

## Detection and Characterization of Structural Changes in the Hard-Disk Fluid under Freezing and Melting Conditions

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(Received 11 October 2004; published 4 February 2005)

The fluid of two-dimensional hard disks is investigated over a range of densities by Monte Carlo simulations in order to detect and characterize structural changes which take place when the condition of freezing and melting is approached. A novel method is proposed based on the use of the Voronoi tessellation and a certain shape factor which turns out to be a clear indicator of the presence of different underlying substructures (domains). Close to the freezing condition the probability distribution of the shape factor develops a second distinct maximum corresponding to a predominant presence of near-regular hexagons, whereas the original peak, having its origin primarily in pentagons and distorted hexagons, diminishes and disappears at melting density.

DOI: 10.1103/PhysRevLett.94.040601

PACS numbers: 05.20.Jj, 61.20.Ja

With changing thermodynamic conditions a restructuring of molecules in fluid systems may take place leading ultimately to a phase transition. Such changes may be difficult to quantify and hence also difficult to detect. This applies particularly to the fluid-solid phase transition in two-dimensional systems, which differs qualitatively from that in three-dimensional systems [1,2] and whose nature remains an unresolved problem. An open question is whether melting in 2D systems occurs as a common one-step first-order phase transition or whether it goes via a continuous two-step scenario as proposed by Halperin and Nelson [3,4] and Young [5] using the ideas of Kosterlitz and Thouless [6]. According to the KTHNY theory, the first continuous transition transforms the solid into a hexatic phase (the phase with the long-range orientational but no positional ordering), and the second transition transforms then the hexatic phase to an isotropic phase. The problem intimately associated with the above question is what structural rearrangements of molecules take place in the transition region and their characterization.

The common technique to monitor the fluid-solid transition on the microscopic level has been an analysis of the bond-orientational order parameter (for its definition and recent results see, e.g., [7,8], and references therein). Another possibility is to use Voronoi tessellation and make use of certain properties of Voronoi cells (e.g., average edge length, surface, etc.), but the results have provided only a vague picture (see, e.g., [9,10]). Thus, despite a large number of computer simulation results, even for the simplest possible 2D system, the fluid of hard disks, no consensus about the existence of a hex-

atic phase and associated structural changes has been reached.

It has been known that the pair correlation function of the hard-disk fluid starts exhibiting a shoulder within about 5% of freezing (which occurs at the packing fraction about  $\eta \approx 0.69$ ). Truskett *et al.* [11] consider this phenomenon a precursor of a phase transition and analyzed *visually* configurations in this region. According to their analysis this shoulder seems associated with the development of a distinct next-nearest-neighbor shell.

As an attempt to find a more mathematical and quantitative characterization of these structural changes near the phase transition region, we consider also the fluid of hard disks and use the Voronoi tessellation but employ a certain shape factor of Voronoi polygons,  $\zeta$ , to analyze its structure. We show that this factor is able to identify the occurrence of different domains. Whereas at low densities the distribution of  $\zeta$  (the occurrence probability of different 2D figures) exhibits a broad and flat maximum, at pretransition conditions the distribution of  $\zeta$  develops a second distinct maximum at lower values of  $\zeta$  indicating the existence of domains made up of more regular (round) figures; the original maximum then gradually diminishes with increasing density and finally disappears in the crystalline phase.

To study the structure of hard-disk fluids we used the standard Metropolis Monte Carlo simulations in an *NVT* ensemble with 256 and 2500 particles in a rectangular cell with the aspect ratio  $\sqrt{3}:2$  [12]. The former number of particles is a typical value used in simulations, and the latter number was used to check a possible size dependence of results; no detectable difference was found. After a long

equilibration period about  $3.5 \times 10^4$  equilibrium configurations were analyzed using the Voronoi tessellation. To characterize the Voronoi cells we used a shape factor  $\zeta$  defined as

$$\zeta = \frac{C^2}{4\pi S}, \quad (1)$$

where  $C$  is the circumference of the cell and  $S$  is its surface. (We note that in the case of figures made up of line segments this shape factor is identical to the parameter of nonsphericity used in convex figure geometry [13].) For circles  $\zeta = 1$  and for all other shapes  $\zeta > 1$ . For a square  $\zeta = 1.273$ , for regular pentagons  $\zeta = 1.156$ , and for regular hexagons  $\zeta = 1.103$ . If the regular hexagon is distorted to a figure with the length-to-breadth ratio 2:1, then  $\zeta = 1.836$ .

