Structural precursor to freezing in the hard-disk and hard-sphere systems

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We show that the simplest model fluids in two and three dimensions, namely, the hard-disk and hard-sphere fluids, exhibit a structural precursor to the freezing transition, which manifests itself as a shoulder in the second peak of the radial distribution function. This feature is not present in the radial distribution function of the low-density fluid. Close examination of the two-dimensional fluid configurations in the vicinity of the freezing transition reveals that the shoulder corresponds to the formation of a distinct structural motif, identifiable as a four-particle hexagonally close-packed arrangement. As the dense fluid approaches the freezing transition, the ordered arrangements form large embryonic domains, commensurate with those seen in the crystal at the melting point. Contrary to the notion that the split second peak is a signature of the amorphous solid, our results support the idea that it is a precursor to the development of long-range order. [S1063-651X(98)00109-3]

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I. INTRODUCTION

Phenomenological rules associated with the liquid-solid phase transition can be found for systems in both two and three dimensions [1–3]. Perhaps the most successful criterion for determining the freezing transition in three-dimensional (3D) monatomic liquids was introduced in 1969 by Hansen and Verlet [4]. They noticed that the amplitude of the first peak in the liquid structure factor $S(k)$ is nearly 2.85 at the freezing line, a seemingly universal feature that has been verified both by simulations [4–7] and experiments [8–12]. Nonetheless, studies of 2D liquids [13–15] reveal that the peak in the liquid structure factor is much larger at the freezing line, indicating that the simple Hansen-Verlet rule does not carry over to arbitrary spatial dimension. For the 3D monatomic crystal, one can appeal to the celebrated Lindemann melting criterion [16], which states that, on average, the root-mean-square (rms) displacement of the atoms scaled by their interparticle separation is approximately 0.15 at the melting line. Proposed in 1910, the Lindemann criterion has been found to be valid for a variety of real and model crystals [17], quite independent of the specific atomic interactions. Preliminary studies by Stillinger and co-workers [18,19] suggest that a *reverse* Lindemann criterion holds for the displacement of liquid atoms about their *inherent structures* [20,21] at the freezing line, indicating that the criterion provides a somewhat symmetric description of the liquid-solid equilibrium. It is worth noting that the rms displacement diverges logarithmically with system size in 2D crystals and thus the Lindemann criterion is not a suitable rule for melting in two dimensions [22].

Two-dimensional systems have provided a fertile medium for the study of phase transitions. Indeed, the topological simplification relative to three dimensions has allowed considerable theoretical and computational progress [3,23]. Underlying the physics of low-dimensional condensed phases is the role of long-wavelength fluctuations. Most notably, 2D crystals do not possess long-range translational order [24,25]; rather, the translational order is *quasi*-long-ranged, with a density-density correlation function that decays algebraically to zero [26,22]. 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. The defect-mediated theory of Kosterlitz, Thouless, Halperin, Nelson, and Young [27–30] addresses the effect of long-wavelength fluctuations on the 2D melting transition. It predicts that the crystal undergoes a continuous melting transition via the unbinding of dislocations into a (possibly metastable [31]) *hexatic* phase, with short-range translational order and quasi-long-range orientational order. The hexatic phase is predicted to undergo a second continuous transition to the equilibrium fluid via the unbinding of disclinations. Of course, the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) scenario does not rule out the possibility of a first-order melting transition occurring by another mechanism. In fact, there is strong evidence to support a first-order phase transition in the hard-disk system [32–34]. While the validity of the KTHNY theory is still an interesting open question (see, e.g., [3,23]), many of its predictions have been verified by simulations and experiments. Of special relevance here is the prediction that the dimensionless combination $K \equiv 4\tilde{\mu}(\tilde{\mu}+\tilde{\lambda})/(2\tilde{\mu}+\tilde{\lambda})$ is equal to 16π on the melting line, where $\tilde{\mu}$ and $\tilde{\lambda}$ are reduced Lamé constants. It has been recognized [35] that while the KTHNY melting criterion is found to hold for 2D solids [14,36], there is no analog in three dimensions.

