Nonperiodic Solid Phase in a Two-Dimensional Hard-Dimer System

K. W. Wojciechowski,[1] D. Frenkel,[2] and A. C. Brańka[1]

[1]*Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17/19, 60-179 Poznań, Poland*

[2]*Foundation for Fundamental Research on Matter (FOM)–Institute for Atomic and Molecular Physics, P.O. Box 41883, 1009 DB Amsterdam, The Netherlands*

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We report Monte Carlo simulations of a system of two-dimensional, hard, homonuclear dimers. The equation of state and the Gibbs free energy were computed for the fluid phase and several crystalline and noncrystalline (aperiodic) solid structures. We observe that the differences in Gibbs free energy between the various solid structures are much less than the contribution to the entropy due to degeneracy of the "ground state" of the aperiodic solid. Hence, the thermodynamically stable solid structure of the system corresponds to an *aperiodic* arrangement of the molecular centers of mass and orientations. The melting point determined for this aperiodic solid is located within the observed narrow hysteresis region.

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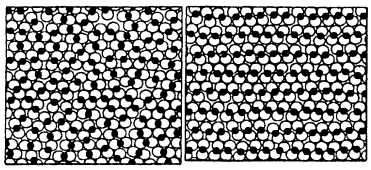
Most atomic and molecular substances that occur in nature form thermodynamically stable crystalline phases at low temperatures. The most characteristic feature of crystals is their periodicity. For a long time, it was assumed that all thermodynamically stable solids have periodic lattices. In other words, nonperiodic solids were considered as metastable. In recent years, however, several theoretical and experimental studies have indicated the possibility that *thermodynamically stable aperiodic solid phases* exist. Examples are incommensurate crystals,[1] quasicrystals,[2] and "turbulent crystals."[3]

There are at least three distinct microscopic mechanisms that may lead to an aperiodic solid. The first, usually relevant for incommensurate crystals, assumes competing interactions, e.g., between nearest and next-nearest neighbors.[1] The second mechanism, recently suggested by Narasimhan and Jarić, assumes that it may be possible that the intermolecular interaction in a dense system is such that the energy of the system is minimal in an aperiodic state.[4] The third mechanism assumes that entropy is the driving force.[5] In particular, it is assumed that the configurational entropy may exceed the energy contribution to the free energy or the excluded-volume effects. (The latter two contributions usually favor periodic structures.) As a result a thermodynamically stable disordered structure may occur.[6] According to this idea, candidates to form aperiodic solids are systems with a large configurational degeneracy of the ground state or states close to it.[7] Certain molecular models exhibit such a property.[8]

The simplest molecule in nature is a homonuclear diatomic molecule. In the crudest approximation, in which atoms can be thought of as hard spheres, the homonuclear diatomic molecule can be represented by a hard dumbbell, consisting of two fused hard spheres of the same diameter σ (from now on we choose σ as our unit of length) and with centers at distance $d=d^*\sigma$ (d^* plays the role of an anisotropy parameter). The hard dumbbell is the simplest hard nonconvex body.[9] However, its equation of state (EOS) and structural properties are not known quantitatively except for the (low-density) fluid phase, both in three and in two dimensions (2D).[10] A hard dimer is a special case of the hard dumbbell with the spheres just touching each other, i.e., with $d^*=1$. It is easy to verify that hard homonuclear dimers (HHDs) have a large configurational degeneracy at close packing.[11] In the case of a 2D system of HHDs, which is the subject of the present work, it has been shown that the degeneracy entropy per particle at close packing is equal to $k_B \ln 2.356\ldots \simeq 0.857 k_B$.[12] At lower densities this entropy competes with the excluded-volume effects (vibrational entropy). The high degeneracy entropy of the 2D HHD system follows from the possibility of arranging the disks forming dimers into a perfect triangular lattice at close packing; the molecular mass centers are then distributed on a Kagomé lattice.[8] At lower densities, for typical aperiodic structures of the 2D HHDs, like that in Fig. 1(a), the distribution of the molecular centers of mass is expected to preserve the symmetry of the Kagomé lattice. In contrast, the free energy of some of the periodic structures, e.g., that in Fig. 1(b), may be lowered by breaking the symmetry. It is not obvious *a priori* what solid structure is the more stable one at



