

## Local structure analysis of the hard-disk fluid near melting

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(Received 19 December 1996)

The local structure of the hard-disk fluid is studied across its melting transition by means of Monte Carlo simulations and measurement of a local order parameter. Evidence for a linear behavior of this quantity in an intermediate density range is found, as well as indications for a possible ensemble difference between constant volume and constant pressure simulations within the presently accessible system sizes.

[S1063-651X(97)01505-5]

PACS number(s): 61.20.Ja, 61.20.Ne, 64.70.Dv

### I. MOTIVATION

The melting transition of strictly two-dimensional fluids, discovered as early as 1962 by Alder and Wainwright for hard disks [1], has been under debate since Nelson, Halperin, and Young proposed, based on ideas of Berezinskiĭ, Kostelitz, and Thouless, a novel continuous two-step scenario [2] in addition to the usual first-order one-step transition. This possibility spurred on the simulation community to search for this Halperin-Nelson-Young (HNY) transition in a variety of simple and complex fluids. We refer to the extensive reviews and discussions in Ref. [3] for more information. Despite this longstanding quest to solve the puzzle of melting in two dimensions more recently quite a few computational studies [4–17] reexamined the problem within various models and using many different techniques. For novel theoretical approaches see Refs. [18–20]. Stimulated by this renewed interest, we focus in the present paper on structural changes along the best studied two-dimensional melting transition, the hard-disk transition [1,21–24,4–7,10,11,14,15]. In particular, we investigate the behavior of the *local* order parameter based on a local structure analysis method [25,26] and constant volume Monte Carlo simulations and obtain bounds for the extension of the fluid-solid coexistence region. Our data lead us to suspect possible systematic discrepancies between results based on constant volume and constant pressure simulations.

### II. METHODS

The standard canonical Metropolis Monte Carlo algorithm with local moves was used to generate the configurations of the hard-disk fluid. The simulations were performed in a rectangular box of area  $V$  with an aspect ratio of  $2/\sqrt{3}$  subject to periodic boundary conditions, see Sec. III in Ref. [11] for details. The systems consisted of  $N=4096$  hard disks. Note that this relatively small system size is sufficient because we are at present not aiming to analyze a long-range order parameter, but rather focus on *local* properties. The systems were set up on a triangular lattice and were equilibrated for  $10^6$  attempted moves per particle each. After equilibration, 100 configurations were generated at each value of the density, with a propagation of 200 attempted

moves per particle between each two configurations. Previous investigations [10] had shown that the *global* bond-orientational correlation function typically decays on a time scale of 50 attempted moves per particle. The generated configurations can thus safely be regarded as statistically independent.

Densities are reported as usual in reduced units  $\rho = \sigma^2 N/V$  where  $\sigma$  denotes the hard-disk diameter. The conversion between this reduced density and the corresponding reduced volume  $v$  is given by  $\rho = 2/(\sqrt{3}v)$ . The maximally compressed solid attains a close-packed density of  $\rho_{\max} = 2/\sqrt{3} \approx 1.15$  in these units.

The technique we selected to monitor the fluid-to-solid transition relies on the analysis of local structures in the fluid [25], see Refs. [25,26] for more details. We quantify the local order near a point particle located at  $\vec{r}$  by the two-dimensional *local* version [25] of the rotationally invariant bond-orientational order parameter [27]

$$Q_l^2(\vec{r}) = \frac{4\pi}{2l+1} \sum_{m=-l}^l \left| \frac{1}{N_0} \sum_{i=1}^{N_0} Y_{lm}(\theta_i, \phi_i) \right|^2, \quad (1)$$

where  $N_0=6$  nearest neighbors are included. The variables  $(\theta_i, \phi_i)$  measure the angle between the imaginary bond between the central particle and the  $i$ th neighbor relative to some arbitrary but spatially fixed reference axis, and we choose  $\theta_i = \pi/2$  for the two-dimensional case. Two-dimensional systems with a sixfold orientationally modulated structure of the solid phase can be analyzed [25] via the local order parameter  $Q_6$ , henceforth denoted by  $Q$ . Contrary to other approaches, see the discussion in Ref. [26], the following analysis is based on the distribution function  $P(Q)$  itself, i.e., without defining any *global* order parameter obtained by averaging  $Q(\vec{r})$  over all bonds in the system [27]. The central idea [25,26] is to decompose a given configuration into patterns of typical local structures fluctuating around some “reference structures” sampled from distributions  $P_k(Q, \xi_k)$  for ideal local patterns  $\Gamma_k$  assuming that the fluid and the solid are characterized by different  $\Gamma_k$  and thus  $Q$  values. The natural choice  $\Gamma_h$  for a two-dimensional solid is the symmetric hexagonal seven-atom cluster with a sixfold coordinated central particle. Other patterns that we call