More recently, Löwen, Palberg, and Simon [7] introduced a dynamical criterion for the freezing of three-dimensional colloidal fluids. It states that the ratio of the long-time to the short-time diffusion coefficient D_L/D_0 in the liquid is ≈ 0.1 at the freezing line. The criterion has been verified by forced Rayleigh scattering experiments on charged-stabilized colloi-

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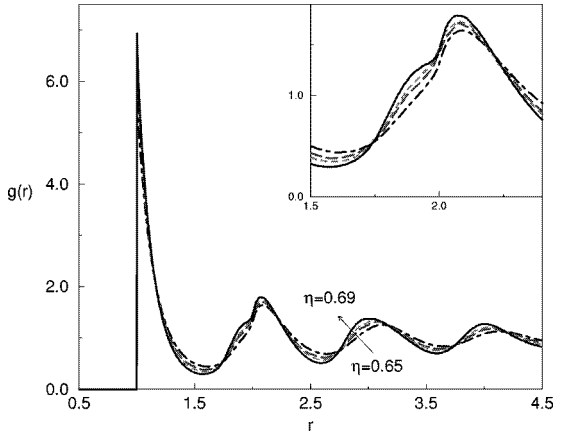


FIG. 1. Radial distribution function $g(r)$ for hard disks plotted versus distance r (in units of diameters). Curves represent the fluid phase with $\eta=0.65$, 0.67, 0.68, and 0.69 (freezing point).

dal suspensions and Brownian dynamics simulations [7] for varying interparticle interactions. Furthermore, Löwen [35] has shown that the criterion does reasonably well for 2D colloidal fluids, making the Löwen-Palberg-Simon rule the only freezing criterion to hold simultaneously in two and three dimensions. Clearly, such a rule is not applicable for atomic liquids, which are governed by Newtonian dynamics and are therefore characterized by a single diffusion coefficient.

The criteria presented above are useful because they provide a means for locating the liquid-solid transition without resorting to free-energy calculations. Of course, such convenience is obtained at the cost of rigor, since thermodynamics dictates the equality of pressure, temperature, and chemical potential as the only criteria to be satisfied for coexisting bulk phases in equilibrium. Nevertheless, these rules suggest that some features of the freezing transition, at least for simple fluids, are universal in character. This is not surprising in light of the fact that dense liquids can be treated as a perturbation on the hard-sphere fluid [37,38], which itself (most likely [39]) exhibits an entropy-driven freezing transition in both two and three dimensions [40–42]. In fact, Longuet-Higgins and Widom [43] demonstrated that the freezing parameters for argon could be obtained from an extended van der Waals treatment of the hard-sphere fluid. This line of reasoning was instrumental in motivating the early order-parameter (density-functional) theories of freezing [13,44,45].

In this paper we present evidence that the simplest model fluids, namely, the hard-disk and hard-sphere fluids, exhibit a structural precursor to the freezing transition. This feature manifests itself as a shoulder just before the second peak of the fluid-phase radial distribution function (RDF) at densities close to (but below) to the freezing transition (see Figs. 1 and 2). The shoulder first becomes visible at a D-dimensional packing fraction $\eta\sim0.67$ for hard disks and $\eta\sim0.47$ for hard spheres. The D-dimensional packing fraction is defined as

$$\eta=\rho v(\sigma/2), \tag{1}$$

where ρ is the number density and $v(r)$ is the volume of a D-dimensional sphere of radius r,

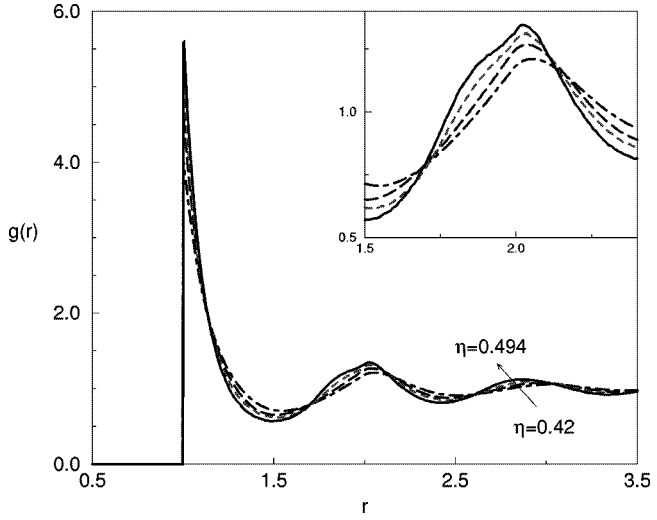


FIG. 2. Radial distribution function $g(r)$ for hard spheres plotted versus distance r (in units of diameters). Curves represent the fluid phase with $\eta=0.42$, 0.45, 0.47, and 0.494 (freezing point).

$$v(r)=\frac{\pi^{D/2}r^{D}}{\Gamma(1+D/2)}. \tag{2}$$

For example, for $D=1$, 2, and 3, $v(r)=2r$, πr^2, and $4\pi r^3/3$, respectively.