(a) (b)

FIG. 1. Typical configurations of $N=112$ hard dimers: (a) in the DC phase ($p^*=9.0$) and (b) in the HB crystal ($p^*=9.0$). Dimer centers are marked by black dots.

lower densities. Mechanical simulations[13] and a theoretical study based on the free-volume approximation[8] suggested that the degeneracy entropy prevails, and in the solid state the molecular mass centers and orientations of the 2D HHDs do not show any periodicity; this aperiodic phase will be further referred to as a disordered (or degenerate) crystal (DC).

As both the mechanical simulations and the free-volume theory are only approximations we performed computer simulations to test the thermodynamic stability of the DC phase. As will be shown below, we do indeed find that the DC phase is stable. To our knowledge, this is the first example of a continuous homomolecular model with an aperiodic distribution of the molecular mass centers and orientations.

The EOS of the 2D HHDs was simulated using the Monte Carlo (MC) method in the *NPT* and *NVT* ensembles. The details of the simulations will be described elsewhere.[14]

Crystalline structures were represented by lattices which at close packing contain one or two molecules in the unit cell. There exist only four such lattices:[14] an oblique Bravais lattice and three lattices with two molecules per unit cell. We restrict our discussion here to the herringbone (HB) structure, Fig. 1(b), as the EOS and free energy of the HB structure differed only a little from that of any of the other three crystalline lattices that were studied. In fact, the thermodynamic properties of any specific realization of the aperiodic solid [for an example, see Fig. 1(a)] were also quite close to those of the solid with the HB structure.

Of course, the *structure* of the other ordered solids is very different from that of the HB lattice. These structural aspects will be discussed elsewhere.[14]

The simulations of the crystalline and the aperiodic solids were started at high pressures. The pressure was then gradually reduced in subsequent runs down to the point where the solid melted spontaneously (these "melting" pressures differed slightly from one solid structure to the next but they were never less than $p^* \equiv p\sigma^2/k_BT = 8.25$, where p is the pressure, T is the temperature, and k_B is Boltzmann's constant). Some aperiodic structures were also generated by freezing the fluid. In these cases the pressure was increased in the subsequent runs. No self-diffusion was observed in solids during the simulations and the molecular arrangements were preserved, except at melting. Hence, in order to sample different realizations of the DC phase, a few series of runs were performed in which, except for standard motions of single molecules, certain groups of molecules were moved cooperatively[15] (the idea of these additional motions is shown in Fig. 2).

The *NPT* simulations of the fluid were performed using a square periodic box. In subsequent runs the pressure was increased from $p^* = 0.5$ up to the spontaneous freezing point of the sample, at $p^* = 8.75$.

In Fig. 3 the EOS branches corresponding to the HB crystal, the DC phase, and the fluid are plotted. As can

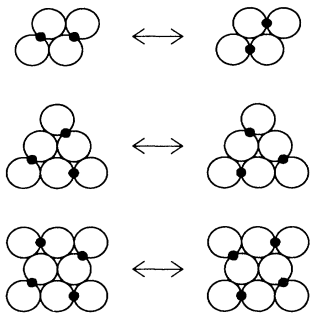


FIG. 2. Schematic changes of the molecular mass centers and orientations for the cooperative motions mentioned in text. It can be shown, see Ref. 14, that (i) any close-packed structure of the 2D HHDs has to contain at least one kind of the presented clusters (obviously, different orientations are possible), and (ii) any close-packed structure of the 2D HHDs in the thermodynamic limit can be obtained from the closely packed Bravais lattice of the 2D HHDs by such motions only (obviously, motions of such clusters have to be allowed also at different orientations).

