

Ground state of a dipolar crystal

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We provide some of the strongest evidence to date that the ground state structure of an infinite collection of point dipoles with hardcore sphere interactions is body-centered tetragonal. The structure with the next highest binding energy is not face-centered cubic; a particular honeycomb structure has lower energy.

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I. INTRODUCTION

One of the most fundamental, the most interesting and also the most difficult tasks in understanding a physical system is the determination of the ground state structure. Much work has been carried out to better understand the ground state structure in dipolar systems such as electrorheological (ER) and magnetorheological (MR) fluids [1–16], both in the case where one dimension is finite and where all three dimensions are infinite. In this study we take the simplest model of such a system and try to establish more convincingly than heretofore the ground state structure in the case where all dimensions are infinite.

All previous studies [1–15] indicate that the thermodynamic ground state of a dipolar system is body-centered tetragonal (bct) rather than another crystalline structure. Why do we consider further work along these lines warranted? To answer this question we need to briefly review the theoretical evidence presented to date. These fall into two basic classes. The first class consists of comparing the exact energy of a handful of infinite structures, e.g., bct, face-centered cubic (fcc), etc., as was carried out in Ref. [1]. There is no guarantee that the ground state structure has been included among the few that have been studied. Assuming the structure is crystalline, there are 14 different kinds of Bravais lattices, and 230 different space groups of a Bravais lattice and its basis [17]. Most of these groups allow for rescalings and changes of orientation, as well as an infinite number of basis representations. The point is that the ~ 10 structures which have been considered for ground state candidates are by no means exhaustive.

The second class of theoretical studies seeks to perform simulated annealing to determine the ground state. Here one generally been restricted to a small number of degrees of freedom, e.g., 122 particles in the case of Ref. [13], or a small number of rigid, uniform chains of particles (without gaps), such as the 16 chains of Ref. [2]. In these studies the ground state of the finite system is compared with the bct structure, e.g., by a computation of bct order parameters, and one sees indications that the bct structure is being approached as the temperature goes to zero. The concern with these studies is that the number of degrees of freedom may be insufficient to reach the thermodynamic ground state structure. It turns out, for example, that a cloud of ions spinning in an ion trap has a thermodynamic ground state which

is simple cubic. Amazingly, however, some 10^5 ions are required before that structure appears [18].

An interesting work outside of these two classes of studies involved simulations with a fairly large number of dipolar particles: 10 000 [15]. In this study a large fraction of particles were seen to have nearest neighbors in an approximate bct arrangement; however, this was never more than about 30%. With so many degrees of freedom, the problem of metastability was severe and, for example, the average coordination number never reached 6. (The coordination number for an infinite bct structure is 10.) Nevertheless this study provided some complementary evidence that the ground state of a dipolar system is bct.

The model we will consider is one in which spherical dipolar particles interact only via the dipole-dipole interaction and a hardcore repulsive term which prevents any overlap. The dipole moments will be taken to all point in the same direction. All dimensions are infinite. This model corresponds at least roughly to a saturated ER or MR fluid in the limit of infinite sample thickness. The perfect alignment of the dipole moments can be considered to be the result of a sufficiently strong external field. This sort of physical system is plagued by metastability problems (also known as “aging”), making it very difficult to experimentally access the ground state structure [16]. As we shall see, the theoretical situation is not immune to this problem, though it has some advantages.

II. CASE FOR GAPS

Dipolar particles tend to most easily form chains and therefore it is natural that the structures considered to date have been almost exclusively able to be constructed from straight chains with no gaps between the particles in each chain. For example the bct and fcc structures which have been considered are of this type.

We wish to carry out a somewhat wider search for ground state candidates and as a first step we revisit several of the structures which have been considered before, but now allow the chains which form these structures to have gaps. By allowing for gaps we are able to pack the chains more closely thereby increasing the inter-chain binding energy at the expense of reducing the intra-chain binding energy.

In Fig. 1 we show part of one layer of an fcc or hexagonal closed packed (hcp) structure. By adding layers of the form

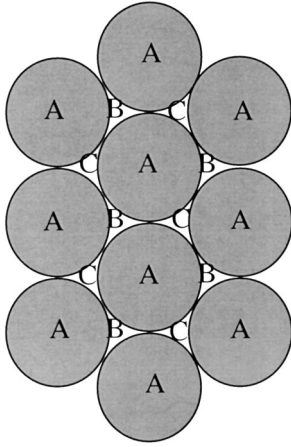


FIG. 1. The fcc and hcp structures.

