Freezing of two-dimensional hard disks

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We argue that structural rearrangements experienced by an assembly of hard disks under increasing disk density are accompanied by the mutual caging of each disk by its three *alternating* Voronoi nearest neighbors. This caging becomes effective at a packing fraction $\eta=\pi\sqrt{3}/8\approx 0.680$ when the average gap width between neighboring disks in the system shrinks to about 15% of the disk diameter. The freezing occurs when the fraction of caged disks is about 40%.

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The freezing transition (FT) of a two-dimensional (2D) substance was first seen in the computer simulation studies of 870 hard disks (HD's) by Alder and Wainwright [1] more than 40 years ago. Since then, a number of papers, both theoretical and computational, have been published discussing different aspects of the fluid-to-solid transformation in 2D. Is this transformation an ordinary first-order FT or a more complex continuous transition or a superposition of both? It is very probable that the fluid-to-solid transition scenario in 2D is sensitive to the details of the interparticle interaction [2]. In the case of HD's, recently there has been growing evidence [3,4] to demonstrate that the observed phase transformation consists of a first-order FT that may be followed by the so-called hexatic phase (HP) predicted by the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory [5–7]. Therefore, the issue of a HP is of importance to understand the melting mechanism of a 2D solid. The problem is complicated since observation of the HP seems to be sensitive to the size of the simulated system (millions of disks are necessary [3,4]) and very possibly the HP is metastable [8]. On the other hand, the FT can be studied by simulating reasonably small systems (thousands of disks is enough [1]); however, the reason why a HD fluid freezes is not clear as well. Insight into the mechanism and driving force of the FT in a HD system is the main purpose of this paper.

In a recent computer simulation study of the HD structuring, Truskett *et al.* [9] turned their attention to a shoulder that developed on the second maximum of the disk radial distribution function (RDF) in the vicinity of the FT (the dashed curve in Fig. 1). The observed shoulder was attributed to the formation of a four-disk hexagonally close-packed arrangement and has been suggested to be considered as a precursor of HD freezing. Indeed, as the disk density increases beyond the FT region (the solid line in Fig. 1), the shoulder gradually transforms into two subpeaks. One closely follows the position of the original second maximum, which is located at distances larger than twice the disk diameter σ, but the other subpeak is clearly shifted to shorter distances in the region $r/\sigma<2$. When the density further increases towards the close-packing (CP) density, these two subpeaks eventually are transformed into two distinct δ-like peaks centered at the distances $r/\sigma=2$ and $r/\sigma=\sqrt{3}$, respectively, representing a loose crystalline hexagonal ordering in a HD solid.

On the other hand, the relevant studies by Huerta *et al.* [10] and Moučka and Nezbeda [11] indicate a notable increase in the formation of quasiregular hexagonal configurations already on approaching the FT. By quasiregular hexa-

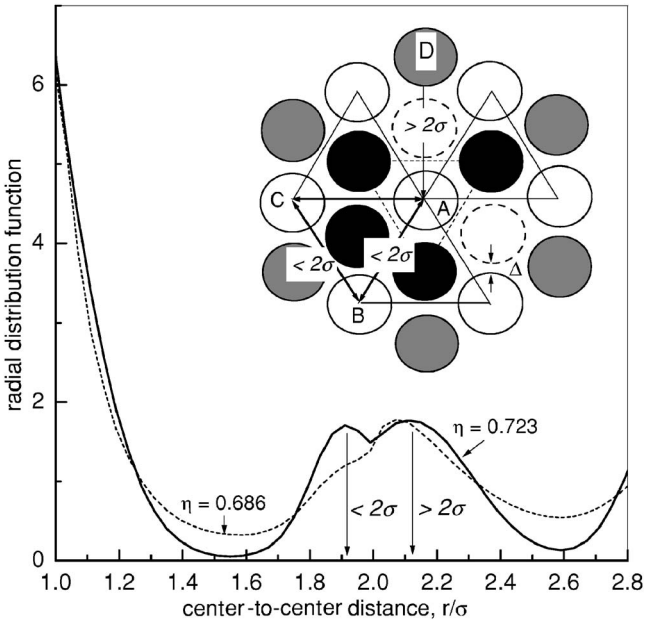

FIG. 1. MC data for the RDF of a HD system at two packing fractions: before melting, $\eta=0.723$ (solid line), and before freezing, $\eta=0.686$ (dashed line). Inset: sketch of the quasiregular hexagonal configuration with an average gap width Δ between VNN's. The disks filled with black and those drawn by the dashed line are the VNN's of the central disk *A* while disks filled with gray and those drawn by the solid line are *farther* and *closer* next-VNN's, respectively.

