Role of Rigidity in the Fluid-Solid Transition

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We examine the fluid-solid transition for a hard-disk system. By counting the near neighbors in the average configurations of a grand-canonical Monte Carlo simulation, this enables us to relate the thermodynamical transition with the rigidity theory, since we find that the coordination number in the fluid-solid transition is close to the coordination number predicted by a mean field rigidity theory, due to dynamical jamming of particles, where the contact region between disks is the radial ring outside a disk with a maximum allowed coordination number that is not bigger than six . Using these ideas, we were able to produce a continuous glasslike transition when nucleation of rigidity is suppressed.

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Although the fluid-solid transition has been studied for many years, it is surprising that even for the simplest systems, like the hard-disk (HD) and sphere models, there are still many unsolved questions [1,2]. For example, it has not yet been determined for the HD system whether the freezing transition is a simple first-order phase change, whether a single higher order transition is involved [1], or whether hexatic domains appear before the transition [3,4]. The simplicity of the HD and sphere models provided the frame for the development of very important theories, namely, the integral equations (like the Ornstein-Zernike) and thermodynamical perturbation theories [5,6], and also the earlier computer simulations on fluids [7] and experimental models [8]. Because of the importance of these simple systems to a wide variety of related applications in the physical and biological sciences (like colloids and biological membranes [9]) and to the development of new theories, many recent studies have been making interesting progress [10]. However, there are some obscure aspects which have not been solved to date, like the complete description of a glass transition in this simple system [11] or the packing of hard-disk and sphere models, for which even the concept of a random close packed structure, considered as the paradigm of amorphous models, has been put in doubt very recently [12], and the concept of *jammed state* has arisen [12]. A system is in a jammed state if all the particles are jammed, in the sense that a sphere or disk cannot be translated while their neighbor contact particles are kept fixed. In fact, a random packing is ill defined [12], because there is always a certain degree of order [13] that can be measured by an orientational order parameter (ψ_6). In a different context, i.e., in the study of the difficult problem of the glass transition, in 1979 Phillips [14] proposed that the glass formation was optimized when the number of constraints, given by the number of bonds and angles between them, was equal to the number of freedom degrees given by the dimensionality of the configurational space of the system ($2N$ in two dimensions and $3N$ in three dimensions). After this successful idea, Thorpe [15] refined the concept by showing that if the number of constraints is lower than the degrees of freedom, there are zero frequency vibrational modes called floppy [15,16], and the resulting network is underconstrained or floppy. A transition occurs when the lattice becomes rigid, and at the corresponding chemical composition, the glass is easy to form due to the configurational limbo in which the system sits. The rigidity transition (RT) occurs for a certain average coordination of the lattice, which is universal in the sense that it depends only on the dimensionality of the system. Many important features of this transition have been experimentally observed for chalcogenide glasses [17,18]; however, it has been elusive to understand the effects of rigidity in thermodynamics, and only very recently were some advances made [19]. In this Letter, we show that the RT plays a very important role in the freezing transition, since our results suggest that both occur at the same time, as seen from our computer simulations with HD. Furthermore, here we show that the suppression of rigidity nucleation in the sense of self-organization [20] can inhibit crystallization and produce a glasslike transition, while overconstraints produce crystallization, as was predicted by Phillips [14].

Using a standard Monte Carlo Metropolis algorithm for a grand-canonical ensemble, we performed simulations for a HD system with disk diameter σ. In Fig. 1, with circles we present the inverse of the numerical density (ρ^{-1}) as a function of the reduced chemical potential ($\beta\mu$), where $\beta = 1/kT$. The results were obtained from equilibrium and productive runs, each averaged over 400 configurations, relaxed by 4×10^5 iterations, where the acceptation rate was fixed to oscillate between 20%–30%, in a square box of size 20σ. The fluid-solid transition that we obtain is similar to that found by many other authors [2,7]. The obtained solid phase presents hexatic domains, although 2D crystals do not possess long-range translational order [2]; rather, the translational order is quasi-long-ranged, with a density-density correlation function that decays algebraically to

