$ is an exponentially decaying function of its argument when x exceeds 1, so this is a very short-range field. This is not unexpected; since the potential must be a solution of the Laplace equation, periodic in z , we would expect it to be roughly exponential in the perpendicular direction. This implies that lines out of registry with one another will experience an attractive interaction.

One way to calculate the field in a dipolar crystal is to divide the crystal into a series of lines and sum up the field from each line. We will also need the field at a lattice site due to other dipoles in the same line

$$E_0 = 2d \sum_{n=1}^{\infty} \frac{2}{(nc)^3} = \frac{4d}{c^3} \zeta(3) = \frac{4.8060d}{c^3} , \quad (2.6)$$

where ζ is the Riemann zeta function.

III. FIELD DUE TO A PLANE

We also wish to calculate the field due to a plane of dipoles at positions $(x_m = ma, y_n = nb)$ where x, y are Cartesian coordinates in the plane and m, n label the dipole positions. Here the dipole moments are perpendicular to the plane. Start by considering the expression

$$\psi(x, y, z) = \sum_m \sum_n \frac{1}{[(x - x_m)^2 + (y - y_n)^2 + z^2]^{1/2}} . \quad (3.1)$$

This can be written

$$\psi(x, y, z) = \int \int dx' dy' \frac{1}{(x'^2 + y'^2 + z^2)^{1/2}} \sum_m \sum_n \delta(x' - (x - x_m)) \delta(y' - (y - y_n)) . \quad (3.2)$$

We now use the Poisson sum formula to obtain

$$\psi(x, y, z) = \frac{1}{ab} \sum_m \sum_n \exp[i(k_m x + q_n y)] \int \int dx' dy' \exp[i(k_m x' + q_n y')] / (x'^2 + y'^2 + z^2)^{1/2} , \quad (3.3)$$

where $k_m = 2\pi m/a$ and $q_n = 2\pi n/b$. We can evaluate the necessary integral (see the Appendix) with the result that

$$\begin{aligned} I(k, q, z) &= \int \int dx dy \frac{\exp[i(kx + qy)]}{(x^2 + y^2 + z^2)^{1/2}} \\ &= [2\pi / (k^2 + q^2)]^{1/2} \exp[-z(k^2 + q^2)^{1/2}] . \end{aligned} \quad (3.4)$$

Now $I(k, q, z) = I(\pm k, \pm q, z)$, so we write ψ as

$$\psi(x, y, z) = \frac{4}{ab} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \cos(k_m x) \cos(q_n y) I(k_m, q_n, z) + \frac{2}{ab} \sum_{m=1}^{\infty} \cos(k_m x) I(k_m, 0, z) + \frac{2}{ab} \sum_{n=1}^{\infty} \cos(q_n y) I(0, q_n, z) . \quad (3.5)$$

Once again we can obtain the desired field as the second derivative with respect to z of ψ ,

$$E(x,y,z) = \frac{4\pi d}{ab} \left[2 \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \cos(k_m x) \cos(q_n y) (k_m^2 + q_n^2)^{1/2} \exp[-z(k_m^2 + q_n^2)^{1/2}] + \sum_{m=1}^{\infty} k_m \cos(k_m x) \exp(-k_m z) + \sum_{n=1}^{\infty} q_n \cos(q_n y) \exp(-q_n z) \right]. \tag{3.6}$$

Just as with a line of dipoles, the field due to a plane of dipoles, evaluated at a point a distance z away from the plane, is exponentially small when z exceeds the lattice spacing within the plane.

For dipoles at an angle ϕ to the normal to the plane, it is simple to generalize these results. For simplicity, we take the dipole moments to be in the x - z plane, at an angle ϕ to the z direction. As a further simplification, we compute only the field in this direction, at the position x,y,z as in the above. A simple computation shows that this field is

$$E_\phi(x,y,z) = \left[\cos^2\phi \frac{d^2}{dz^2} + 2 \cos\phi \sin\phi \frac{d}{dz} \frac{d}{dx} + \sin^2\phi \frac{d^2}{dx^2} \right] \psi(x,y,z). \tag{3.7}$$

This is useful for the computation of the surface energy in the [101] direction (see Sec. V below).