$ABCABC \dots$ we form the fcc structure. By adding layers of the form $ABABAB \dots$ we form the hcp structure. These structures can be considered to consist of chains with no gaps. (Parts of three chains made up of A particles are shown in the figure.) If we put in a gap η between successive particles in each chain, while laterally moving the chains as close as possible to each other without overlapping, we form a family of structures with an energy per particle which can be calculated as a function of η . The result for the fcc lattice is shown in Fig. 2. One might expect the energy per particle to increase monotonically with η because the binding energy between particles in a chain is normally much greater than between particles in different chains, because of the character of the dipolar interaction. It is therefore somewhat of a surprise to find that the energy per particle does not increase monotonically but peaks at a gap of $\eta \approx 0.16$ (in units of the particle diameter) and then turns down. At $\eta = \sqrt{2} - 1 \approx 0.41$, the binding energy per particle is exactly the same as in the no gap case, namely, 2.961921952 (For convenience we express the energy in units of the dipole moment squared divided by the particle diameter cubed). This is related to the fact that the $\eta = \sqrt{2} - 1$ structure is in fact also an fcc structure, but with a different orientation. At this value of η , particles which were not in contact for $\eta < \sqrt{2} - 1$ now become in contact. Because of this, any further increase of η does not reduce the energy per particle.

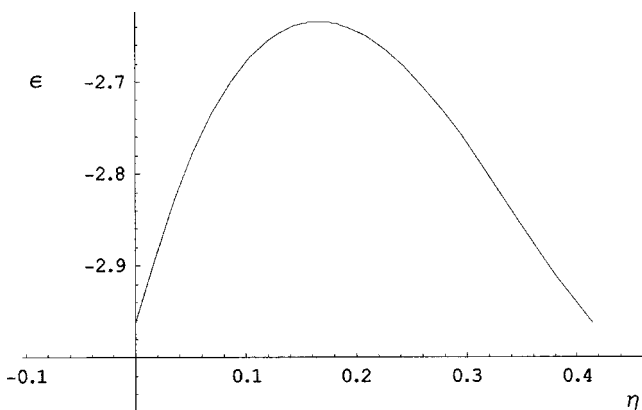


FIG. 2. The energy per particle for the fcc structure with gap η between spherical particles.

Given that the binding energy per particle can decrease with increasing gap, yet no structures formed from chains with gaps have been examined previously, a study of other structures with gaps might be useful. We looked specifically at the following structures with gaps: hcp, bct, and honeycomb. In the latter case, the structure is a two-dimensional honeycomb pattern of chains such that each chain has three nearest neighbor chains, each of which is shifted vertically by half the distance between successive particles in a chain. We found that in none of these three cases was the binding energy greater than in the bct structure formed from chains with no gaps. In particular, the honeycomb structure had a maximum binding energy of 2.984 per particle with a gap of 0.5993 which was larger than fcc but less than the bct energy per particle of 3.050099872. Thus the energy of this structure lies in between that of bct and fcc, which suggests that studies which have compared the bct to fcc structures including the effects of higher multipoles [4] or boundaries [10,11] should be expanded to include the honeycomb structure. We also carried out importance sampling on the space of configurations which can be formed out of chains, with and without gaps, as described in the next section.

III. SIMULATED ANNEALING IN GEOMETRY SPACE

We now turn to the main results of this study, which involve carrying out simulated annealing in the space of all candidate ground state structures for an *infinite* dipolar crystal. We make the modest requirement that these crystals must be able to be formed out of uniform chains of particles parallel to the dipole direction. While the chains can be allowed to have different spacings (by “spacing” we mean the distance between the *centers* of successive particles in a chain, whereas “gaps” refers to the distance between the closest boundaries of successive particles in a chain), it is easy to show that if the chain spacings are not commensurate, there can be no attractive interaction between the chains. This is seen by examining the interaction energy between a chain with spacing ω and a particle which is a lateral distance ρ away and shifted by a vertical distance s with respect to one of the particles of the chain [1,2,19],

$$E = \frac{16\pi^2}{\omega^3} \sum_{n=1}^{\infty} n^2 K_0(2n\pi\rho/\omega) \cos(2\pi ns/\omega). \quad (1)$$

Forming a second chain by replacing s by $s + l\omega'$ and summing over all integers l , one sees that the phase factors will cancel out unless the spacings ω and ω' are commensurate. Thus, to minimize the energy per particle, we can assume the chains have commensurate spacings.

But if the spacings are commensurate, they may as well be chosen as equal, as seen from the example of Fig. 3. The two chains on the left of the figure have spacings 2 and 1 in units of the particle diameter, but it is equivalent to view them as 3 chains, each with the spacing 2.