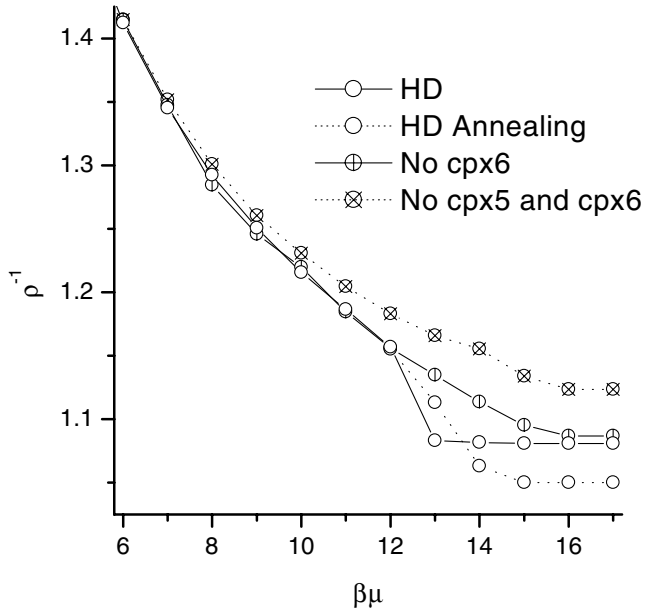

FIG. 1. Inverse of the numerical density versus chemical potential for the HD without (with) annealing, represented by the solid line with circles (dotted line with circles), and by the exclusion of overconstrained configurations of 6 (5) disks, denoted by crosses (dotted line).

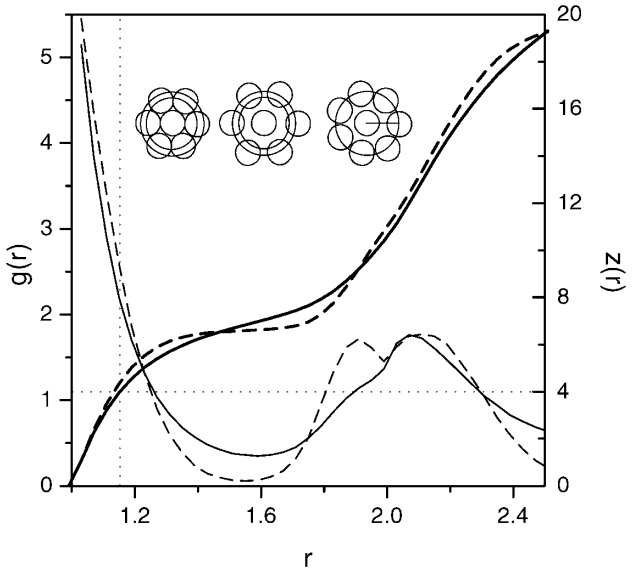

FIG. 2. Radial distribution function (left scale) of the HD system before and after the fluid-solid transition $\beta\mu = 12, 13$, shown as thin solid and thin dashed lines, respectively. The corresponding integral of $g(r)$, which gives the coordination number for the same chemical potentials, is shown in darker lines (right scale). The inset represents the contact region, as described in the text.

zero [21]. However, there is true long-range bond-orientational order in the crystal, while both translational and orientational order are short ranged in the equilibrium fluid. For comparison purposes, in Fig. 1 we also include the obtained results after an annealing process of the solid phase that allows one to obtain higher densities.