IV. FIELD OF VARIOUS LATTICE STRUCTURES

We can use these expressions for the field due to a line and a plane of dipoles to calculate the field at a lattice site in various structures. One must be careful to include the field due to distant surfaces. To illustrate the method, we will start by examining lattices with cubic symmetry. Here, we already know what the field at a lattice site must be, from classical dielectric theory

$$E = (4\pi/3)d\phi, \tag{4.1}$$

where ϕ is the number density of dipoles and d is the dipole strength. Let us recall how this is calculated [11]. We consider an infinite lattice of dipoles, of cubic symmetry. To calculate the field at a point, we draw an imaginary "sphere of exclusion" around the point (Fig. 1). We then calculate the field as the sum of the field due to the dipoles within the sphere and the dipoles outside the sphere. The sphere is assumed to be large enough that macroscopic electrostatics can be used to calculate the field due to those dipoles located outside of the sphere,

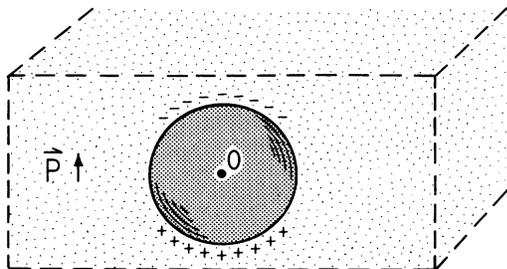


FIG. 1. A sphere of exclusion about the point O . The macroscopic field in the cavity due to the external medium of polarization \mathbf{P} is $4\pi\mathbf{P}/3$. The contribution from the dipoles within the cavity vanishes for lattices with cubic symmetry.

while we actually sum the field due to the individual dipoles within the sphere. Now, if we sum the dipole field due to particles in a cubic lattice over a spherical volume, the field is zero by symmetry, so the total field is just that due to a macroscopic spherical hole in a uniformly polarized body, of polarization density $d\phi$, or $E = (4\pi/3)d\phi$.

Let us calculate the same field as a sum over lines of dipoles. For definiteness, we will consider a close-packed fcc lattice of particles of radius r_d , with number density $\phi = 1/(4\sqrt{2}r_d^3)$. We will imagine drawing an infinitely long "cylinder of exclusion" (Fig. 2). The field is then the field due to all the dipoles within the cylinder, plus the macroscopic field due to an infinite cylindrical hole in a uniformly polarized body. From elementary electrostatics this macroscopic field is zero, so the total field is that from the nearby dipoles. Figure 3(a) shows the lattice structure; Fig. 3(b) shows a view looking down the \hat{z} axis, showing the neighboring column positions [12]. Dipoles in the same column are spaced at $2\sqrt{2}r_d$ apart, so Eq. (2.6) implies that the field due to the same column is $E_0 = 0.60102d/(\sqrt{2}r_d)^3 = 0.21249d/r_d^3$. There are four attractive nearest-neighbor chains, located at a distance $\rho = \sqrt{2}r_d$ away, and displaced vertically by a distance $z = \sqrt{2}r_d$. From Eq. (2.5), each of these contributes a field

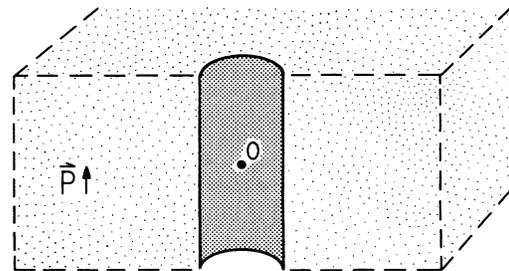


FIG. 2. A cylinder of exclusion about the point O . The macroscopic field in the cavity due to the external medium vanishes in this geometry. The only contribution to the field comes from the dipoles within the cylindrical cavity, whose field may be summed by lines.