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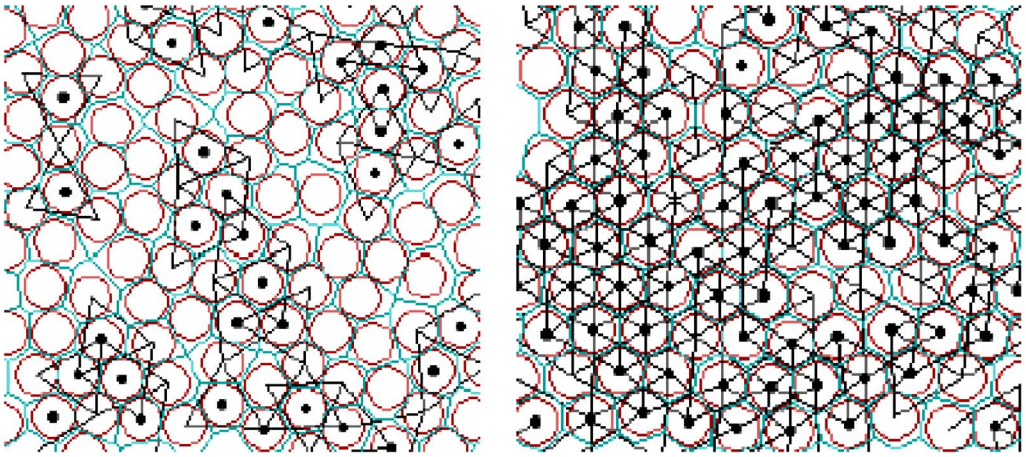

FIG. 2. (Color online) Snapshots of a part of the configuration of $N=1000$ disks at two different densities. Left: $\eta=0.686$—i.e., before freezing. Right: $\eta=0.723$—i.e., before melting. Disks with a dot mean that they are caged using the criterion that CTC distances between three pairs of its *alternating* VNN's be less than 2σ while lines show the *alternating* VNN disks that cage the central disk.

gons we mean the sixfold configurations (see the inset in Fig. 1) with on average the same gap width $\langle\Delta\rangle$ between the Voronoi nearest neighbors (VNN's). It already has been shown [10,12] that the upper limit of such a gap for regular hexagons is $(1/[2\sin\pi/7]-1)\sigma\approx 0.152\sigma$; gaps larger than 0.152σ will allow for a ring of seven disks to be formed around the central disk; $\langle\Delta\rangle=0$ in the CP limit when all disks are in immediate contact. Since the freezing density [2,13] is far lower than the CP density, $\eta_{\mathrm{cp}}=\pi/(2\sqrt{3})\approx 0.907$, the regular but loose hexagons in a prefreezing region are formed on average by noncontacting disks—i.e., with a gap width $\langle\Delta\rangle\neq 0$. Therefore, it seems reasonable to suggest that the phenomenon of disk freezing somehow is linked to the shrinkage of the average gap width between disks.

Based on these observations, as well as on our own computer simulation data, we believe that during the structural rearrangements that take place in an assembly of HD's with increasing density, there exists a gap width $\langle\Delta\rangle$ that favors a local environment characterized by the mutual caging of each disk provided by only a single set of its three *alternating* VNN's. The FT occurs when about 40% of the disks are caged in this way.

