Fluid/solid transition in a hard-core system

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We prove that a system of particles in the plane, interacting only with a certain hard-core constraint, undergoes a fluid/solid phase transition.

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I. INTRODUCTION

It is generally believed that the classical statistical mechanics of particles in 3 dimensions, interacting through a strong, short-range repulsion and weak, short-range attraction, would exhibit a solid/fluid phase transition. It has not been possible to control this analytically, and this has been an important open problem for many years [1–5]. There were proofs long ago within lattice gas models of order/disorder transitions [6, 7], as well as convincing molecular dynamics and Monte Carlo simulations, showing a transition in continuum models (particles in 2 or 3 dimensions; see [8] or [9] for a review). In particular, simulations indicate such a transition even for the conceptually simple hard-sphere model in which the interaction is just a hard-core, and even in 2 dimensions, though the ordered phase may not have translational long-range order in 2 dimensions [10].

Two notable analytic proofs of a phase transition in a system of particles moving in a continuum rather than a lattice were those by Ruelle [11] and the recent paper by Lebowitz et al. [12]. The first is concerned with breaking the discrete symmetry between particle species rather than the spatial symmetry. The latter uses a long-range attraction and therefore, like the Curie-Weiss model, is more relevant to the gas/liquid transition [12].

The melting transition concerns an ordered structure breaking apart. This is often modeled as a competition between the influences of energy E and of entropy S on the distribution over states that minimizes the (Helmholtz) free energy $F := E - TS$ [13]. But this competition cannot be the mechanism for a system with only hard-core forces since the energy is then just kinetic and can be integrated out; for such a model the mechanism must be purely geometric, a competition between random and ordered configurations as the dominant contribution to the entropy.

There have been various approaches to determine which close-packed crystal would be most stable at high density for the hard-sphere model, by expansion about close packing [14, 15], and by simulations [16, 17], but little has been done to show analytically that the high density phase is ordered in this model.

One attempt to give a geometric mechanism for the hard-sphere or hard-disk transitions is through the geometric constraint, at high density, which prevents neighboring parallel planes of molecules from sliding past one another [9]. We are therefore introducing a new hard-core model, closely related to the hard-disk model, specifically in an attempt to elucidate in what way this mechanism (roughly related to resistance to shear) may be relevant to the fluid/solid transition in hard-core models.

In this new 2-dimensional model we replace the round disk by a "zipper molecule", a solid unit hexagon with a fringe of projections and holes on its edges (see Figure 1). This is really a family of models, in which a parameter ρ controls the size and shape of the fringe elements (see Figure 2); our results hold for any fixed, sufficiently small value of ρ. As in the hard-disk model, our model is defined by allowing all arrangements of nonoverlapping molecules in the plane, with no other interaction.

The geometry is such that a molecule can accept the holes and projections of neighboring molecules in one of two modes, "tightly linked" and "loosely linked", the latter when the projections are less than half way into the holes of the neighboring molecule, as in Figure 1. Any tight link geometrically forces all projections and holes on the corresponding edges to be used, and any motion of one molecule forces a like motion of the other. Loose links on an edge do not require all projections on that edge to be used, but if three molecules are each pairwise linked (as in Figure 1) then indeed all projections/holes on the corresponding edges are used. Loose links allow small relative motions.

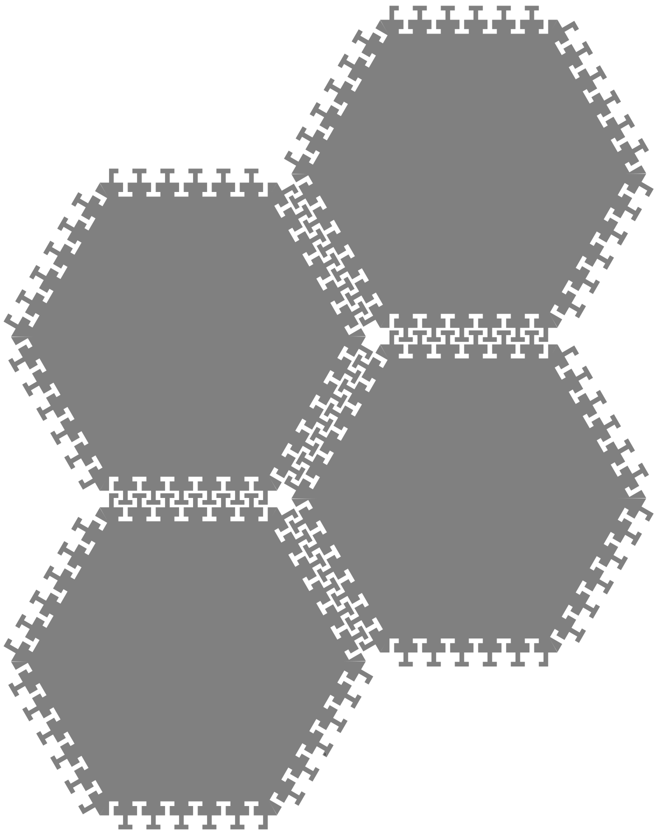

FIG. 1: Four zipper molecules, loosely linked together.