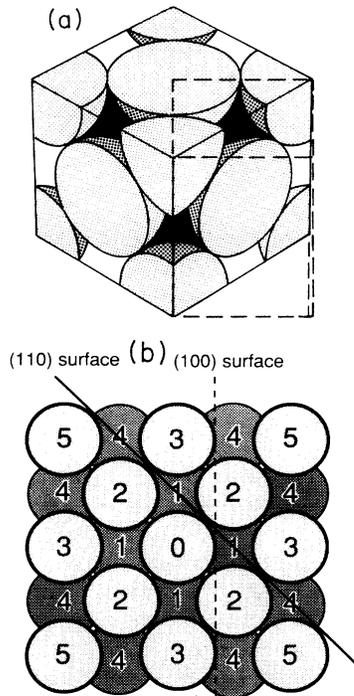


FIG. 3. (a) A close-packed face-centered-cubic (fcc) lattice. The dashed line shows the conventional unit cell of the corresponding body-centered tetragonal lattice. (b) A close-packed face-centered cubic (fcc) lattice, viewed along the z direction. The different numbers indicate lines of particles at various distances from line 0. The interaction between line 0 and lines 1 and 4 is attractive, while the interaction with lines 2, 3, and 5 is repulsive. The dashed line shows the cut for computing the (100) surface energy; the solid line shows the cut for computing the (110) surface energy. Note that this diagram could equally well show a body-centered structure, though with a conventional unit cell rotated with respect to that of the face-centered structure.

$$E_1 = (\pi^2/\sqrt{2}) \sum_1^{\infty} (-1)^{m+1} m^2 K_0(m\pi) d / r_d^3 = 0.18226d / r_d^3 .$$

The next four chains are repulsive next-nearest neighbors, located a distance $\rho = 2r_d$ away, contributing a field

$$E_2 = -(\pi^2/\sqrt{2}) \sum_1^{\infty} m^2 K_0(\sqrt{2}m\pi) (d / r_d^3) = -0.04922d / r_d^3 .$$

If we add up these fields, we get a total field of $E = E_0 + 4E_1 + 4E_2 = 0.745d / r_d^3$. The exact result to five figures is $E = (4\pi/3)(1/4\sqrt{2}r_d^3) = 0.74048d / r_d^3$, so we get 1% accuracy already at the next-nearest-neighbor level.

We can also calculate the field as a sum over planes. To do this, we draw an infinite “box of exclusion” (Fig. 4) and sum the field due to the planes of dipoles within the box with that due to the macroscopic continuum located

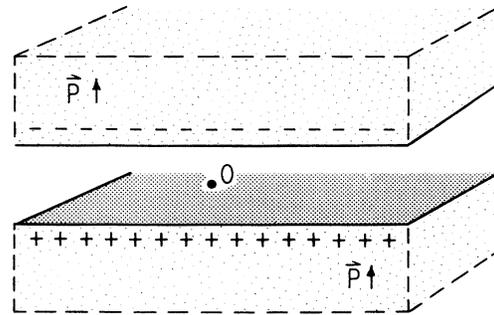


FIG. 4. A slab of exclusion about the point O . The macroscopic field in the cavity due to the external medium of polarization \mathbf{P} is $4\pi\mathbf{P}$. The contribution to the field from the dipoles within the cavity can be summed by planes.

outside of the box. The macroscopic field is equal to that within an infinite parallel-plate capacitor with charge density $d\phi$ on each plate, or $E_{\text{mac}} = 4\pi d\phi = 2.2214d / r_d^3$.

The field due to dipoles in the same plane has been evaluated numerically [5], with the result that $E_0 = -9.0336d / (2r_d)^3 = -1.1292d / r_d^3$. Here note that the dipoles in the plane act to lower the local field.

There are two nearest-neighbor planes, located a distance $z = \sqrt{2}r_d$ away. The field due to each plane, evaluated using Eq. (3.6), is $E_1 = -0.17868d / r_d^3$. Note that the nearest-neighbor field is negative, so the nearest-neighbor planes are repulsive. The next-nearest-neighbor planes are located at a distance of $2\sqrt{2}r_d$, and each contributes a field of $E_2 = 0.00282d / r_d^3$. Then the total field is

$$E = E_0 + \sum_{n=1}^{\infty} 2E_n + E_{\text{mac}} = 0.74048d / r_d^3 .$$

We can apply this technique to other lattice structures, obtaining the known results for the other cubic-lattice structures. We also apply it to a hcp structure and a bct lattice that is close-packed along the field direction, shown in Fig. 5. The bct lattice arises naturally as a possible ground state of an electrorheological fluid at low

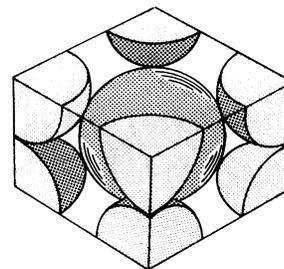


FIG. 5. A body-centered tetragonal lattice. This lattice has been compressed so that the particles are close-packed along the z direction, the direction of the field. This lattice has a lower bulk energy than do the close-packed fcc or hcp (hexagonal close-packed) structures.