The average gap width between hexagonal VNN's can be estimated assuming that disks are spread uniformly,

$$\langle\Delta\rangle/\sigma=\left(\frac{\eta_{\mathrm{CP}}}{\eta}\right)^{1/2}-1, \tag{1}$$

where $\eta=\pi\sigma^2/(4a)$ is the packing fraction with a denoting the area per disk. To proceed, let us consider what different values of $\langle\Delta\rangle$ imply and why this could be important for HD's before FT. Analyzing the schematic drawing in Fig. 1, it is easy to find that for $\langle\Delta\rangle/\sigma=2/\sqrt{3}-1\approx 0.155$, the average center-to-center (CTC) distances between a central disk and what we call *farther* (circles filled with gray) and *closer* (white solid circles) next-VNN's in a hexagonal arrangement are $AD=2.31\sigma>2\sigma$ and $AB=AC=BC=2\sigma$, respectively. The fact that for $\langle\Delta\rangle<0.155\sigma$ the average CTC distances between a central disk and its *closer* next-VNN's will be shorter than 2σ—i.e., $AB=AC=BC<2\sigma$—is crucial. In particular, it means that in such a case the corresponding gaps between pairs of disks A and B, A and C, and B and C will be on average shorter than σ and, consequently, the central disk (circle filled with black) becomes caged. In contrast, if $\langle\Delta\rangle>0.155\sigma$, then distances $AB=AC=BC>2\sigma$ and the corresponding gaps are large enough for the central disk to escape. Because of this, the gap width $\langle\Delta\rangle/\sigma=2/\sqrt{3}-1$ can be referred to as the caging gap. An estimate made by substituting this gap value into relation (1) gives the corresponding caging density $\eta_{\mathrm{cage}}=\pi\sqrt{3}/8\approx 0.680$.

More careful examination of the hexagonal arrangement similar to that in Fig. 1 reveals that any disk in a 2D array being chosen as a central disk (e.g., disk A) and its two *closer* next-VNN's (e.g., disks B and C) serve simultaneously as the pair of *alternating* VNN's of common neighboring disks (the disks filled with black in Fig. 1). Thus, the formation of the subshell of *closer* next-VNN's, which reveals itself as a shoulder on the disk RDF, signals that the corresponding gaps between the pairs of *alternating* VNN's in the entire array become on average shorter than σ. The latter means that the disks considered as wanderers (e.g., the disks filled with black in Fig. 1) can no longer squeeze out of the triangular cells formed by their three *alternating* VNN's—i.e., become caged.

The caging by the *alternating* VNN's in a qualitative manner can be seen from the snapshot of the disk configuration obtained from computer simulations of 1000 disks. The canonical ensemble Monte Carlo (MC) method that we used in the present study is quite standard and identical to that used in our previous study [10] as well as in the relevant studies by Truskett *et al.* [9] and Moučka and Nezbeda [11]. The snapshots in Fig. 2 correspond to two different densities: $\eta=0.686$ and $\eta=0.723$, which are on either side of the FT region [2,13]. The dots mark those disks that are caged using the criterion that gaps between their *alternating* VNN's be less than σ while lines connect these VNN's. From the snapshot that corresponds to the density before freezing, we can see that practically all disks in the array already have their six VNN's. Nevertheless, only some of the disks are caged;

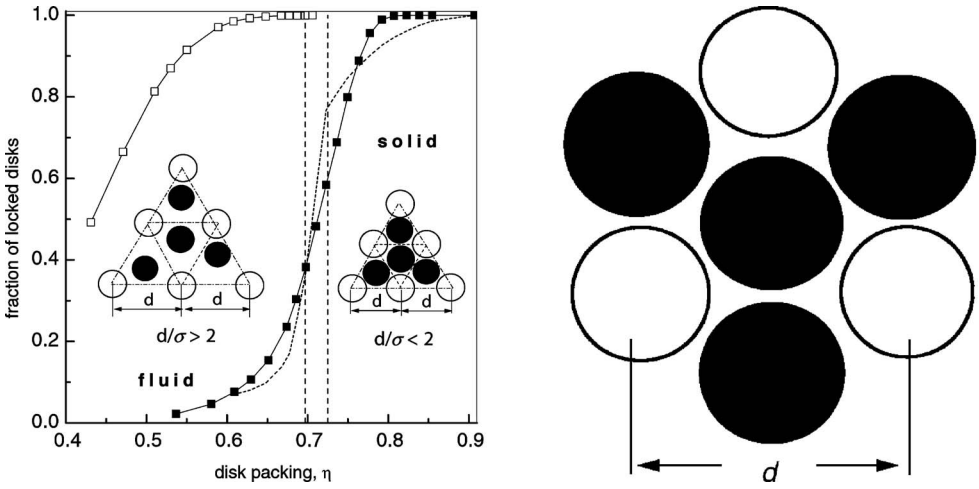

FIG. 3. Left: fraction of caged disks that follows from our MC simulations by using two different criteria: (i) the CTC distances between all six VNN's must be less than 2σ (line with open squares), i.e., the criterion used in a *conventional* CM [15], and (ii) the CTC distances between three *alternating* VNN's must be less than 2σ (line with filled squares), i.e., the criteria that follows from the present analysis. The short-dashed curve corresponds to the global bond orientational order parameter while vertical dashed lines mark the freezing and melting densities all obtained from our MC simulations. Right: triangular unit cell formed by the *alternating* VNN's.