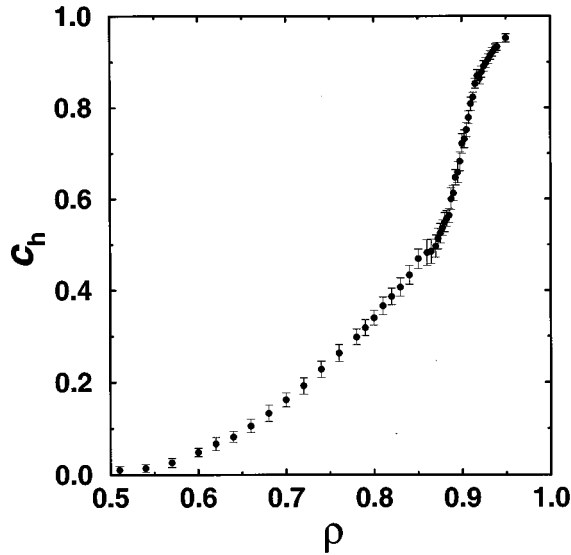


FIG. 1. Raw data for the local bond-orientational order parameter  $c_h$ , see text for the definition, as a function of the reduced density of the  $N=4096$  particle hard-disk fluid. Statistical error bars are shown.

$\Gamma_d$  correspond to nonhexagonal defect structures and reflect the arrangement of particles in the vicinity of dislocations. The statistical displacements of the particles constituting the clusters are taken into account as Gaussian fluctuations with a mean fluctuation amplitude  $\xi_h/\sqrt{2}$ . The simulated distribution  $P(Q, \rho)$  is decomposed into solidlike and fluidlike contributions

$$P(Q, \rho) = c_h(\rho)P_h(Q, \xi_h) + c_d(\rho)P_d(Q, \xi_d), \quad (2)$$

using three fit parameters  $c_h$ ,  $\xi_h$ , and  $\xi_d$ ; note that  $c_h + c_d = 1$  in this case. The distribution  $P(Q, \rho)$  was obtained from the Monte Carlo trajectories at 51 values of the density ranging from  $\rho = 0.51$  in the dilute fluid phase to  $\rho = 0.95$  in the solid phase.

### III. RESULTS AND DISCUSSION

The data including statistical error bars for the measure  $c_h$  of the contribution of local hexagonal order are shown in Fig. 1 as a function of density over the full range covered. The ideal solid phase in two dimensions is characterized by local (and in fact global, i.e., long-range) sixfold orientational order. Thus the function  $c_h(\rho)$  is expected to reach its largest value in the dense phase. The fluid phase, on the other hand, contains a large number of local defect structures with relative angles between the bonds that deviate from  $60^\circ$ , which leads to a small value of the local hexagonal order parameter  $c_h$ . In the limit of a very dilute fluid  $c_h$  should vanish. These expectations are borne out by the data. In the displayed density range spanning the regime from the dilute fluid up to the solid,  $c_h$  increases from essentially zero to nearly unity in the dense phase as expected. We note that the value in the solid phase is slightly smaller than unity because of a well-defined average number of defect and interstitial sites that are present in thermodynamic equilibrium.

A closer inspection of the data in Fig. 1 reveals that  $c_h$

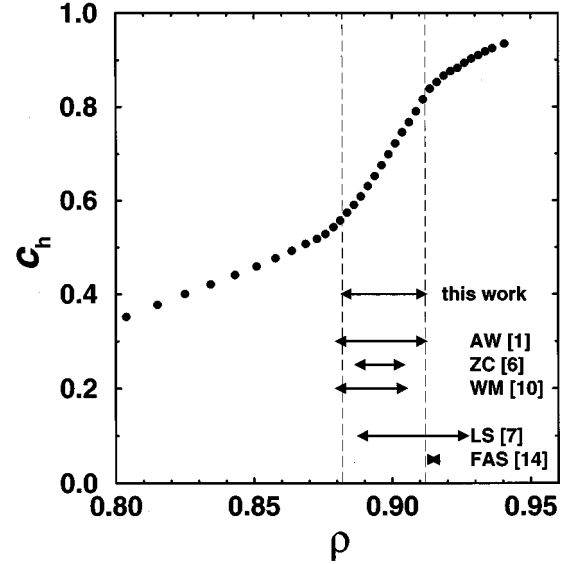


FIG. 2. Smoothed  $c_h$  data from Fig. 1, see text for more details, as a function of the reduced density of the  $N=4096$  particle hard-disk fluid close to the transition region. Previous simulation estimates of the coexistence region or transition point are included for comparison, see Table I for further details.