TABLE I. Local fields in units of d/r_d^3 for various lattice structures. The compressed bct lattice has the highest field, and thus the lowest energy. The close-packed lattices (fcc and hcp) are quite close in energy to the bct lattice.

Lattice	Local field
bct	0.762 52
fcc	0.740 48
hcp	0.740 06
bcc	0.680 17
sc	0.523 60

temperatures or high fields [6]. Our results confirm those of Tao and Sun; in particular, we find that the bct lattice has the largest field of the lattices that we examined. Table I shows the field for these lattices.

Note that while the bct structure has the largest field, and thus the lowest energy, the energy differences with the close-packed fcc and hcp structures are small, approximately 3%. Thus, at finite temperature entropic terms in the free energy will play an important role in determining the structure. To find the lattice with the lowest free energy, one must take into account the contribution of lattice vibrations and other thermally excited modes. In principle, we might expect a series of structural transitions as the dipolar strength is increased, if these contributions are significantly different for different structures. Note also that this calculation has ignored higher-order multipolar interactions. For particles with appreciable polarizabilities, these interactions will contribute terms of the same order of magnitude as the dipolar terms, and could change the preferred lattice structure.

It is also interesting to understand *why* the bct lattice has a larger field than the close-packed fcc. We can write the field in each case as

$$E = E_{\text{near}} + (4\pi/3)\phi d, \quad (4.2)$$

where E_{near} is the field due to the nearby dipoles within a sphere that is large microscopically but small macroscopically and $(4\pi/3)\phi d$ is the long-range field due to the rest of the body. We see that

$$E_{\text{near}} = \begin{cases} 0 & \text{for a fcc lattice} \\ 0.064\,38d/r_d^3 = 0.384\phi & \text{for a bct lattice,} \end{cases} \quad (4.3)$$

and the long-range field is

$$(4\pi/3)\phi d = \begin{cases} 0.740\,48d/r_d^3 & \text{for a fcc lattice} \\ 0.698\,13d/r_d^3 & \text{for a bct lattice.} \end{cases} \quad (4.4)$$

We see that the long-range field favors the fcc structure, due to the higher density, but that the larger field due to the nearby dipoles favors the bct structure. The fcc and bcc lattices can both be obtained by varying the ratio of the height c of the unit cell in the direction parallel to the field (we refer here to the unit cell of the corresponding simple tetragonal lattice) to its width a in the direction perpendicular to the field. We always fix the distance be-

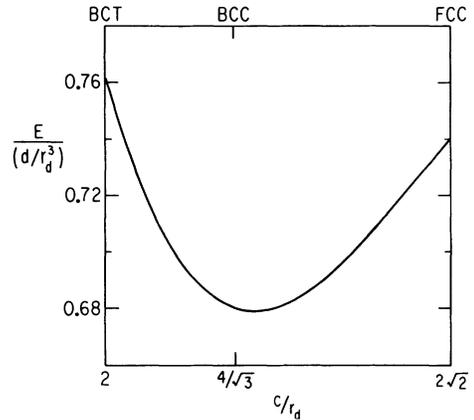


FIG. 6. The local field E as a function of the vertical distance c between the particles for body-centered tetragonal lattices, given in units of d/r_d^3 . The parameter c is measured in units of the particle radius r_d . The closest possible packing is chosen for each value of c . By varying c , we can go from the compressed bct lattice of Tao and Sun to the fcc lattice via the bcc lattice.

tween nearest-neighbor particles as $2r_d$. The case of a bct lattice is then the case with a minimum possible value of $c = 2r_d$, with $a = \sqrt{6}r_d$; that of the bcc lattice is the symmetric case $a = c = 4r_d/\sqrt{3}$; and that of the fcc lattice corresponds to the minimum possible value of $a = 2r_d$, with $c = 2\sqrt{2}r_d$. It is interesting to calculate the local field as we go continuously from the fcc structure to the bct structure by varying c/a . Figure 6 shows the field as a function of c as we go from the bct lattice to the fcc lattice via the bcc lattice. The bcc lattice not only has a smaller local field, but has a lower density, and thus a lower long-range field than the bct structure.

