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 $\mathbb{R}^3$ 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], [2],[3],[4],[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 $\mathbb{R}^3$; see [8] 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 be crystalline in 2 dimensions [9].

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 [10] and the recent paper by Mazel et al. [11]. A weakness of the first is that it is more concerned with breaking the discrete symmetry between particle species than the spatial symmetry. A weakness of the latter is that it uses a long-range attraction and therefore, like the simpler Curie-Weiss model, it is more relevant to the gas/liquid transition [11].

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 configurations which minimizes the (Helmholtz) free energy $F := E - TS$ [12]. 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.

One attempt to give a geometric mechanism for an order/disorder transition is through "orientational order" in the two dimensional hard-disk model, based on the supposed difficulty or cost of rotating a pair of neighboring disks past other neighbors [9]. Assuming this mechanism is significant, a geometric proof of a transition should be simpler if the relative orientation between neighboring pairs were constrained, as this would make it easier to detect and quantify long range order.

In this paper we simply change the shape of the disks in the hard-disk model, introducing three well-defined levels of constraint for the relative orientation between neighboring pairs and allowing a proof to go through. We call the shape a molecule, and it is basically a solid unit hexagon, but with a fringe of projections and holes on its edges (see Figure 1) which can accept the holes and projections of neighboring molecules in one of two modes, "tightly linked" and "loosely linked", the latter when the projection is less than half way into the neighboring molecule. (See Figure 2.)

We assume the molecule has area 1, so that number density coincides with packing density. A molecule F will be called "fully linked" if all its projections and holes are linked (either tightly or loosely) to neighboring molecules. Molecules not linked to other molecules are called "free", and molecules which 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). For each packing we decompose the container into the Voronoi cells of the molecules and concentrate on the connected components of cells associated to fully linked molecules.

It is easy to see that there exist $1 > d_1 > d_2 > d_3 > 0$ such that the following hold: a large region of fully linked

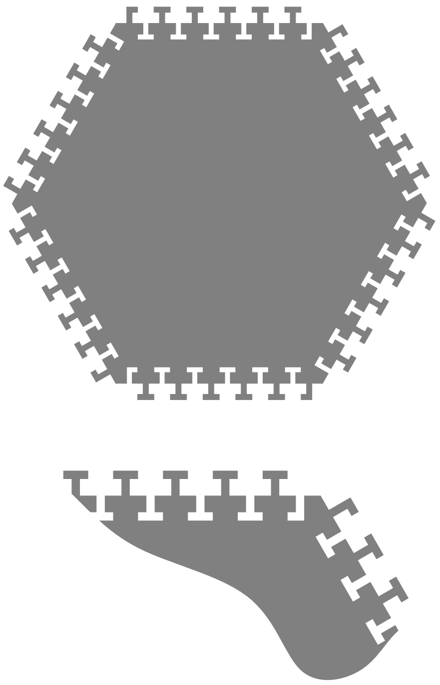

FIG. 1: The “zipper” molecule, including blow-up of a corner.

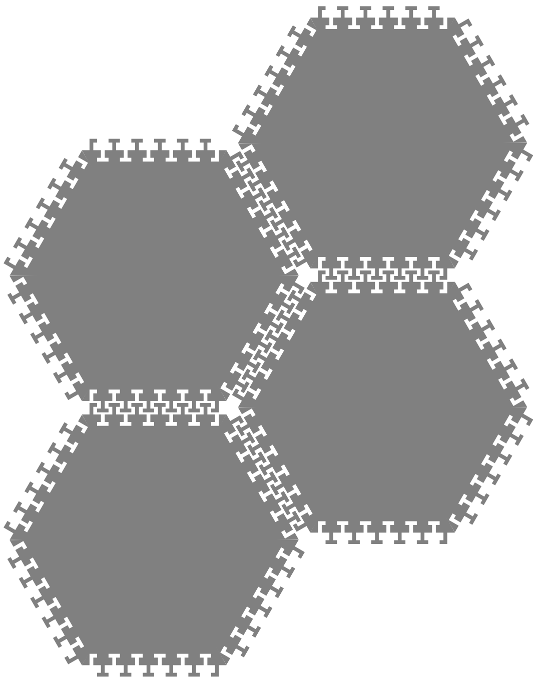

FIG. 2: Loose linked molecules.

molecules in which all links are loose 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 smallest possible upper limit for the corresponding interval.

We are concerned with the infinite-volume canonical ensemble defined as the limit of canonical distributions in an expanding sequence of finite boxes with periodic boundary conditions. In the 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 limit). Among those packings of a given box with fixed density, sets of configurations in which the molecules form fewer tightly-linked components live in a lower-dimensional subspace than those with more, and by any natural approach would have to be accorded zero relative 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 key feature of our model is that the canonical distribution for a finite box at given density is supported on those arrangements of molecules with the largest number of degrees of freedom.

II. RESULTS.

Our main result is the following.

Theorem. Let $P(d)$ be the probability, given by the infinite volume canonical ensemble at density d, that the origin (or any given point) is inside an infinite fully-linked cluster. Then there is some $d_4 > 0$ such that $P(d) = 0$ if $d \in (0, d_4)$, while $P(d) > 0$ for $d \in (d_1, 1)$.

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

Outline of proof of Theorem. We begin with high densities. We shall work directly with invariant measures on configurations in the whole plane, rather than in finite boxes. 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 inradius and 2ρ is the fringe height. At the molecules' densest packing without tight links, the disks of radius $r + \rho$ concentric with the molecules form a hexagonal close packing, whence there is a unique invariant measure λ_1 on packings of molecules whose density is the highest possible out of those without tight links. This measure λ_1 has a number of important optimization properties, the detailed proofs of which will be published elsewhere. First, by choosing ρ to be sufficiently small, we can assume 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. To express the other properties, we need some more notation.

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. Let ν be an invariant measure giving average density $d > d_1$. 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 $\int f\, d\mu \geq \int f\, d\nu$, 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 $\nu = \mu$.

This implies that the thermodynamic limit distribution is μ. In particular, $P(d) = 1$.

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 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 Corollary. We have shown that at density d the probability that the origin is near 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 $P(d)$ 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 [7] we expect that the interval of d in which $P(d) > 0$ 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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