increases in a nonlinear fashion from zero to a value of about 0.5 at a density that is slightly larger than 0.85. From there on it appears to increase linearly to a density of about 0.9, followed again by a nonlinear increase before it reaches its largest value in the densest system investigated. These raw data for  $c_h$  are subject to statistical scatter, and especially so at the onset of the linear regime. Therefore we applied a smoothing procedure to the data of Fig. 1 by taking local running averages of these data. The result is presented in Fig. 2 in the density range of interest; error bars are difficult to assess in this case and were therefore omitted. After reduction of the scatter the three regions, and especially the densities which separate them, appear much more clearly. The low density boundary of the intermediate linear region is  $\rho_f \approx 0.882$ , and its upper limit is  $\rho_s \approx 0.912$ . We applied running averages of different lengths to the raw data; all of them yield very similar results for the extension of the linear region in the plot.

What is the meaning of the special densities  $\rho_f$  and  $\rho_s$  that delimit the linear region? The quantity  $c_h$  as we define it can be viewed as a specific *local* order parameter for sixfold bond-orientational order [3]. In the case of a first-order phase transition in an ensemble that allows for the coexistence of the ordered and disordered phases, such a quantity is expected to increase linearly in the coexistence region from a small value at the boundary with the pure disordered phase to a larger value at the point where the ordered phase becomes stable as a pure phase. This is nothing else than the classic lever rule that governs phase coexistence. The  $c_h$  data in Fig. 2 with the linear region around densities of 0.9 clearly display such a behavior. In addition, it should be kept in mind that  $c_h$  is a *local* measure of the bond-orientational order of the fluid which is defined on the smallest meaningful length scale. On the basis of these considerations we conclude that  $\rho_f$  and  $\rho_s$  are generous estimates for the bounds that separate the fluid-solid coexistence region from

TABLE I. Estimates for the extension in density of the fluid  $\rho_f$  and solid  $\rho_s$  phases of the hard-disk system; see text for a discussion and more details.

Authors	Reference	$\rho_f$	$\rho_s$	$\rho_0$
Alder and Wainwright 1962 Canonical: $N=870$ , PBC <sup>a</sup> van der Waals loop in $p$ vs $\rho$ curve	[1]	0.880	0.912	
Zollweg and Chester 1992 Canonical: $N=16384$ , PBC Tie line from histogram reweighting	[6]	0.887	0.904	
Lee and Strandburg 1992 Constant pressure: $N\leq 400$ , PBC	[7] <sup>b</sup>	0.888	0.927	
Weber and Marx 1994 Canonical: $N=16384$ , PBC Finite-size scaling, cumulant analysis	[10]	0.880	0.905	0.8985 <sup>c</sup>
Fernández, Alonso, and Stankiewicz 1995 Constant pressure: $N\leq 15876$ , HCW <sup>e</sup> Finite-size scaling assuming HNY behavior	[14]	0.916	0.914	0.916 <sup>d</sup>
Present work Canonical: $N=4096$ , PBC Local structure analysis		0.882	0.912	0.897 <sup>f</sup>

<sup>a</sup>Periodic boundary conditions.

<sup>b</sup>Values obtained by extrapolating the data in Fig. 5, quoted from Ref. [6].

<sup>c</sup>Crossing point of order parameter cumulant.

<sup>d</sup>Essential divergence of correlation length from a HNY fit of fluid phase data.

<sup>e</sup>Hard crystalline wall boundary conditions.

<sup>f</sup>According to lever rule  $\rho_0 = \rho_f - (\rho_s - \rho_f)x$  for  $x = 1/2$ .

the pure fluid and pure solid phases, respectively. The midpoint of the coexistence region is simply given according to  $\rho_0 = \rho_f + (\rho_s - \rho_f)x$  for  $x = 1/2$ , where  $x$  is the fraction of the solid phase in the coexistence regime. Using the densities  $\rho_f$  and  $\rho_s$  inferred from Fig. 2, we obtain  $\rho_0 \approx 0.897$  for the density at which the fluid and solid phases contribute with equal weight to the hard-disk system in the coexistence regime.