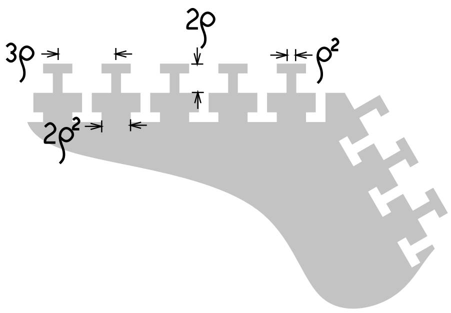

FIG. 2: Blow-up of a corner of a zipper molecule.

Thus the geometry of the molecules allows three well-defined degrees of relative separation between neighboring pairs: tightly linked, loosely linked, and unlinked. We know from simulations for the hard-disk model that there is an interval of densities that represents coexistence of a fluid and a solid phase. We expect the same to hold in our model, though our method of proof does not allow us to examine this intermediate-density region. We introduce an order parameter, which we expect to sense the presence of a solid phase, and show it is identically zero for a range of very low densities, and is nonzero for a range of very high densities, and conclude in the usual way that there must be a transition, without being able to examine the behavior in the intermediate-density regime. As noted above, the order parameter is chosen for its intuitive relation to the degree of resistance to shear. We call our highest density phase "solid" by analogy with the hard-disk model; indeed, from the geometry it is easier for our zipper molecule to cohere in a solid phase than is the case for round disks. Furthermore, we expect that the order parameter which we prove to control the transition in this new model could, with some modification, be made to work in the hard-disk model, though we are far from being able to demonstrate this.

The infinite-volume canonical ensemble that we use is defined as the limit of canonical distributions in an expanding sequence of finite boxes with periodic boundary conditions. In a finite box our canonical probability distribution (restricted to physical space variables; we integrate out the momentum variables, as usual) is uniform on the set of all arrangements of molecules with fixed density d', where $d' \to d$ in the infinite volume limit. The only restriction on arrangements is that the molecules do not overlap, which defines our model. Each molecule has 3 degrees of freedom, two for translation and one for rotation, so a collection of N molecules can be associated with a point in a bounded subset of $3N$ dimensions. This representation is used to define the uniform distribution on the set of all ways to distribute N non-overlapping molecules in the box. However, as noted above, when molecules are tightly linked they lose degrees of freedom. So packings at the same density (that is, the same number of molecules) can be represented by points in spaces of different numbers of dimensions because one uses only 3 coordinates for each cluster of tightly-linked molecules. The set of packings which can be represented in a space of dimension lower than other packings at the same density must be accorded zero probability; this would be the case, for instance, if the model were considered the limit of models in which neighboring molecules could not fit together so perfectly, or of models with softened core. Thus a feature of our model is that the canonical distribution for a finite box at given density is supported only on those arrangements of molecules with the largest possible number of degrees of freedom. This turns out to be very useful to the analysis.

II. RESULTS.

We assume the molecule has area 1 so that number density coincides with packing density. A molecule will be called "fully linked" if all its projections are linked (either tightly or loosely) to neighboring molecules. Molecules not linked to other molecules are called "free", and molecules that are neither fully linked nor free are called "partially linked". Each fully linked molecule is contained in a unique maximal connected set of such molecules (connected by links).

It is easy to see that there exist $0 < d_3 < d_2 < d_1 < 1$ such that the following hold: A configuration of fully linked molecules in which all links are loose (as in Figure 1) has density $d \in [d_2, d_1]$; and the density d of any large collection of free molecules satisfies $d \leq d_3$. We assume d_1 is the highest possible density for loose-linked molecules.

Our main result is the following.

Theorem. Let $\mathbf{P}(d)$ be the probability, given by the infinite-volume canonical ensemble at density d, that the origin (or any given point) is inside a molecule that is linked to infinitely many others through full links. Then if the parameter ρ is small enough there is some $d_4 > 0$ such that $\mathbf{P}(d) = 0$ if $d \in (0, d_4)$, while $\mathbf{P}(d) > 0$ for $d \in (d_1, 1)$.

Corollary. The model exhibits a fluid/solid phase transition.

Outline of the proof of the Theorem. We begin with high densities. If we fix the density d above d_1 then some tight links must be used to achieve the density d. Since the distribution is supported on arrangements with the highest number of degrees of freedom, it uses the fewest number of tight links. Intuitively, this forces the tightly linked molecules to form only one component and the loosely linked molecules to form only one component.