During the fluid-solid transition, the free volume is reduced in such a way that disk diffusion becomes nearly impossible in the solid phase. If the free volume is reduced to zero, we expect a jamming of the disks inside hexagons formed by the contact of the six first neighbors, and thus there are not possible movements. For a Monte Carlo or molecular dynamics simulation, one has the problem of how to define the number of disks that are in contact with another, since statistically the probability of having a perfect contact is zero. Usually, to define a neighbor, the criterion is to look at a circular region with a radius given by the minima between the first and second peaks of the radial distribution function $(g(r))$ [2] (that we show from our results in Fig. 2). However, is clear that if, for example, in the fluid phase we have a disk surrounded by a heptagon formed by seven disks (see inset of Fig. 2), these disks are not able to jam the central one, and thus the definition of the contact region cannot be the same as the region of nearest neighbors. Because of these considerations, it is natural to define the "contact" as those disks that are in a region where the maximal allowed coordination ($Z_{\max}$) is six, i.e., the sector between a circle of radius $r = \sigma$ defined by an hexagon of disks and a heptagon with radius $r = \sigma/[2\sin(2\pi/14)] \approx 1.152\sigma$ which is formed by seven disks, where each disk is in contact with two neighbors.

Our main result is related to the following fact. If we obtain the average number of neighbors ($\langle Z \rangle$) by integrating $g(r)$, we get that $\langle Z \rangle$ is close to 4, for $r \approx 1.15\sigma$ at the fluid-solid transition, as shown in Fig. 2, where the integral of $g(r)$ at the chemical potentials that are closer to the transition are displayed. The surprise is that $\langle Z \rangle = 4$ is the value predicted for a RT in a mean field when angular forces are not present [15]. The value $\langle Z \rangle = 4$ comes from the fact that in 2D there are $2N$ degrees of freedom, but each time that a bond or contact is formed, a constriction is imposed. In a mean field approximation, the RT is obtained by observing that the jth site has Z_j contacts, each contact is shared by two sites, and thus the total number of constraints is $\sum_j Z_j/2$. However, if a disk has maximum coordination, the angles between contacts are fixed due to geometrical hindrance, and extra constraints appear [there are $\sum_j'(Z_{\max} - 1)$ angular contraints, where the sum is carried over sites with $Z = Z_{\max}$]. Taking into account these two contributions, the proportion of floppy modes (given by the difference between the number of freedom degrees minus the number of constraints, normalized to $2N$) is

$$f = 1 - \frac{\langle Z \rangle}{4} - \frac{(Z_{\max} - 1)}{2}\chi_{Z_{\max}}, \qquad (1)$$

where it was used that $\sum_j Z_j/N$ is the average coordination number, and $\chi_{Z_{\max}}$ is the fraction of disks with maximal coordination. If this last fraction is very low, as is the

case of the present system before the thermodynamical transition, the RT occurs when $f = 0$, and thus $\langle Z \rangle = 4$. The present result suggests that a RT occurs at the thermodynamical transition due to overconstraint of the system, as is seen in Fig. 3, where the number of floppy modes, obtained from the numerical data and Eq. (1), crosses the line $f = 0$ at the thermodynamical transition. Notice that after the transition, f is negative due to the fact that the system is overconstrained, and Eq. (1) still can be used if we define a new quantity, the hardness (h), as $h = -f$ where h now gives the fraction of overconstraints. We can understand the value $\langle Z \rangle = 4$ as a dynamical jamming transition (dynamical because contacts are within certain limits) or as a sort of cage effect [22,23], since to jam or to put in a cage a disk, at least four disks are needed. Notice that a disk can be jammed with only three disks, however, there is only one configuration in which this is possible, an equilateral triangle, and the statistical weight of this possibility is nearly zero. With four disks the situation is the inverse; there is only one configuration which is not able to produce jamming.

To further discuss this point, in Fig. 4 we show the evolution of $\langle Z \rangle$ with respect to the chemical potential, now using the idea of defining the contact region as $\sigma \leq r < 1.15\sigma$. As is clearly seen, there is a jump at the fluid-solid transition and $\langle Z \rangle$ cross the value 4 near the transition.

