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Local structure, fluctuations, and freezing in two dimensions

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Starting from the concept of local solidlike order in two-dimensional (2D) liquids we introduce and quantify the corresponding ensembles of fluctuations, using a probabilistic-based method of local-structure analysis (LSA). A systematic LSA (including size dependence) was performed for a hard disk and 2D Lennard-Jones systems, simulated using Monte Carlo and molecular-dynamics methods. We find that the onset of freezing is accompanied by a dramatic crossover between ensembles of fluctuations. Some universal features related to the onset of freezing in two dimensions are found and corresponding freezing criteria are formulated: (i) the liquid starts to freeze when the concentration of solidlike atoms constitutes 0.50–0.56, and (ii) a Lindemann-like freezing criterion: the rms fluctuation constitutes, at the onset, 0.12–0.13. Those criteria offer an effective method for a localization of the onset of freezing in computer simulations. We point out, in this context, that in computer simulations there is a possibility that all quantitative characterizations of the onset of freezing are related to a metastable range. This important methodological topic is discussed briefly in the light of recent results both for 2D and 3D systems.

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I. PHASE DIAGRAMS, LOCAL ORDER, AND FLUCTUATIONS IN CONDENSED MATTER: AN OUTLINE

The liquid-crystal phase transition has been the object of numerous experiments and theoretical studies; more recently, increased computer power allows one to study liquids using computer simulations with realistic potentials. Particularly, the position of the melting and crystallization lines in the thermodynamic (T-ρ) plane can be predicted. Here, T is the temperature and ρ the particle density. The most challenging question is that of the nature of changes in the local and global structure of the system at melting/crystallization, related to the general question of the liquid structure. In this paper we concentrate on two-dimensional (2D) systems, which are known[1] to exhibit some peculiarities as compared to ordinary 3D matter. The origin of special features of 2D liquids lies in large (as compared to the 3D case) long-wavelength fluctuations. We study two simplest models of the 2D melting/freezing transition, the hard disk fluid and Lennard-Jones (LJ) fluid. The strictly 2D LJ systems have been intensively studied by various theoretical approaches[2–6] as well as by computer simulations.[3–7] In general, the phase diagram for 2D LJ systems is quite well known. It exhibits 2D counterparts of all familiar states of matter in three-dimensional space: gas, liquid, and solid. The triple point temperature has been estimated quite accurately as equal to $T_t^* = 0.40 \pm 0.015$.[3,8] The reduced temperature is $T^* = k_B T/\varepsilon$, where k_B stands for the Boltzmann constant and ε sets the energy scale for the Lennard-Jones potential. Existing estimations of the critical temperature[9,10] are much less conclusive, because of well-known difficulties with interpretation of computer simulation results in the vicinity of second-order phase transitions. An up-to-date discussion of this topic can be found in Ref. 11. Freezing/melting phenomena in 2D hard disk systems are reviewed in Refs. 12–28.

The special role of long-range fluctuations in 2D ordered systems was revealed in the papers, published in the 1930s, by Peierls[29] and Landau.[30] They argued that truly long-ranged positional order cannot exist in two-dimensional systems. This was rigorously proven later by Mermin and Wagner.[31] In the 1970s, Kosterlitz and Thouless[32] and Berezinskii[33] proposed a theory of dislocation-mediated melting for two-dimensional systems, later developed by Halperin and Nelson[34,35] and by Young [Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY)].[36] The KTHNY theory confirms that 2D systems may posses only quasi-long-ranged positional order, characterized by algebraic decay of the two-particle correlation function, and predicts a two-step melting in two dimensions, via two continuous phase transitions, first to a hexatic phase characterized by a crystalline local order and some density of paired and free defects, and then to a liquid state. The local structure of this liquid state may differ from what is assumed in the KTHNY theory, making the description of the ‘‘true’’ melting inaccurate. Other theories of 2D systems[37–40] predict a ‘‘usual’’ first-order melting in 2D systems. The concept of first-order melting was advocated by Abraham,[7,41] who argued that the loss of positional order is negligible in real systems due to their limited, though macroscopic, size. Some other theoretical approaches can be found in Refs. 42–44. Computer simulations[1,7,8,19,22,25–27,41,45,46] and physical experiments[47–51] do not give conclusive results regarding the important question of melting in two dimensions. Very recent simulations of a hard disk liquid are compatible with a two continuous transitions scenario. Nevertheless, the possibility of a (very weak) first-order transition from liquid to crystal cannot be firmly ruled out.[28] In both cases there exists two densities, $\rho_l < \rho_s$, which separate liquid and crystal phases. In the former case, at those densities continuous phase transitions take place; ρ_l and ρ_s determine the boundaries of the hexatic phase. In the later case, ρ_l and ρ_s determine the boundaries of the solid-liquid coexistence region; they are called liquidus and solidus densities, respectively.