In Fig. 1 we show the pair correlation function,  $g(r)$ , for a number of densities. With increasing density  $g(r)$  develops a shoulder (at about  $\eta \approx 0.65$ ) which ultimately evolves to a secondary peak. The question is what structural rearrangement of the molecules gives rise to this phenomenon.

In Fig. 2 we show the distribution of the shape factor for the same series of densities as in Fig. 1. As one could expect, at low densities the particles are distributed quite randomly, no specific figures are formed, and we thus get a very flat curve with a broad maximum ( $\eta \approx 0.3$ ). As the density increases, the distribution becomes more localized around the maximum which simultaneously moves to lower values of  $\zeta$  and a shoulder on its rising portion also occurs ( $\eta \approx 0.5$ ). With a further increase of density the shoulder develops to a distinct second maximum ( $\eta \approx 0.65$ ). It means that more regular cells can be observed and their occurrence starts prevailing. This is also the region where the pair correlation function starts exhibiting a shoulder; see Fig. 1. For densities about  $\eta \approx 0.7$  (i.e., in

the vicinity of the melting density,  $\eta = 0.716$  [7]) and higher the original maximum (high values of  $\zeta$ ) disappears and the low  $\zeta$ -value maximum sharply rises and its location moves to  $\zeta \approx 1.1$ .

To understand these changes, we show in Fig. 3 snapshots of configurations at  $\eta = 0.50, 0.65$ , and  $0.70$ . To clearly distinguish domains made up of different figures we classify the polygons according to their  $\zeta$  values as follows: (i) class A polygons are those within the range defined by the location of the minimum on the  $\zeta$  distribution,  $\zeta_A < \zeta_{\min} \approx 1.159$  (which is found to be only marginally density dependent); (ii) class B polygons are those within the range from the minimum to  $\zeta = 1.25$ ; (iii) class C polygons are those with  $\zeta > 1.25$ . (The upper bound,  $\zeta = 1.25$ , has been set so that at  $\eta = 0.65$ , i.e., at the density at which the height of the two maxima are roughly the same, the number of figures belonging to classes A and B are, approximately, the same. The population of these two classes then changes with density.)

To differentiate polygons belonging to different classes we use color coding: polygons of class A are indicated by a darker interior, those of class B by a lighter interior, and the remaining polygons have the white interior. We see that for  $\eta = 0.5$  we observe a mixture of various polygons, although small domains made up of pentagons and hexagons, respectively, can also be detected. For  $\eta = 0.65$  we already find two large domains: one made up predominantly of more or less regular hexagons (figures belonging to class A), and the other made up of distorted hexagons and pentagons (figures belonging to class B). At density  $\eta = 0.7$ , i.e., at density slightly higher than the freezing density, only small islands of pentagons and distorted hexagons are found, whereas the overwhelming majority of the molecules form near-regular hexagons. Ultimately, for densities higher than  $\eta = 0.716$  we end up with configurations

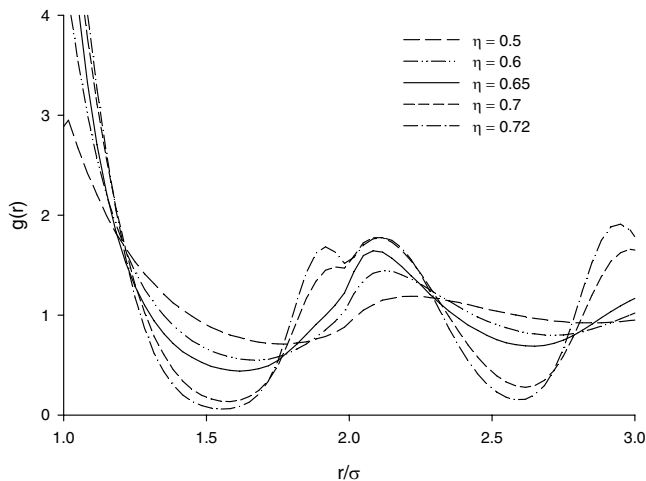


FIG. 1. Pair correlation function of the fluid of hard disks at different densities.