V. LATTICE SURFACE ENERGIES

This technique is particularly useful for calculating surface energies. The surface tension of a dipolar crystal is interesting in order to examine the stability of various lattice structures, and arises in at least one theory of structure formation in electrorheological fluids [7].

To calculate the surface tension along a plane with normal \hat{n} we imagine pulling the lattice apart along the direction \hat{n} , until the planes on either side of the cut are separated by a distance that is small macroscopically, but much larger than a lattice spacing. We then calculate the total energy of this system. The surface energy $\sigma(\hat{n})$ is defined by

$$U_{\text{new}} = U_{\text{old}} + 2\sigma(\hat{n})S, \quad (5.1)$$

where U_{old} is the energy before the separation, U_{new} is the energy after the separation, and S is the surface area created (on one side of the cut). Thus, we need to calculate the change in energy per unit surface area. Note that the condition that both of the planes be retained in computing the field is crucial in order to avoid spurious long-range contributions to the surface energy. The long-range contributions should be included in the expression for the *bulk* electrostatic energy of a body of arbitrary

shape.

Once again, to illustrate the technique we will consider a fcc lattice. Let us first calculate the surface energy along a plane parallel to the dipole axis. Figure 3(b) shows the view looking down along the z axis. The number 0 indicates the particle at which we calculate the field. Each of the numbers represents a line of dipoles; 1 indicates a nearest-neighbor line, 2 indicates a next-nearest-neighbor line, and so forth. The dashed line indicates the new surface. To calculate the field, we include all dipole chains on the left side of the cut; thus, the difference in field at a point on the inside of the lattice is equal to the field due to all the chains on the right-hand side of the cut. Thus, the difference in the field at the point indicated is $\delta E_a = -(E_1 + 2E_2 + E_3 + 4E_4 + 2E_5 + \dots) = -0.087816d/r_d^3$. We can also ask what the change in field is for a particle sitting one row back; in this case $\delta E_b = -(E_3 + 2E_4 + 2E_5 + \dots) = +0.001512d/r_d^3$. Then the change in energy, per particle, is $\delta U = -\frac{1}{2}d(\delta E_a + \delta E_b + \dots) = 0.043132d^2/r_d^3$. Because of the exponential decay in field strength we only need consider the field of a few lines near the cut in order to achieve high accuracy. To get the surface energy, we just divide by the surface area per particle, $4r_d^2$, to get

$$\sigma(100) = 0.010783d^2/r_d^5. \quad (5.2)$$

Typically the dipole moment $d \propto r_d^3$, so that $\sigma \propto r_d$. This proportionality between the surface energy and the size of a particle is an explicit indication of the dependence of this effect on the short-range ordering of the lattice.

Now let us calculate the surface energy along a plane perpendicular to the dipole direction. The change in field at the plane next to the cut is just the sum $\delta E_a = -(E_1 + E_2 + E_3 + \dots) = +0.17588d/r_d^3$, where E_n is now the field due to the n th plane. The change in the field at the next plane in is $\delta E_b = -(E_2 + E_3 + E_4 + \dots) = -0.00280d/r_d^3$, so the total change in energy per surface particle is $\delta U = -\frac{1}{2}d(\delta E_a + \delta E_b + \dots) = -0.086556d^2/r_d^3$, and the surface energy is

$$\sigma(001) = -0.021639d^2/r_d^5. \quad (5.3)$$

Note that the surface energy in this direction is negative, indicating that the total energy is actually lowered by splitting the lattice along this direction, as long as the bulk density is maintained, so that the long-range macroscopic field of $4\pi d\phi$ is now lowered. This is a microscopic analog of the well-known Taylor instability of a liquid dielectric in a field normal to its surface [13]. This instability is due to the fact that a protuberance parallel to the field will have a larger local field, and therefore a lower energy, so that the protuberance will tend to grow. Thus, the only stable shapes are those highly elongated along the field direction, for which there is very little (001) surface area [7]. The more physically relevant surface tensions will be those in directions perpendicular to the dipole axis. This can also be seen by directly considering the contribution of the bulk depolarization energy (as in Ref. [7]), which directly favors elongated shapes.