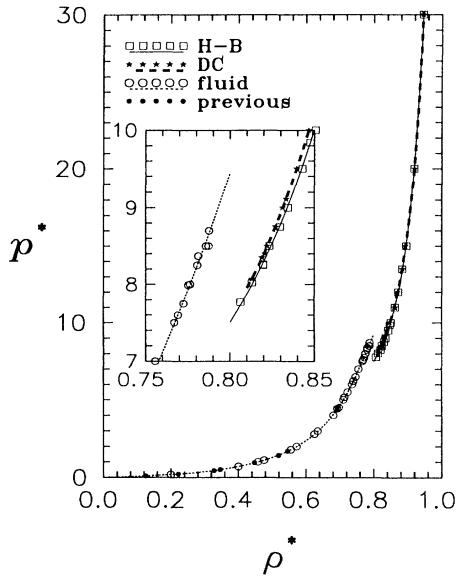


FIG. 3. The EOS for the three structures discussed in the text: the HB crystal (squares), the DC phase (pentagonal stars), and the fluid [circles represent our data, solid dots represent the data of Refs. 10(b)–10(d)]. A few points in the solid branches for which $p^* < 8.25$ were obtained in the *NVT* ensemble. The lines are drawn to guide the eye; ρ^* is the relative density (the ratio of the density $\rho \equiv N/V$ to its value at close packing $\rho_{cp} = 3^{-1/2}\sigma^{-2}$; N and V are, respectively, the number of molecules and the area of the system).

be noted, close to melting the densities of the DC phase are slightly lower than those of the HB crystal at the same pressures; at higher pressures the corresponding densities are the same, to within the simulation error.

In order to determine the stability of the solid structures and to locate the melting transition, we calculated the free energies per particle of the fluid, f_{fluid}, and solid, f_{solid}, respectively. For the fluid this was done by integrating numerically the fluid branch of the EOS. The free energy of the solid structures considered was computed using the Einstein crystal method.[16] From the free energy and the EOS one can immediately obtain the Gibbs free energy:

$$g = f + pv . \quad (1)$$

The Gibbs free energies per particle of the HB crystal, a typical aperiodic solid structure,[17] and the fluid, obtained at the two pressures bracketing the melting hysteresis region, are shown in Table I. As can be seen, the values for the solids differ only slightly (the HB crystal appears to be slightly more stable than the average aperiodic structure). All these values are considerably higher than the corresponding values of the fluid. The Gibbs free energy per particle of the DC phase, g_{DC}, is, however, lower than the average value, $g_{\text{DC}}^{(\text{average})}$, of individual realizations of this phase because of the degeneracy entropy per particle mentioned above: $s_{\text{DC}} \simeq 0.857 k_B$. Taking this into account, we located the melting transition at $p^* = 8.6(2)$ corresponding to $\rho^*_{\text{solid}} = 0.824(3)$ and $\rho^*_{\text{liquid}} = 0.787(4)$, i.e., inside the observed hysteresis region.

The analysis of the solid branches of the EOS shows that the Gibbs free energy of the DC phase is lower than that of the HB crystal over the entire pressure range that we studied. In Ref. 14 it is argued, on basis of a free-volume argument, that the DC phase is also more stable than the ordered crystalline structures near close packing. Hence we expect that the DC phase is thermodynamically stable over the whole range of the densities corresponding to the 2D HHD solid. Thus, the 2D HHDs do *not* form a thermodynamically stable, periodic crystal at any density.

The present work constitutes a starting point for a more extensive study of the complete phase diagram of general 2D hard dumbbells ($0 \leq d^* \leq 1$). The latter study will be the subject of forthcoming papers.[14,18]

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TABLE I. The Gibbs free energies of the structures discussed in the text at the dimensionless presure in the hysteresis region.

p^*	g_{HB}	$g_{\text{DC}}^{(\text{average})}$	g_{fluid}	g_{DC}
8.35	21.84	21.92(2)	21.03	21.06(2)
8.7	22.57	22.66(2)	21.81	21.80(2)

[1]See, e.g., *Incommensurate Phases in Dielectrics,* edited by R. Blinc and A. P. Levanyuk (North-Holland, Amsterdam, 1986).

[2]D. Schechtman, I. Blech, G. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984); D. Levine and P. J. Steinhardt, Phys. Rev. Lett. **53**, 2477 (1984).

[3]D. Ruelle, Physica (Amsterdam) **113A**, 619 (1982).