We now discuss the algorithm used to carry out simulated annealing in the space of crystals made out of infinite parallel chains, each with the same spacing. Any such configuration can be constructed from a parallelogram unit cell which is filled with nonoverlapping chains at various locations within the cell, and with various relative vertical shifts. The

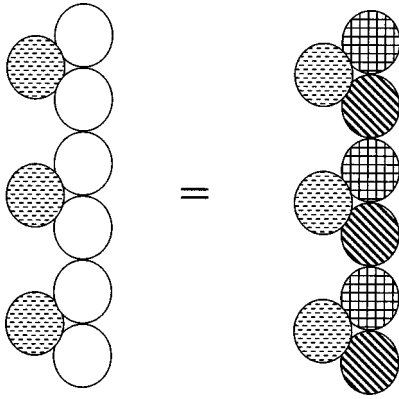


FIG. 3. An example of how chains with commensurate but distinct particle spacings can be relabeled as chains with the same spacing.

unit cell is then translated by the vectors which form its edges in order to generate an infinite crystal. Figure 4 shows a possible unit cell which contains three chains. The parameters which must be varied in the simulated annealing algorithm are $a, b, \theta, x_1, y_1, x_2, y_2, x_3, y_3$, the vertical shifts of the chains relative to some reference plane, s_1, s_2, s_3 , and the particle spacing ω . Actually using s_1, s_2 , and s_3 rather than the two relative vertical shifts is redundant, though quite acceptable. The energy per particle must be repeatedly calculated as a function of all these parameters, as this quantity is minimized by the procedure of simulated annealing. This is done separately for each possible number of chains per unit cell, and so one is forced to stop at some number of chains per unit cell depending on computational limitations.

The interaction energy between each pair of chains was calculated efficiently and accurately by using the Euler-Maclaurin formula to approximate the infinite double sum as a finite sum plus remainder terms. This approximation was tailored to ensure that the error for the interaction energy per particle between two chains was of order the machine precision, or about 10^{-15} . Since the interaction energy between chains falls off exponentially with distance, we were able to cut off the sum over pairs of chains at a certain distance. This distance was chosen so as to include all terms which contributed to the interaction energy by an amount of order the machine precision or greater. Finally the internal energy per particle for each chain is simply given by $-2\zeta(3)/\omega^3 = -2.40411380631919/\omega^3$.

In any algorithm in which a minimization process takes

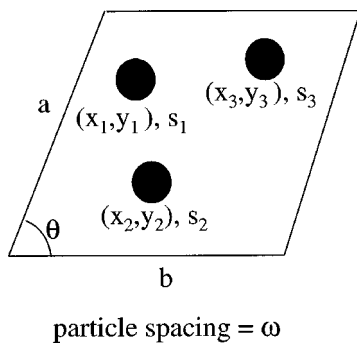


FIG. 4. A possible unit cell with 3 chains, showing the parameters which are varied in the simulated annealing work.

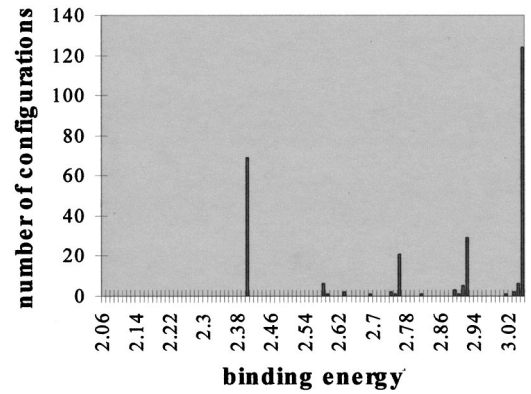


FIG. 5. A histogram of binding energies from 275 simulated annealing runs for structures containing two chains per unit cell.

place, the system is likely to get “stuck” in local minima. This was quite a serious problem in our simulations, in part because of the geometrical constraints which restricted the particles from overlapping with each other or from crossing the boundary of the unit cell.

IV. RESULTS AND SUMMARY

For practical reasons, most of our work was done with two chains per unit cell. These configurations include bct, fcc, honeycomb, and infinitely many others. Figure 5 shows a histogram of the results of 275 runs, each using a different set of random numbers for the simulated annealing. Although the initial configurations were the same for each run, the initial temperature was taken so large that the configurations were quickly randomized. From these runs it was found that nearly half of the configurations ended up bct, or very close to bct, and no other configuration was found with a larger binding energy per particle. Certain other states were metastable with respect to our algorithm, including honeycomb with no gap ($-E \approx 2.92$), wall-like structures ($-E \approx 2.76$), and two chains with spacing 2 superimposing to form one chain with spacing 1 per unit cell ($-E \approx 2.40$). In the last case, since the cell size was variable, and the widely separated chains with the same shift repelled one another, the cell size moved off toward the maximum cutoff value allowed in the program.