We also calculate the (110) surface energies. Our con-

TABLE II. Surface energies in units of d^2/r_d^5 for various lattice structures in various directions. The Miller indices are defined with respect to the simple cubic (or simple tetragonal) lattices. The dipole moment is always taken in the z direction.

Lattice	(100)	(110)	(101)	(001)
bct	0.008228	0.005250	-0.005753	-0.024265
fcc	0.010783	0.023120	-0.011576	-0.021639
bcc	0.013535	0.008064	-0.004032	-0.027070
sc	-0.002567	-0.003428	0.001714	0.005134

vention is to determine the Miller indices from the unit cell of the corresponding simple cubic or simple tetragonal system. This implies, for instance, that for the body-centered structures the (100) energies are determined by making a 45° cut across Fig. 3(b) (and then computing the field of the missing lines), while for the (110) body-centered energies the cut is made in the vertical direction. Except for this subtlety, the computation of the (110) surface energies is entirely analogous to the computation of the (100) surface energies.

Finally, using Eq. (3.7), we can compute the (101) surface energy. This surface of a cubic or tetragonal crystal can be represented as a square or rectangular lattice (or as a sum over such lattices for the body-centered structures), so the surface energy can be expressed as a sum over planes. Note that for the tetragonal lattices, this direction is *not* at a 45° angle to the field direction. For the preferred body-centered structure of Tao and Sun, the [101] direction is at an angle of $\arctan(\sqrt{2}/3)$ to the field direction. As with the (001) surface energy, it is necessary to include the electric field induced by the second surface created when the lattice is separated. This second surface is set a macroscopic distance from the first, and is parallel to it. Also reminiscent of the (001) surface energy is the fact that these surface energies are negative for the more closely packed lattices.

Table II shows the results of surface energy calculations for various lattice structures. Note that the simple cubic structure has a negative surface energy in the [100] direction. This is due to the fact that all the lines of particles are in registry with each other, so that if we calculate the field by summing over lines, all lines are repulsive. All of the attractive contribution comes from the particles in the same line, so the energy is lower for an isolated line than for a simple cubic structure.

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APPENDIX: EVALUATION OF $I(k, q, z)$

In order to evaluate the field of a plane of dipoles we need an expression for

$$I(k, q, z) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx dy \frac{\exp[ikx + iqy]}{(x^2 + y^2 + z^2)^{1/2}}. \quad (A1)$$

We first perform the integral over y , making the change of variables $y' = y / (x^2 + z^2)^{1/2}$, $q' = q (x^2 + z^2)^{1/2}$, so that the y integral becomes

$$2 \int_0^\infty dy' \frac{\cos(q'y')}{(1+y'^2)^{1/2}} = 2K_0(q'). \quad (\text{A2})$$

Then $I(k, q, z)$ is

$$I(k, q, z) = 4 \int_0^\infty dx \cos(kx) K_0[q(x^2 + z^2)^{1/2}]. \quad (\text{A3})$$

We change variables again, to $w = (x^2 + z^2)^{1/2}$, to get

$$I(k, q, z) = 4 \int_z^\infty \frac{w dw}{(w^2 - z^2)^{1/2}} \cos[k(w^2 - z^2)^{1/2}] K_0(qw). \quad (\text{A4})$$

This is a tabulated integral, [14], and the final result is that

$$I(k, q, z) = \frac{2\pi}{(k^2 + q^2)^{1/2}} \exp[-z(k^2 + q^2)^{1/2}]. \quad (\text{A5})$$

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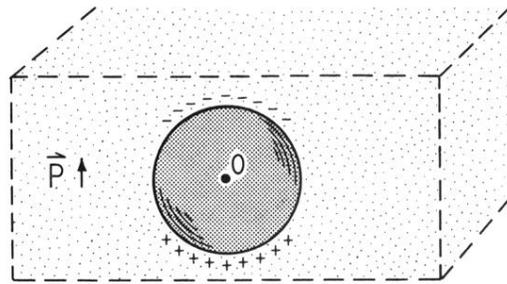


FIG. 1. A sphere of exclusion about the point O . The macroscopic field in the cavity due to the external medium of polarization \mathbf{P} is $4\pi\mathbf{P}/3$. The contribution from the dipoles within the cavity vanishes for lattices with cubic symmetry.