Once the connection between rigidity and the thermodynamical phase transition is revealed, one is led to ask if it is possible to inhibit the thermodynamical transition by avoiding the development of an overconstrained lattice. This can be done if nucleation of rigidity is forbidden, in the same spirit of the self-organization of rigidity, as was proposed very recently by Thorpe *et al.* [20], and experimentally confirmed by the group of Boolchand [17,18].

This inhibition can be achieved by including in the potential a term that depends on the number of neighbors in the contact region. The potential is built in such a way that a disk cannot move inside the contact region if the number of disks already present in that region is five. In that way, nucleation of six disks around a disk is not permitted, since they give extra constraints that overconstrain the system. A similar biased simulation can be done by avoiding five disks in the contact region. Notice that a model with this kind of potential, but in the context of lattice systems, has been considered [24] as a possible source for a glass transition. In Fig. 1 we present the results of avoiding constraints in the lattice by rejecting configurations with six and five disks in the contact region. As can be seen, the phase transition is avoided and a transition that is glasslike occurs. This graph can be compared with the corresponding evolutions of $\langle Z \rangle$ as a function of the chemical potential (Fig. 4), where the rigidity transition is clearly avoided, since the line $\langle Z \rangle = 4$ is not crossed, and as a result, supercooling is possible. Furthermore, when the nucleation of rigidity is avoided, all the systems fall in the line $f(\langle Z \rangle) = 1 - (\langle Z \rangle/4)$ (see Fig. 3), which, in fact, is the line defined by self-organization of rigidity [20].

An interesting confirmation of the glassy nature of the solid, is the distribution of volume in each of the Voronoi

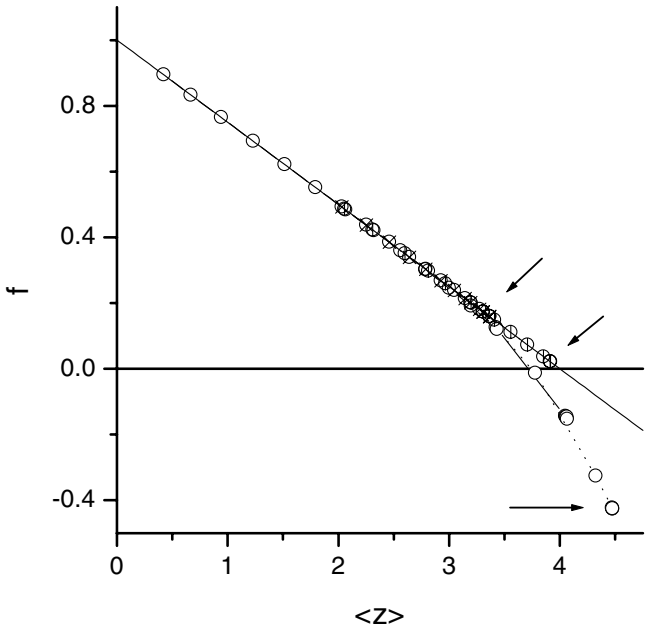

FIG. 3. Number of floppy modes calculated from Eq. (1), using the same symbols described in Fig. 1.