Our study is focused on the onset of freezing, i.e., the phenomena taking place close to the density ρ_l both in the liquid phase and in the transition region (hexatic phase or coexistence region). For historical reasons we interpret the occurring phenomena using the terms of liquidus, solidus, and liquid-solid coexistence, which by no way excludes the quite probable, in light of Ref. 28, KTHNY scenario. Note that a study of long-range correlations in the hexatic phase requires massive simulations of systems much larger than those considered in our study. While elaborate and effective methods for calculation of the phase diagrams in computer simulations were worked out, a sound understanding of what actually happens in the coexistence region is still a challenge. Therefore, to clarify the physical picture of a freezing transition is important; only when this task is completed can one introduce appropriate physical quantities that characterize freezing phenomenon in computer simulations.

Lever-rule-like arguments (see, e.g., Ref. 52), various thermodynamic integration schemes and integral equation approaches for studying the phase diagrams, allow to calculate the thermodynamic properties. We are, however, interested in understanding the changes in the local structure in the coexistence region. This aspect of a freezing is very important both from material science and theoretical points of view. We discuss briefly the two main concepts related to the local structure, that of ideal local structure, and fluctuations of the structure.

The hypothesis of local order in liquids has a long history. Numerous experimental results yielding indirect proof of the existence of some kind of local order in liquids have resulted in local-order hypotheses formulated years ago at various qualitative and quantitative levels, see, e.g., Refs. 53 and 54. A qualitative description of a typical liquid configuration, based on the concept of solidlike clusters, was formulated by Frenkel,[55] who underlined their kinetic rather than thermodynamic character. The quantification of those ideas in terms of particle correlation functions is rather difficult. Both computer-based calculations[56,57] and experimental[58–61] measurements of triple correlation functions are technically very difficult. As a rule,[62] liquid is described in terms of a pair-correlation function $g_2(r)$ only, which contains little information about local symmetries. This technical problem limits the area of physical effects studied within statistical-mechanics methods in liquids, in comparison to solids. We point out that solid-state physics owes a rich variety of physical effects to the underlying concept of the symmetry of the crystalline lattice (Curie principle). The question whether the physics of liquids is actually much more rich than physics described in terms of $g_2(r)$ remains open. A liquid with local order is globally disordered; recent progress in disordered systems might justify efforts to construct theories of liquids based on concepts of local symmetries, reminding of local symmetries in field theories. Ideas of this kind has lead to the concept of structural discontinuous liquid-liquid phase transitions,[63] reported in experiments[64] and simulations,[65] taking place not only in classical systems, but also in 2D vortex matter.[66]

One of the ways out of this difficulty is an introduction, *a priori*, of local-structure order parameters. The attempts of a quantification of the concepts of Frenkel in the language of fields of local-order tensor parameters and effective Hamiltonians[67–69] have initialized statistical-mechanics treatment of equilibrium liquids as locally ordered matter. In two dimensions it is KTHNY theory; in three dimensions a theory was formulated,[70] but quantitative analysis is still a challenge. An explicit form of an order parameter depends on physical assumptions concerning details of the local structure. Starting from noncrystalline patterns based on icosahedron, much progress in understanding structure of glasses, metallic glasses, and undercooled liquids[71–74] was achieved. On the other hand, studies based on local crystalline order[69,75] have contributed to a better understanding of some general features connected with melting (see, e.g., Ref. 76).