[4]S. Narasimhan and M. V. Jarić, Phys. Rev. Lett. **62**, 454 (1989). It is not obvious, as yet, whether the quasicrystalline structures obtained in that paper are really *stable* because periodic structures with large unit cells may have lower energy.

[5]An early example of such a model is Pauling's ice model: L. Pauling, J. Am. Chem. Soc. **57**, 2680 (1935).

[6]This is a mechanism of many order-disorder phase transitions [for hard spheres see, e.g., M. Baus, J. Stat. Phys. **48**, 1129 (1987)]. The typical disordered phases are, however, either of periodic lattice of the molecular mass centers [e.g., orientationally disordered crystals: J. M. Rowe, J. J. Rush, D. G. Hinks, and S. Susman, Phys. Rev. Lett. **43**, 1158 (1979)] or—if translationally disordered—not solid (e.g., liquid crystals or liquids).

[7]Examples of strongly degenerated systems are, e.g., the low-temperature solids formed by molecules like CO, NO, etc. [E. A. Guggenheim, in *Encyclopedia of Physics,* edited by S. Flügge (Springer, Berlin, 1959)]. It should be noted, however, that the mass centers of the molecules forming these materials are arranged in (slightly disturbed, at most) periodic lattices.

[8]K. W. Wojciechowski, Phys. Lett. A **122**, 377 (1987).

[9]As nonconvex bodies are qualitatively different from the convex bodies, one can expect qualitatively new behaviors in systems composed of the first ones. An example is a negative value of the Poisson ratio in a solid phase of certain 2D model system of hard nonconvex bodies: K. W. Wojciechowski and A. C. Brańka, Phys. Rev. A **40**, 7222 (1989). One could add here that "cells" of real materials exhibiting negative values of the Poisson ratio are also nonconvex: R. Lakes, Science **235**, 1038 (1987).

[10]Results of the computer simulations of the hard dumbbells in the three dimensions are reviewed in (a) T. Boublik and I. Nezbeda, Collect. Czech. Chem. Commun. **51**, 2301 (1986). Concerning the two-dimensional case, see (b) A. Bellemans, J. Orban, and D. Van Belle, Mol. Phys. **39**, 781 (1980); (c) J. Talbot and D. J. Tildesley, J. Chem. Phys. **83**, 6419 (1985); (d) K. G. Honnel and C. K. Hall, Mol. Phys. **65**, 1281 (1988).

[11]There exist finite clusters of the same shape and different arrangements of dimers. A few pairs of such clusters are shown in Fig. 2 for the 2D case.

[12]When the continuous translations and rotations of the close-packed structure are neglected the problem reduces to complete decoration of a triangular lattice by dimers. This problem has been solved approximately by R. H. Fowler and G. S. Rushbrooke, Trans. Faraday Soc. **33**, 1272 (1937). For better estimates of the degeneracy entropy, see J. F. Nagle, Phys. Rev. **152**, 190 (1966); see also A. J. Phares and F. J. Wunderlich, J. Math. Phys. **27**, 1099 (1986).

[13]A. C. Brańka and K. W. Wojciechowski, Mol. Phys. **56**, 1419 (1985).

[14]K. W. Wojciechowski, A. C. Brańka, and D. Frenkel (unpublished).

[15]It is worthwhile to add that the trial cooperative motions, typically 20 times less frequent than the standard trial motions, allowed for observing structural changes in the solid. For example, in the presence of such motions structural transformation from a periodic crystal (for example, the HB one) to the DC phase required only a few (about five) thousand trial steps per molecule (typical Monte Carlo runs in the DC phase were 4–10 times longer).

[16]D. Frenkel and A. J. C. Ladd, J. Chem. Phys. **81**, 3188 (1984); D. Frenkel and B. M. Mulder, Mol. Phys. **55**, 1171 (1985).

[17]This free energy was computed as a mean value of the free energies obtained for a few random aperiodic solid structures of the 2D HHDs. Another possibility would be by applying the cooperative motions. In the second case, the reference state for the Einstein solid varies with "time."

[18]K. W. Wojciechowski (unpublished).