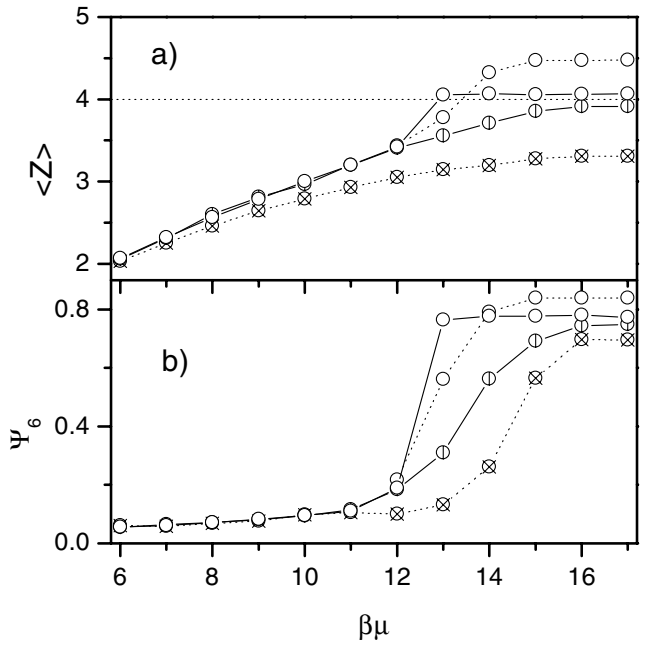

FIG. 4. (a) Average coordination versus chemical potential; the neighbors were determined using the contact region criteria. (b) Order parameter as a function of the chemical potential calculated using Voronoi polygons to define the neighbors. The symbol code is the same used in Fig. 1.

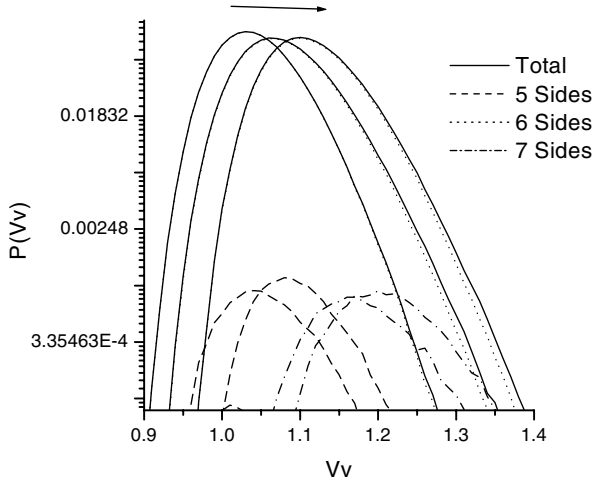

FIG. 5. Voronoi volume distribution when the solid is already formed ($\beta\mu = 16$); we can observe an increment of the total Voronoi volume (solid lines) as we decrease the stress in the system (arrow). The left, middle, and right curves correspond to HD without rejecting any configuration, rejecting maximal coordination 6, and rejecting maximal coordination 6 and 5, respectively. The increase in the free volume is paid by the corresponding increase in defects (5 and 7 sides Voronoi polygons). For the case of the pure HD with annealing, no defects are observed, while if we reject configurations of 6 disks (6 and 5 disks), the middle (right) set of curves is obtained.

polygons ($P(V_V)$), presented in Fig. 5. In the fluid to solid phase transition, all the pentagons and heptagons that were present in the fluid disappear at the transition, while for the case of the inhibition of rigidity nucleation, there are pentagons and heptagons that are frozen in. Notice that there is a relation between the average volume and the rigidity of the lattice, since for maximal rigidity the volume is smaller, and the contrary is true for less rigidity, as shown by the arrow in Fig. 5 (each of these configurations is also indicated with arrows in the corresponding plot of the floppy modes). The relation between Voronoi volume and rigidity conduces to a dynamical jamming, which is reflected in the order parameter ψ_6, shown in Fig. 4(b), defined as $\psi_6 = \sum_k \sum_j \exp(6i\theta_{kj})/N_{\text{Bonds}}$ where θ_{kj} is the angle between two neighbors k and j, now *obtained from the Voronoi polygons*, N_{Bonds} is the total number of bonds, and the sum is carried over all pairs of disks. For the case of the usual fluid-solid transition, we find the same results reported in Ref. [2]. Notice that the maximum value is not 1 due to the size of fluctuations in 2D, as was said previously.

In conclusion, we have found that there is an intimate connection between rigidity and the fluid-solid transition in a hard-disk system. By avoiding nucleation of rigidity, in the sense of self-organization, we were able to produce a glasslike transition.

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