The second aspect of the local order in liquids is that it manifests itself in the presence of strong fluctuations, so that a physically meaningful definition and practical recognition of this order is far from being a trivial task. Intuitively, one expects the order in a small cluster to represent a special arrangement of particles. For example, in a hard sphere or 3D LJ system, one looks for icosahedric, fcc, or hcp structure in a 13-particle cluster that includes a central particle and its first coordination shell.[71] With this assumption, one represents the physical positions of particles in the cluster in terms of small displacements from their ideal positions in the arrangement.

If the idea of an ideal local order is accepted, it immediately invokes the next question: how many different ideal structures are necessary to describe all the local situations in the liquid? Introduction of the minimal full set of ideal local structures results in a natural division of the configuration space of a cluster into domains representing the ideal structures; each domain includes, together with an ideal structure, all fluctuations of this structure. The ensembles of those fluctuations play a decisive role in determination of local and global physical properties of the system.

Those general ideas and, in particular, the role of various ensembles of the fluctuations, are readily applied to supercooled liquids and glasses. In those systems, a particle is assumed to vibrate in a relatively stable cage made by surrounding particles. The lifetime of this cage is much larger than the vibration period. The particle and its cage constitute the smallest cluster that can be described in terms of structure. At low temperatures and high pressures, in supercooled metastable liquids, various ideal configurations of the cluster are separated by high enough energy barriers, and the lifetime of a chosen local structure in a cluster becomes very large compared to the particle vibration period. A dramatic increase of the local-order lifetime is seen in the increase of viscosity and in the rapid shift of the α-peak frequency upon supercooling in glass formers.[77] For those systems, a classification of typical configurations as fluctuations around configurations corresponding to local minima of the energy can be done using the energy landscape picture in the theory of the liquid state, see, e.g. Ref. 76. The Hamiltonian assigns a potential energy to each point of the configuration space. In general, the energy landscape is assumed to have many local minima of the potential energy and barriers intervening between them. The division of the configuration space into basins of attraction, closely related to the concept of inherent structures,[78] provides a basis for a classification of typical configurations. A physical picture of the process of changing the basin was formulated in terms of local rearrangement in glassy materials.[79] The problem of an ensemble of the fluctuations in one basin was studied recently;[80] the interbasin fluctuations were analyzed in Ref. 81. The crossover between various types of ensembles is one of the most important topics in the physics of supercooled liquids and glasses.

The situation for the equilibrium liquids is more difficult. At higher temperatures the fluctuations are larger, and larger parts of the configuration space have to be taken into account, leading to difficulties with the concept of a typical configuration in a liquid. On the other hand, one expects intuitively that the ensembles describing the fluctuations in liquid and solid differ noticeably. In this case, freezing should be accompanied by a dramatic crossover between them. Thus, finding a quantitative measure for those ensembles constitutes an important task for equilibrium liquids, which may cast some light onto the physics of the coexistence region.

The above considerations applied to 3D equilibrium liquids have rather a speculative character. In two dimensions the situation is quite different. Local-structure analysis of various 2D liquids, based on probabilistic concepts discussed in the next section, has revealed a high concentration of local solidlike structures close to the two-phase region[25,82,83] (see also Ref. 76). Thus, at least for those solidlike structures, one can (hopefully) introduce ensembles of fluctuations and analyze their behavior in the coexistence region. The emerging hypothetical physical picture looks as follows. Two important processes occur at 2D freezing. First, the concentration of solidlike structures just continues to increase. Second, the character of the fluctuations of the atoms constituting solidlike structures changes from a liquidlike-type to a solidlike-type. In a 2D solid, long-wavelength phonons play a crucial role (actually, they lead to a restoration of translational symmetry in the thermodynamic limit). Density of those phonon states is proportional to the wavelength vector k ($k \ll 1/a$, where a stands for the lattice constant), to be compared with k^2 in three dimensions. Thus, a highly correlated motion of small groups of the atoms is expected to occur to a much higher extent than in 3D solids. Contrary to the case of a solid, a quantification of an ensemble for a liquid requires sound physical assumptions. We deal with this task only for the local solidlike part of the liquid. Under the assumption that only short-range correlations between the motions of atoms are present in this part of a liquid, we introduce an ensemble of independent Gaussian fluctuations (IGF) for the description of the movements of the atoms belonging to locally solidlike ordered structures. In this scenario, freezing corresponds to a breakdown of IGF, because of a rapid onset of correlations between the fluctuations, typical for 2D solids. Since those correlations are strong in a solid phase, this breakdown may have a well-defined, spectacular character, and may provide means, complementary to the existing ones, oriented to localization of the freezing in computer simulations.