The onset of this significant structural change appears within 5% of the freezing transition, which occurs at $\eta_f\approx 0.69$ in two dimensions and $\eta_f\approx 0.494$ in three dimensions. Unlike the familiar split second peak that occurs in the RDF of the dense, metastable hard-sphere system (see, e.g., [46,47]), the appearance of the shoulder in the stable fluid phase is, for the most part, unrecognized. Labík and Malijevský [48] noticed the shoulder in their Monte Carlo simulations of the hard-sphere fluid. Upon further investigation [49,50], it was concluded that the shoulder marked the onset of the supercooled liquid, whose structure is similar to that of the amorphous solid. Giarritta, Ferrario, and Giaquinta [51] noted the shoulder in their curved space simulations of dense, hard-disk systems. It is interesting to note that both subpeaks and shoulders have appeared on the experimentally measured RDFs of several simple liquids. Their presence was originally attributed to finite truncation of the Fourier inversion integral of the structure factor. However, Fehder [52] has suggested, based on his study of Lennard-Jones disks, that the subsidiary features may actually result from alternative patterns of local ordering in the fluid.

In the present work we demonstrate that the appearance of the shoulder in the hard-disk and hard-sphere fluid corresponds to a salient structural feature that is not present in the low-density fluid. Furthermore, the data suggest that the structural motif is indeed a precursor of the crystalline solid.

II. RESULTS AND DISCUSSION

For our study of the fluid phase, molecular dynamics simulations were performed for systems of 500 particles in both two and three dimensions. The systems were equilibrated for a period of $5000N$ collisions, which was sufficient to guarantee reproducible thermodynamic properties. A slightly larger system of 780 particles was chosen to simulate