A key to our proof that this is correct is to work directly with (translation- and rotation-) invariant probability measures on configurations in the whole plane, rather than in finite boxes. For each packing we decompose the plane into the Voronoi cells of the centers of the molecules and concentrate on the connected components of cells associated to tightly linked molecules. Our molecules have the property that two of them that are not tightly linked have centers at distance at least $2r + 2\rho$, where r is the in-radius of the hexagon. At the molecules' densest packing without tight links the disks of radius $r + \rho$ that are concentric with the molecules form a hexagonal close packing so there is a unique invariant measure λ_1 on packings of molecules whose density is the highest possible among those without tight links. This measure λ_1 has a number of important optimization properties the proofs of which are much too long to present here and will be published elsewhere. The first (which does not have a simple analogue for 3-dimensional models) is that by choosing ρ to be sufficiently small we obtain that the area of the Voronoi cell of the center of a molecule without tight links is at least $1/d_1$, with equality if and only if its neighbors are arranged as in λ_1 [18].

Intuitively, packings of molecules that use molecules that are not fully linked will waste space, which will force more tight links than necessary. Making this intuition rigorous is the primary difficulty we had to face. The first ingredient in its treatment involves the following notation. If C is a finite tight-linked component with $j(C)$ molecules let $p(C)$ denote the perimeter of the union of hexagons corresponding to these molecules. Also, let $a(C)$ denote the area of the union of the Voronoi cells of the centers of the molecules in C. Let $p_1 := p(C)$ when $j(C) = 1$. Although it is not hard to show, a key estimate is that for small ρ there exist $\epsilon > 0$ and $\delta \in (0, \epsilon/100)$ such that $d_1 = 1/(1 + \epsilon p_1 + \delta)$ and $a(C) \geq j(C) + \epsilon p(C)$ for all finite C.

The rest of the proof requires a bit more notation. The idea is to replace quantities in finite boxes, such as areas and degrees of freedom, by average quantities for infinite-volume measures. If P is a packing with a molecule m containing the origin let $j(P)$ be the number of molecules in the tightly linked connected cluster containing m and $f(P) := 3/j(P)$, which is the number of degrees of freedom per molecule for these molecules. Let $j(P) := f(P) := 0$ if the origin is not contained in a molecule. Let λ_0 be the unique invariant measure on tilings by the molecules (tilings are configurations in which all molecules are fully tight-linked). Let ν be an invariant measure giving average density $d > d_1$. With this notation we have been able to prove the following concerning the measure λ_1.

If we put $s := (1-d)/(1-d_1) \in [0,1]$ and $\mu := s\lambda_1 + (1-s)\lambda_0$, then the average density with respect to μ equals that with respect to ν. If ρ is sufficiently small then one can use the bounds above relating areas and perimeters to show that $\int f\, d\mu \geq \int f\, d\nu$, with equality only if $j(P) \in \{0, 1, \infty\}$ for ν-almost every P, and only if, when $j(P) = 1$, the area of the Voronoi cell of the molecule containing the origin equals $1/d_1$. It follows that if $\int f\, d\mu = \int f\, d\nu$, then $\nu(j(P) = 1) = s$ and thus, since the density of any P with $j(P) = \infty$ is strictly less than 1 if P is not a tiling, $\nu = \mu$.

In particular, if ν is an infinite-volume canonical ensemble then since ν maximizes the number of degrees of freedom per molecule we have from the preceding paragraph that $\int f\, d\mu = \int f\, d\nu$, whence $\nu = \mu$. This proves that there is exactly one thermodynamic limit at density d, namely μ. In particular $\mathbf{P}(d) > 0$.

The case of low density is straightforward. For low density we can compare a block of fully linked molecules with a geometrically similar collection of free molecules in which each has twice the room to move as do the linked molecules. (This argument ignores the presence of molecules near the linked molecules; this is permissible at small enough d_4 for this crude estimate.) Therefore at low density the probability of a block of M fully linked molecules is less than $(1/3)^M$, which goes to 0 as $M \to \infty$. (We are simply showing that at low density the canonical ensemble looks like a gas of independent molecules.) This proves the desired result for low density, and thus the theorem. □

Proof of the Corollary. We have shown that at density d the probability that the origin is in an infinite fully linked block of molecules is zero for $d \in (0, d_4)$, while it is positive for $d \in (d_1, 1)$. This implies that $\mathbf{P}(d)$ is not analytic in d, which we take as the hallmark of the transition. □

By analogy with the simulations on hard-sphere and hard-disk models [8, 9], we expect that the interval of d in which $\mathbf{P}(d) > 0$ continues below d_1, which we would interpret as implying that the melting transition in this model occurs at density below d_1, but we do not know how to prove this.

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