In the case of three chains per unit cell, structures such as bct, hcp, fcc, and honeycomb are not allowed, because these require half the chains per unit cell shifted by a particle radius with respect to the other half. Correspondingly, the result of all our three-chain simulations were wall-like structures of various types. In other words the chains of different cells joined with each other to form quasi-two-dimensional objects, with spaces between each of these walls. None of the structures had a binding energy larger than bct. See Fig. 6.

In the case of more than three chains per unit cell, practical difficulties set in because of the large number of geometrical constraints necessary to prevent overlaps. 36 runs were carried out in the range of 4 to 8 chains per unit cell, and none had a binding energy larger than bct. However, the bct structure itself only appeared only two times, indicating that more runs or longer runs would be necessary in order to more conclusively show that bct is the ground state for the dipolar system.

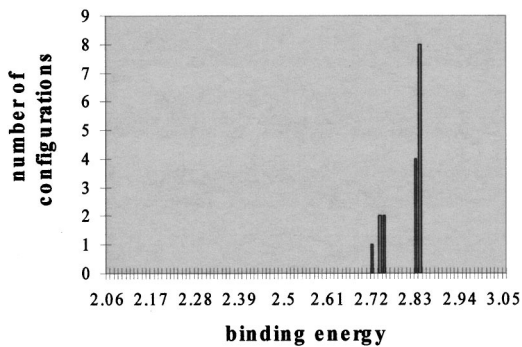


FIG. 6. A histogram of binding energies from 17 simulated annealing runs for structures containing three chains per unit cell.

In summary, we have examined various regular structures formed out of chains with gaps and discovered that in some cases gaps reduce the energy of the dipolar lattice. We found that a honeycomb lattice with a gap of 0.5993 has an energy of -2.984 per particle, closer to the value for bct (-3.050) than any other state previously studied, including fcc

(-2.962). We used a method which allows one to carry out simulated annealing in geometry space. This basic method may have applicability in a wide variety of situations in which the ground state crystalline structure is unknown. In the dipolar example considered here, the lattices considered were actually two-dimensional with a fixed number of chains per unit cell, but this need not be the case. After numerous independent simulated annealing runs with two chains per unit cell and a smaller number of runs with more chains per unit cell, we have obtained the strongest theoretical evidence to date that the ground state structure of a system of dipolar particles with hard sphere repulsions is body-centered tetragonal.

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- [1] R. Tao and J. M. Sun, Phys. Rev. Lett. **67**, 398 (1991).
 - [2] R. Tao and J. M. Sun, Phys. Rev. A **44**, R6181 (1991).
 - [3] T. Chen, R. N. Zitter, and R. Tao, Phys. Rev. Lett. **68**, 2555 (1992).
 - [4] R. Friedberg and Y.-K. Yu, Phys. Rev. B **46**, 6582 (1992).
 - [5] L. C. Davis, Phys. Rev. A **46**, R719 (1992).
 - [6] H. J. H. Clercx and G. Bossis, Phys. Rev. E **48**, 2721 (1993).
 - [7] R. Tao and Q. Jiang, Phys. Rev. Lett. **73**, 205 (1994).
 - [8] G. L. Gulley and R. Tao, Phys. Rev. E **56**, 4328 (1997).
 - [9] W. Y. Tam, G. H. Yi, W. Wen, H. Ma, M. M. Y. Loy, and P. Sheng, Phys. Rev. Lett. **78**, 2987 (1997).
 - [10] L. Zhou, W. Wen, and P. Sheng, Phys. Rev. Lett. **81**, 1509 (1998).
 - [11] M. Gross, Phys. Rev. E **58**, 6124 (1998).
 - [12] H. Zhao, Z. Liu, Y. Liu, and J. Shen, Phys. Lett. A **239**, 393 (1998).
 - [13] R. Tao and Q. Jiang, Phys. Rev. E **57**, 5761 (1998).
 - [14] A. Lukkarinen and K. Kaski, Int. J. Mod. Phys. C **9**, 591 (1998).
 - [15] J. E. Martin, R. A. Anderson, and C. P. Tigges, J. Chem. Phys. **9**, 3765 (1998).
 - [16] C. Djurberg *et al.*, Phys. Rev. Lett. **79**, 5154 (1997).
 - [17] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976), Chap. 7.
 - [18] W. M. Itano *et al.*, Science **279**, 686 (1998).
 - [19] T. C. Halsey and W. Toor, Phys. Rev. Lett. **65**, 2820 (1990) J. Stat. Phys. **61**, 1257 (1990).