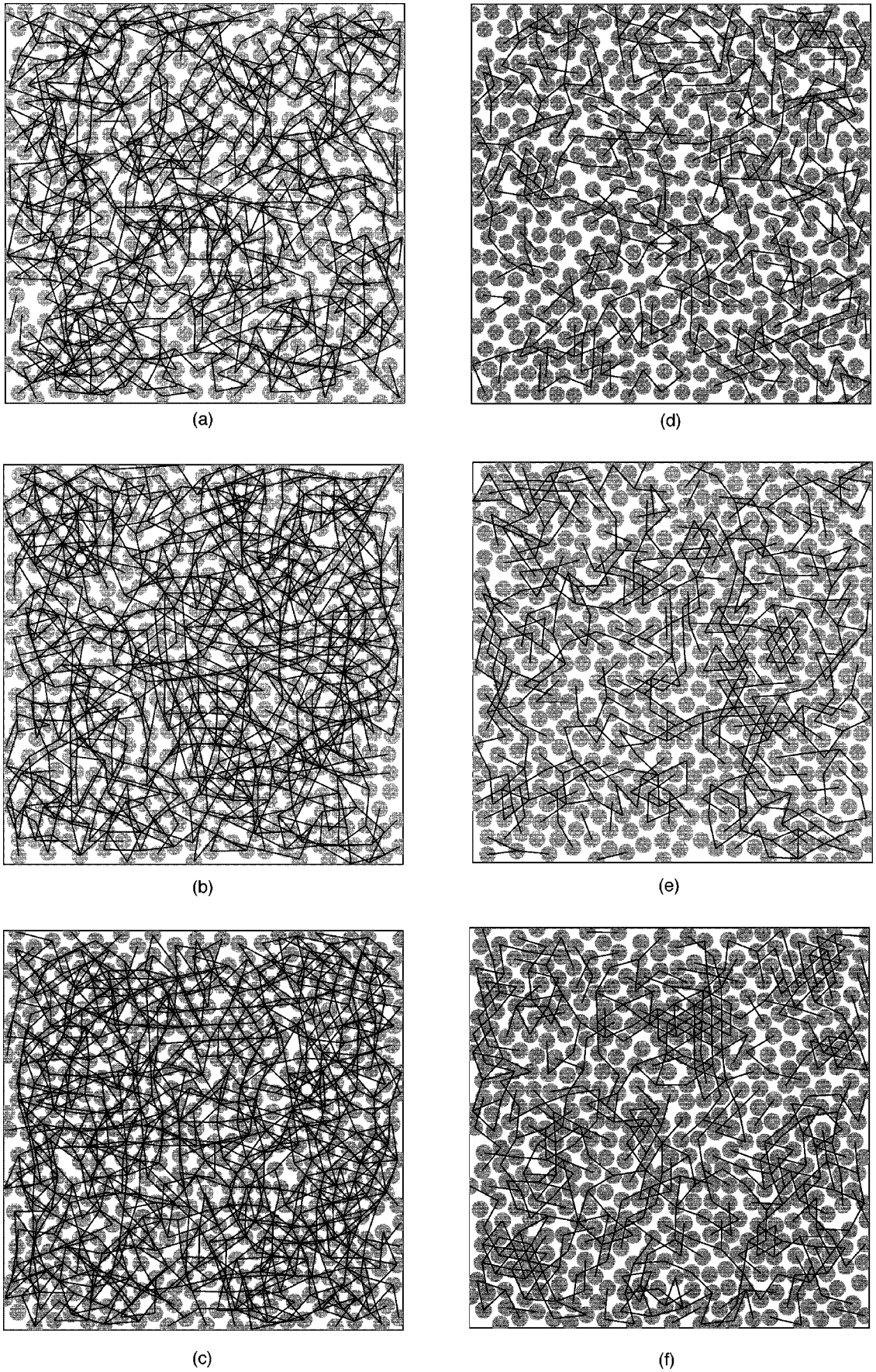
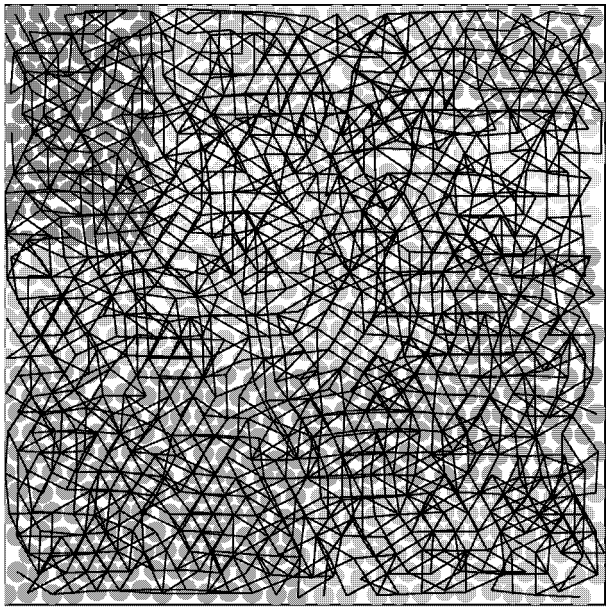
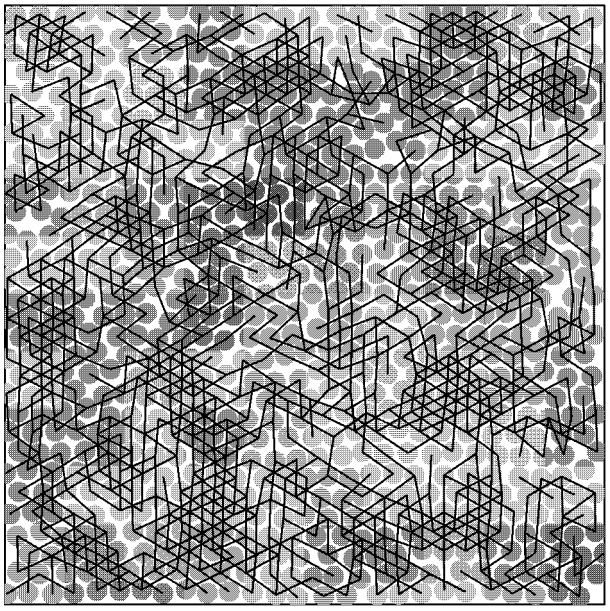


FIG. 3. Hard-disk fluid configurations are shown with second peak bonds ($r=1.95$–2.17) (a) $\eta=0.63$, (b) $\eta=0.67$, and (c) $\eta=0.69$ and with next-nearest-neighbor bonds ($r=\sqrt{3}$–1.95) (d) $\eta=0.63$, (e) $\eta=0.67$, and (f) $\eta=0.69$ referred to in the text.