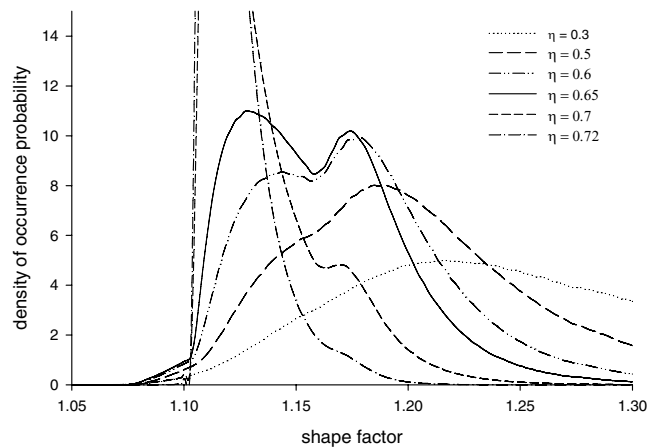


FIG. 2. Probability distribution of the shape factor in dependence on density.

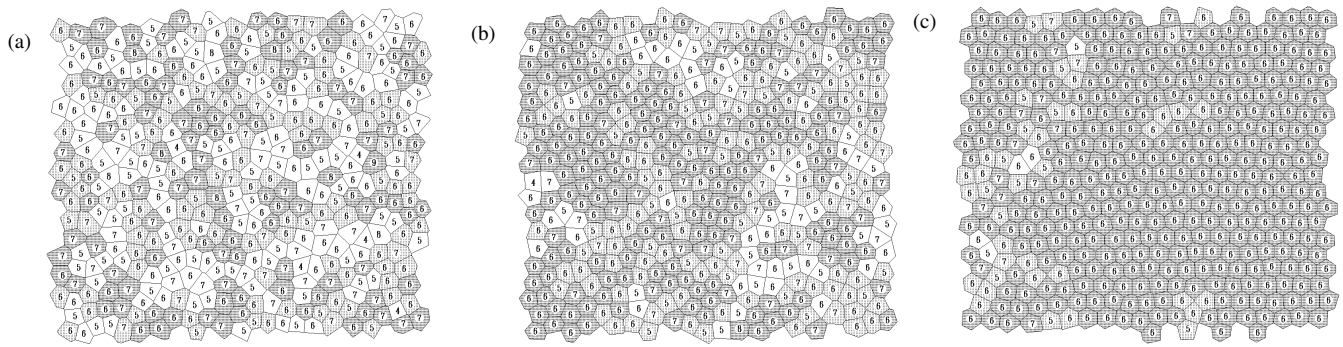


FIG. 3. Snapshots of configurations at  $\eta = 0.5$  (a),  $\eta = 0.65$  (b), and  $\eta = 0.7$  (c), with Voronoi cells. Darker cells correspond to polygons of class A [ $\zeta \in (1.108; 1.159)$ ], lighter cells to polygons of class B [ $\zeta \in (1.159; 1.25)$ ], and the numbers indicate the type of polygon (number of vertices).

where only more or less regular hexagons are found (the peak of  $\zeta$  approaches the value 1.108), i.e., in the ordered crystalline phase.

The common tool to describe the structure of fluids, the pair correlation function, provides only a sort of an average arrangement and is thus not able to characterize in detail tiny structural effects. A better indicator of such details and structural changes is usually the structure factor, but it tells only that there are patches of another phase. Similarly, the individual characteristics of Voronoi cells, as, e.g., the average surface, circumference (edge length), etc., are also of little use yielding just smooth curves with one broad maximum. However, we have found that the simultaneous use of the circumference and surface combined into a shape factor is sensitive to changes in the 2D structure and clearly marks domains made up of different figures. Particularly, it gives a clear physical picture of competition between less and more ordered domains and of gradual building of a regular hexagonal arrangement in the region of the phase transition. The question whether some of its features, as, e.g., the inflection point on the distribution through which the second maximum disappears, may have deeper meaning and can be also related, e.g., to the melting, should be a subject of further investigations. The proposed method based on the use of a shape factor may also be conveniently used to analyze the structure of fluids at interface, i.e., of pseudo-two-dimensional layers.

This research was supported by the National Research Program “Information Society” (Project No. 1ET400720409).

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