The aim of this paper is to propose an effective method for a localization of the onset of freezing in two dimensions, starting from fluctuation-oriented physical arguments based on local-structure features of two-dimensional liquids.

The paper is organized as follows. In the next section we present briefly the method for local-structure analysis in 2D liquids. Section III is devoted to a study of various local-structure aspects of freezing in a liquid of hard disks; an analogous study for a 2D LJ liquid (along various paths in the ρ-T plane) is presented in Sec. IV. The emerging physical picture is discussed in Sec. V, in particular, the aspect of applications for an effective localization of an onset of freezing in 2D liquids.

II. LOCAL-STRUCTURE ANALYSIS (LSA)

Local order in a 2D system in the neighborhood of an atom located at the point $\vec{r}$ is described by a 2D local version of the bond-order parameter of Nelson *et al.*:[68,71,82]

$$Q_{6m}(\vec{r}) = \frac{1}{N_0} \sum_{i=1}^{N_0} Y_{6m}(\pi/2, \phi_i), \tag{1}$$

where $Y_{6m}(\theta,\phi)(m=-6,\ldots,6)$ denotes the spherical harmonic function, where the sum is taken over the N_0 nearest neighbors of the atom located at the point $\vec{r}$, and the pair of azimuthal and polar angles, (θ_i, ϕ_i), describes the direction between the central atom $\vec{r}$ and its ith nearest neighbor. The invariant $Q(\vec{r})$ for an (N_0+1)-atom cluster with the central atom at $\vec{r}$ is defined as[71,82]

$$Q^2(\vec{r}) = \frac{4\pi}{13} \sum_{m=-6}^{6} |Q_{6m}(\vec{r})|^2. \tag{2}$$

In the spirit of the method of analysis of local 2D structures,[82,25,83] we use two patterns as the candidates for the local structure in the system. Pattern Γ_6 is a 2D hexagon, i.e., a $N_0+1=7$-atom cluster from a 2D triangular lattice. The nearest-neighbor distance is taken as the unit of length. Pattern Γ_5 is a seven-atom cluster centered around a five-coordinated atom (disclination in a 2D triangular lattice). Fluctuating patterns Γ_6 and Γ_5 are described in terms of the probability density functions (PDF) $\rho_6(Q,\xi)$ and $\rho_5(Q,\xi)$. Following the arguments presented above, we use an independent Gaussian ensemble for the modeling of the fluctuations of the atoms. Each of the six neighbors of the central particle fluctuates independently of the other atoms, according to a Gaussian distribution

$$P(\delta\mathbf{r};\xi)=\frac{1}{\xi\sqrt{\pi}}\exp[-(\delta\mathbf{r})^2/\xi^2], \tag{3}$$

with random displacement vectors $\delta\mathbf{r}$ and root-mean-square (rms) displacement ξ. The resulting PDF $\rho_6(Q,\xi)$ and $\rho_5(Q,\xi)$ for Γ_6 and Γ_5, respectively, are then dependent on the amplitude ξ of the fluctuations. The role of the averaged (over the atoms) root-mean-square displacement in our simulation of patterns is played by quantity $\sqrt{(\Delta\vec{r})^2}=\xi/\sqrt{2}$.[25,83]

The statistics of invariant Q in the trial configuration is described by PDF $\rho(Q)$ which are approximated by the histogram of the random variable Q, calculated from the set of data $\{Q(\vec{r}_i)\}, i=1,\dots,N$, where N denotes the total number of the atoms in the configuration.

The analysis of local structures is done using the methods of mathematical statistics.[82] We assume that $\rho(Q)$ depends linearly on PDF $\rho_k(Q,\xi_k)(k=5,6)$:

$$\rho(Q)=\sum_{k=5,6} c_k\rho_k(Q,\xi_k). \tag{4}$$

The ‘‘best’’ decomposition (4) is obtained by maximizing the significance level

$$\alpha(c_5,c_6,\xi_5,\xi_6) \quad (c_5+c_6=1, c_5,c_6\geqslant 0),$$

calculated from a χ^2-test (see, e.g., Ref. 84) verification of the hypothesis which states that the data corresponding to the left-hand side and the right-hand side of Eq. (4) are drawn from the same distribution. Very small values of α (of order of 10^{-6} and smaller) indicate that the decomposition (4) is statistically not reliable. Significance level α plays a central role in our analysis of ensembles of fluctuations.