(a)



(b)

FIG. 4. Hard-disk crystal at its melting point ($\eta_s = 0.716$) shown with (a) second peak bonds ($r = 1.95$–2.17) and (b) next-nearest-neighbor bonds ($r = \sqrt{3}$–1.95) referred to in the text.

the hard-disk solid at the melting point, i.e., at a volume fraction of $\eta_s = 0.716$ [53].

We have focused on the two-dimensional system, where it is possible to easily visualize the configurations. Close examination of the RDF reveals that the shoulder spans from $r \approx \sqrt{3}$ to $r \approx 1.95$ (in units of diameters). These values correspond to the next-nearest-neighbor distances in the triangular lattice at the close-packed density ($\eta_c = \pi/2\sqrt{3}$) and at the melting point density ($\eta_s = 0.716$), respectively. This indicates that the shoulder corresponds to the development of a distinct next-nearest-neighbor shell. To illustrate the structural change accompanying this feature in the RDF, we present in Fig. 3 a series of dense fluid configurations with

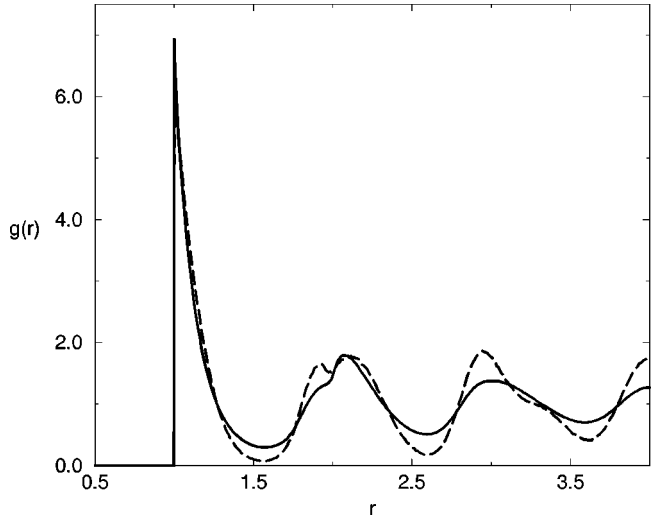


FIG. 5. Radial distribution function $g(r)$ for the hard-disk system plotted versus distance r (in units of diameters). The solid line represents the fluid at the freezing point ($\eta_f = 0.69$) and the dashed line represents the crystal at the melting point ($\eta_s = 0.716$).

bonds drawn between pairs of disks separated by distances $r = \sqrt{3}$–1.95. Typical fluid configurations at $\eta = 0.63$, 0.67, and 0.69 are shown. Bonds corresponding to an equivalent interval around the second peak ($r = 1.95$–2.17) are also shown. The comparison is striking. It is apparent that the next-nearest neighbors compose ordered, hexagonal domains that increase in size appreciably as the freezing transition is approached. In stark contrast, the bonds representing the second peak interval lack coherent orientational order.

Inspection of the ordered domains reveals that the bonds in the so-called shoulder interval ($r \approx \sqrt{3}$–1.95) correspond to a distinct structural motif: the four-particle hexagonal-close-packed configuration. In other words, the bonds connect pairs of particles that straddle another pair of particles at (or near) contact. Perhaps more surprising is the degree of orientational order that is exhibited at this length scale. The bond network associated with the equilibrium crystal at the melting point (Fig. 4) clearly supports the claim that the shoulder is a signature of ordered, crystalline domains rather than of the amorphous solid. Thus far, there is no numerical evidence for a kinetically stabilized extension of the fluid branch in the one-component hard-disk system. The nonexistence of a metastable fluid branch would remove the possibility that the shoulder corresponds to a precursor of the supercooled liquid or glass.

The hexagonal-close-packed motif and the corresponding shoulder that appear in the RDF should not be affected by an increase in system size if indeed the observed phenomena are real. As a check, a system of 2000 disks was also simulated. There were no distinguishable differences in the radial distribution function or in the configuration snapshots. This might have been expected since the box size is many times larger than the length scale associated with the observed shoulder.