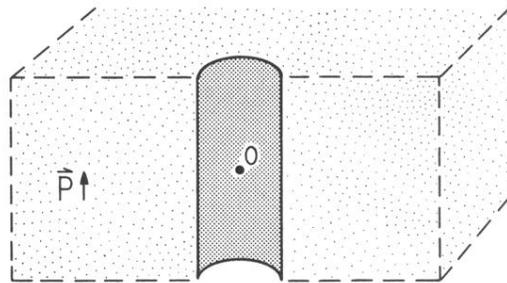


FIG. 2. A cylinder of exclusion about the point O . The macroscopic field in the cavity due to the external medium vanishes in this geometry. The only contribution to the field comes from the dipoles within the cylindrical cavity, whose field may be summed by lines.

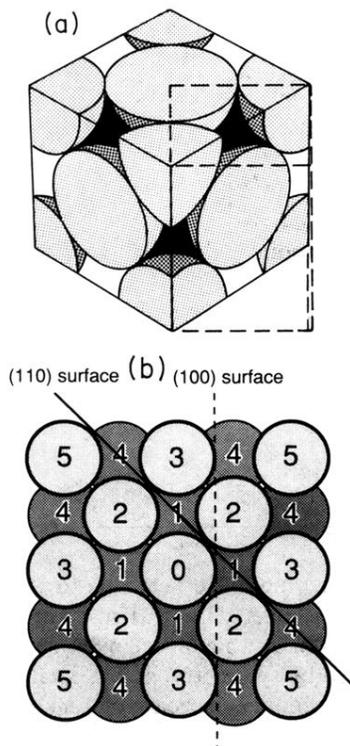


FIG. 3. (a) A close-packed face-centered-cubic (fcc) lattice. The dashed line shows the conventional unit cell of the corresponding body-centered tetragonal lattice. (b) A close-packed face-centered cubic (fcc) lattice, viewed along the z direction. The different numbers indicate lines of particles at various distances from line 0. The interaction between line 0 and lines 1 and 4 is attractive, while the interaction with lines 2, 3, and 5 is repulsive. The dashed line shows the cut for computing the (100) surface energy; the solid line shows the cut for computing the (110) surface energy. Note that this diagram could equally well show a body-centered structure, though with a conventional unit cell rotated with respect to that of the face-centered structure.

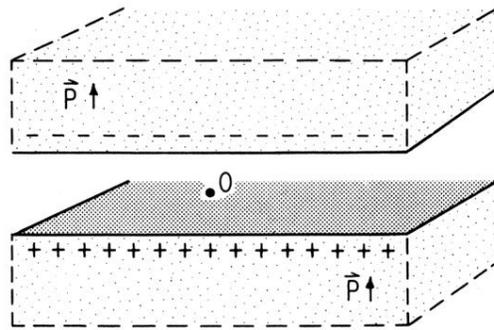


FIG. 4. A slab of exclusion about the point O . The macroscopic field in the cavity due to the external medium of polarization \mathbf{P} is $4\pi\mathbf{P}$. The contribution to the field from the dipoles within the cavity can be summed by planes.

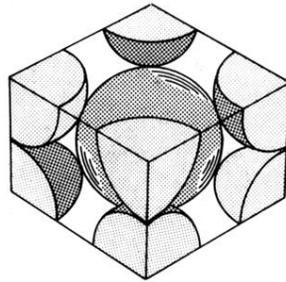


FIG. 5. A body-centered tetragonal lattice. This lattice has been compressed so that the particles are close-packed along the z direction, the direction of the field. This lattice has a lower bulk energy than do the close-packed fcc or hcp (hexagonal close-packed) structures.