Let us compare these data inferred from the local structure analysis with data based on different approaches. Some of the previous estimates for the coexistence region of the hard-disk system are indicated by arrows in Fig. 2 in an obvious notation, and are collected with more information in Table I. Our upper bound agrees best with the classic estimate of Alder and Wainwright (AW) [1]. This is consistent since this estimate was obtained from small systems of only  $N=870$  particles, which should compare well to a bound that is derived from a *local* order parameter. The two remaining much more recent estimates of Zollweg and Chester (ZC) [6] and Weber and Marx (WM) [10] based on constant volume simulations fall into the coexistence region as delimited by our present bounds. However, the coexistence region from ZC [6] and WM [10] is much narrower, which is again consistent as these estimates were obtained with much larger systems and finite-size scaling [10]. We mention in passing that the estimate  $\rho_0$  that we obtained by making use of the simple lever rule and our coexistence boundaries is close to the value obtained from the cumulant intersection method [10], see Table I and Refs. [10,11] for more information. This is consistent because both procedures should yield an estimate for that density at which the two coexisting phases

contribute with equal weight to the system under coexistence.

The remaining two calculations of Lee and Strandburg (LS) [7] and Fernández, Alonso, and Stankiewicz (FAS) [14] resulted in melting densities that are not contained in the bounds obtained from the analysis of the local orientational properties of the hard-disk system. It should be noted that Lee and Strandburg [7] did not themselves report these estimates for the extension of the coexistence region since they conclude that they “are not in the scaling regime yet;” here, we use the values as quoted in Ref. [6], which can be obtained by linear extrapolation of the data plotted in Fig. 5 of Ref. [7]. But nevertheless, Lee and Strandburg state “that the melting density is somewhat higher than previously believed” [7]. In the most recent investigation by Fernández and co-workers (FAS) [14] based on quite large systems the authors used finite-size scaling of the bond-orientational susceptibility assuming HNY-type behavior (see, however, Ref. [15] for a critical discussion). They argue that a single continuous transition from the fluid to the solid occurs at a density of about  $\rho_0 \approx 0.916$ ; the corresponding boundaries depicted in Fig. 2 indicate the inferred mutual overlapping extensions of the fluid and solid phases [14]. This density is higher than any other estimate, except for the extrapolated melting density of Lee and Strandburg [7]; we mention that nonperiodic boundary conditions, the hard crystalline wall boundary conditions [8], were used by FAS [14], whereas periodic boundary conditions were applied in all other hard-disk simulations. The common feature of the two calculations, LS [7] and FAS [14], which both lead to higher  $\rho_s$  values, is that they were both performed in the constant pres-

sure ensemble, and not in the constant volume ensemble like all the other simulations. In the present context, this could be interpreted as an indication that constant pressure simulations tend to yield a higher density  $\rho_s$  above which the pure solid phase becomes stable than constant volume simulations based on similar particle numbers.

At this point it should be mentioned that standard constant volume simulations impose periodic boundary conditions based on a fixed box which especially for small system sizes tend to bias the system. This might lead to a stabilization of the ordered phase in cases where for a given volume the fixed shape of the simulation box is chosen to be commensurate with the expected lattice structure of the stable solid phase. Constant pressure simulations, on the other hand, should be less biased in favor of the solid as the volume is allowed to fluctuate during the simulation. FAS [14], however, do not use periodic boundary conditions in their constant pressure simulations, but rather the nonperiodic hard crystalline wall boundary conditions [8] in order to facilitate the nucleation of crystal growth [14]. Thus the reflecting boundary of their fluctuating simulation box is given by that of a rectangular box superimposed on a triangular lattice where all sites on the boundary are occupied by disks. This again seems to favor the ordered phase for small system sizes, which is similar to the bias in constant volume simulations. The least bias in simulations using a constant number of particles is expected for the Parrinello-Rahman method where both the volume and the shape of the box are allowed to fluctuate [28]. Of course, all these considerations become the less important the larger the system.

#### IV. SUMMARY AND CONCLUSIONS

Constant volume Metropolis Monte Carlo simulations of systems of 4096 hard disks were performed. For many densities spanning the range from the dilute fluid to the dense solid, the configurations were analyzed in terms of a *local* order parameter that is sensitive to the degree of local sixfold bond-orientational order. This quantity is found to increase from a minimum value in the fluid phase to its maximum in the solid. We observe an intermediate density region where this increase is effectively linear as expected in the case of a first-order transition, and thus obtain generous bounds for the extension of a possible coexistence region between the fluid phase and two-dimensional solid phase. This estimate for the coexistence region is consistent with the previously published data obtained in the constant volume ensemble. However, those estimates for the melting density that were obtained with constant pressure Monte Carlo methods have a tendency to exceed our bound as well as the other estimates based on constant volume simulations. Based on this observation, one is tempted to speculate that this might be a manifestation of an ensemble difference due to finite particle numbers. A similar conclusion was already reached for a purely repulsive Weeks-Chandler-Andersen soft-disk fluid simulated in the constant volume and constant pressure ensembles [9] using molecular dynamics. Because these observations are most probably also valid for other fluids in two dimensions further clarification of that aspect is certainly warranted.

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