A similar picture is expected to hold for the three-dimensional system, although it is more difficult to visualize. Here we draw attention to the fact that the shoulder in the 3D RDF is not as pronounced as its 2D counterpart. This is related to the fact that, as the dimensionality of space in-

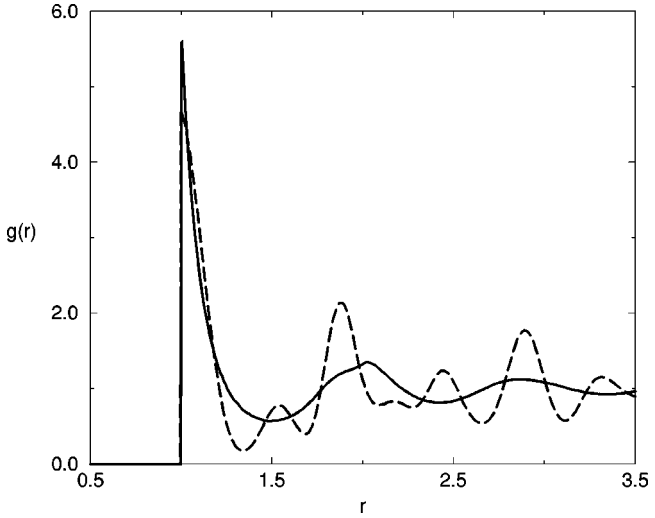


FIG. 6. Radial distribution function $g(r)$ for the hard-sphere system plotted versus distance r (in units of diameters). The solid line represents the fluid at the freezing point ($\eta_f = 0.494$) and the dashed line represents the crystal at the melting point ($\eta_s = 0.545$).

creases, more shells (with varying occupation numbers) are being formed between the first and second peaks in the RDF. For example, the fcc solid has a second-neighbor shell at $\sqrt{2}a$ and a third-neighbor shell at $\sqrt{3}a$, where a is the nearest-neighbor spacing. The RDF of the equilibrium fluid and crystal are shown in Figs. 5 and 6 for the hard-disk and hard-sphere systems, respectively. In both cases, the position of the shoulder in the fluid-phase RDF suggests local crystalline ordering.

The idea that the dense, equilibrium fluid contains ordered domains is not surprising. In fact, it is strongly suggested by other investigations of repulsive 2D liquids, e.g., [3,14,51,54–56]. An impressive example of this feature was put forth by Glaser and Clark [3,54,55], where it was demonstrated that the structure of a 2D Weeks-Chandler-Andersen fluid can be described as a tiling of squares and equilateral triangles. These studies motivated a provocative *generalized tiling model* [3] for melting in two dimensions. Remarkably, these structural features are not captured by many of the best available theories of the hard-disk and hard-sphere fluids. For hard spheres, the RDFs consistent with the Percus-Yevick [57,58] approximation and the generalized mean-spherical approximation [59] show no sign of a shoulder in the second peak. Perhaps this is expected since neither theory contains information about the freezing transition. Apparently the shoulder can be produced using parametrized bridge functions [48–50]. However, this approach is empirical and its physical implications remain unclear. We propose that the ability to reproduce the detailed structure of the hard-sphere and hard-disk fluids near the freezing transition and in particular the shoulder in the second peak of the RDF is a sensitive test of the accuracy of future theories of this important class of systems.

III. CONCLUSIONS

We have found evidence of a structural precursor to the freezing transition in the hard-disk and hard-sphere fluid. This feature can be identified with the development of a shoulder in the second peak of the radial distribution function of the fluid within 5% of the freezing transition. Inspection of the configurations of the hard-disk fluid near the freezing transition reveals that pairs of disks separated by distances in the shoulder interval straddle pairs of disks at contact. In other words, the shoulder in the RDF corresponds to the formation of a four-particle hexagonally close-packed motif. At the freezing transition the ordered regions form appreciably large embryonic domains. Examination of the structural features of the equilibrium crystal at the melting density reveals that the shoulder interval is indeed a signature of the equilibrium solid. It is not known if such a precursor holds for monatomic fluids in general, although this structural characteristic does appear to be associated with the onset of freezing in the 2D Lennard-Jones fluid [60].

Finally, we note that it would be instructive to study the size distribution of the ordered domains that exist near the freezing transition via large-scale simulations, i.e., system sizes that are much larger than the correlation length for orientational order in the fluid. Glaser and Clark [3] report that the ordered domains in the 2D Weeks-Chandler-Andersen system near freezing follow closely the size distribution predicted by the Fisher droplet model [61]. Further studies along this line should provide a benchmark for testing the classical nucleation theory.

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