the majority of this caging is realized by a single set of the three *alternating* VNN's. There are only few disks that experience double caging—i.e., are caged by a hexagonal cell of the all six VNN's which in fact represent double sets of the *alternating* VNN's. As the density increases, more single sets of VNN's merge to form the hexagonal arrangement.

To quantify this caging, we calculated the fraction of caged disks at various packing fractions η. This fraction was obtained as the ratio of the HD's that have three *alternating* VNN's with a CTC distance between them shorter than 2σ to the total number of disks. We can see from Fig. 3 that indeed on approaching the FT there is a sharp increase of the disks caged by three *alternating* VNN's. Moreover, the profile of the fraction of caged disks follows closely the profile of the global bond orientational order parameter [2,6], which was evaluated in the same simulation runs. It follows that around 40% of disks in the array must be caged by their three *alternating* VNN's for the FT to occur. In contrast, the caging by all six VNN's shows little relation to the FT.

The concept of caging is essential in studies of the FT by means of the cell model (CM) approach [14]. Originally this approach considered that each disk in the array always is surrounded by a fixed group of VNN's equal in number to those that surround it in the solid phase. In an approach that we will refer to as a *conventional* CM [15], this group of VNN's was identified as a sixfold hexagonal arrangement. In turn, Alder *et al.* [16] suggested a *correlated* CM in which only four out of six VNN's remain fixed in their hexagonal lattice positions. An important observation from the present study lies in the fact that when the density progressively increases towards freezing, the caging is realized neither by six nor four disks but only by three disks that are the *alternating* VNN's. This finding led us to the conclusion that the triangular cell formed by the *alternating* VNN's could be a natural unit cell for the HD system. Such a unit cell is shown in Fig. 3. The three *alternating* VNN's drawn by open circles are fixed while circles filled with black represent the disks that are allowed to move within their cells or even get out from the cell if the gap between fixed disks allows one to do so. This gap, or better the CTC distance d, between *alternating* VNN's is only a parameter of the proposed CM; the corresponding packing fraction η follows from $(d/\sigma)^2 = \pi\sqrt{3}/(2\eta)$. The free area per disk, a_f, is given by

$$a_f/\sigma^2 = \frac{\sqrt{3}}{4}(d/\sigma)^2 - \frac{\pi}{2} + 3\cos^{-1}\left(\frac{d/\sigma}{2}\right) - \frac{3}{4}(d/\sigma)\sqrt{4-(d/\sigma)^2}, \tag{2}$$

for distances $1 < d/\sigma < 2$; if $d/\sigma > 2$, only the first two terms contribute. Then the pressure $pa/kT = a(\partial \ln a_f/\partial a)$ is

$$\frac{pa}{kT} = \frac{d^2}{2a_f}\left[\frac{\sqrt{3}}{2} - \frac{3}{d/\sigma}\sqrt{1-\left(\frac{d/\sigma}{2}\right)^2}\right], \tag{3}$$

for distances $1 < d/\sigma < 2$; if $d/\sigma > 2$, only the first term contributes. To calculate the derivative $\partial a_f/\partial a$ we used the relation $a = \sqrt{3}d^2/6$.

The pressure resulting from Eq. (3) is shown in Fig. 4 together with the results of the *conventional* CM theory [15]. These two theoretical predictions are compared with three sets of computer simulation data obtained independently for both fluid and solid phases [17] as well as for the FT region [4,13]. We can see that the *conventional* CM, which is based on the hexagonal unit cell, describes the HD system at high densities well but fails for low densities and also fails even to predict a FT region. In contrast, the CM theory, based on the triangular unit cell of *alternating* VNN's, does predict the coexistence region between HD fluid and HD solid phases. Similar results were obtained by Alder *et al.* [16] using a rectangular unit cell. A clear first-order transition is found in both cases. There is a cusp at the caging density $\eta_{\text{cage}} \approx 0.680$, which corresponds to $d = 2\sigma$ or equivalently to $\langle\Delta\rangle \approx 0.155\sigma$. The cusp is inside the coexistence region as determined by a Maxwell construction. Outside the coexist-

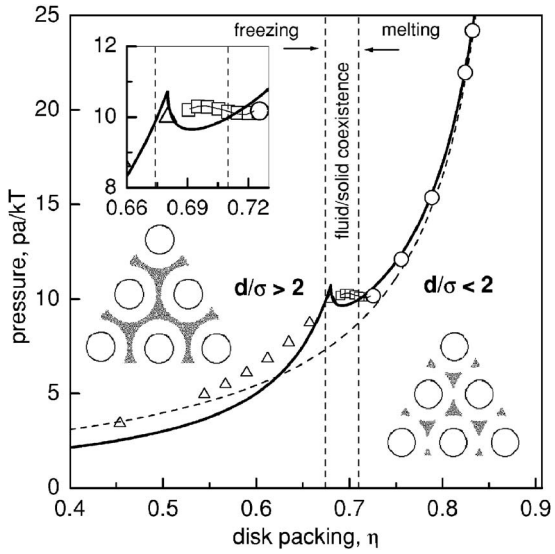

FIG. 4. The equation of state of a HD system. The open symbols are computer simulation data for fluid (triangles) and solid (circles) phases [17] as well as for a transition region (squares) [13], respectively. The thin solid line in the transition region shows the large-scale computer simulation data extracted from Ref. [4]. The thick solid line shows results of the CM theory using the proposed triangular unit cell formed by the *alternating* VNN's while the dashed line gives the results of the *conventional* CM [15]. The vertical dashed lines mark the fluid and solid coexisting densities as obtained by a Maxwell construction from the pressure isotherm given by Eq. (3). The inset illustrates the transition region in detail. Two snapshots show the traces of central disks surrounded by the disks (open circles) that are fixed in the positions of a triangular unit cell formed by *alternating* VNN's. The gaps between fixed disks correspond to the packing fractions η=0.686 (on the left) and η=0.723 (on the right).

ence region, $\partial p/\partial a < 0$. The resultant coexisting densities are $\eta_{\text{fluid}}=0.674$ and $\eta_{\text{solid}}=0.710$.

Two snapshots in Fig. 4 were obtained from MC simulations with fixed *alternating* neighbors (in analogy to the CM approach) to illustrate the qualitative change in the free area (shown as a shaded area) of the HD system across the transition region. One can see that on the fluid side the traces (i.e., available free area) of the central disks from different unit cells are connected—i.e., the central disks wander through the system. In contrast, on the solid side the same traces are separated; i.e., each central disk is restricted to move only in a designed unit cell of its *alternating* VNN's. It is interesting to note that such a restriction finally leads to the overall hexagonal arrangement in the HD solid in accordance with observation.

Summarizing, the formation of local quasiregular hexagons with increasing density in a HD system implies that the average CTC distance between any disk chosen as a central disk and its *closer* next-VNN's begins to be shorter than 2σ. This fact reflects itself as the shoulder on the second maximum of the disk RDF that already has been suggested as a structural precursor to FT in the HD system [9]. On the other hand, within the hexagonal arrangement each central disk and its *closer* next-VNN's are simultaneously the *alternating* VNN's of the common neighboring disk, and when the CTC distance between them becomes shorter than 2σ, this common neighboring disk becomes caged. Based on this observation we have reported a simple mechanism for the freezing of hard disks. This mechanism considers that by taking only *alternating* VNN's into account this is enough to describe fluid and solid phases as well as the transition region. The fluid becomes unstable when the average CTC distance between *alternating* VNN's becomes shorter than 2σ and the resulting gap between them is not large enough for the central disk to wander.

The results presented in Fig. 4 indirectly suggest that caging by the *alternating* VNN's can be the origin of the freezing in a HD system. On the other hand, some recent large-scale computer simulations of a HD system indicate the possibility of the HP existing just after the first-order FT [3,4]. We wish to point out that the mechanism that we proposed for freezing does not exclude the possibility of a continuous HP (probably metastable in the case of a HD system) just after the disks freeze.

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