Each seven-atom cluster can be identified as a fluctuation either of the pattern Γ_5 or Γ_6 via a maximal probability decision rule (MPDR).[82,85] It states that a trial cluster with $Q=Q^*$ is a fluctuation of Γ_6 when $Q^*\geqslant Q_0$, for some fixed value of Q_0. The central atom of such a cluster is called a solidlike atom; the remaining atoms in the liquid are called liquidlike. In the present paper we are interested only in the properties of solidlike atoms. Thus, if not otherwise stated, in the context of LSA the concepts of atoms and their fluctuations refer only to solidlike atoms and their fluctuations.

The MPDR-based classification has a probabilistic character. The total probability of a false classification, a fluctuation of pattern Γ_5 as a fluctuation of pattern Γ_6 and vice versa, is given by the degree of overlap of the corresponding PDF:

$$E(\xi_5,\xi_6)=\int \min[\rho_5(Q,\xi_5),\rho_6(Q,\xi_6)]dQ. \tag{5}$$

$E(\xi_5,\xi_6)$ is a measure of structural identity of two fluctuating patterns. When the overlap is small then the probability of a false classification is also small and fluctuating structures preserve their structural identity. With increasing fluctuation level the overlap of the PDF increases and the structural identity of fluctuating patterns is gradually lost. More information on mathematical aspects of structural identity can be found in Ref. 85. In our simulations, the probability of an erroneous classification of a non-solid-like atom as a solidlike one is small; on the liquidus line it is approximately equal to 0.07. In this sense the fluctuating local solidlike structure is well defined (see also in Ref. 83, where the plots of PDF are presented).

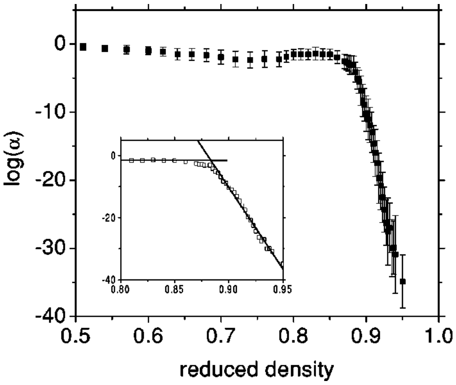

FIG. 1. Plot of the logarithm of significance level, log α, against the reduced density ρ^* for $N=4096$ hard disks. Inset: The same for the densities close to the coexistence region.

III. HARD DISKS

A system of $N=4096$ hard disks at constant volume was simulated using the standard Metropolis Monte Carlo method.[86,87] The details of the simulations were presented in Ref. 25. For the densities spanning the interval from low-density liquid to high-density solid, the concentration $c_6(\rho^*)$ was found ($\rho^*=\sigma^2\rho$, where σ denotes the hard disk diameter). The plot, cf. Fig. 1 in Ref. 25, consisted, for intermediate densities, of three nearly linear parts (Fig. 2 in Ref. 25). The intersection of their linear extrapolation has lead to generous bounds $\rho_l^*\simeq 0.882, \rho_s^*\simeq 0.912$ for the coexistence region between the liquid and two-dimensional solid. The estimate was consistent with previous results obtained for a constant-volume ensemble.[12,19,21] The midpoint of the coexistence region $\rho_M^*\simeq 0.897$ is the density at which the liquid and solid phases contribute with equal weight to the local solidlike structure in the coexistence regime. This value is close to the value $\rho^*\simeq 0.899$ obtained using the cumulant intersection method in Ref. 21 (see also Ref. 22) developed for an estimation of the density at which the two coexisting phases contribute with equal weight to the system under coexistence.

LSA-based analysis of fluctuations in the liquid is done using the significance level. Figure 1 demonstrates a spectacular breakdown of the IGF as the density increases. The plot of $\log\alpha(\rho^*)$, calculated using 50 or 100 configurations (the later for the densities $0.85\leqslant\rho^*\leqslant 0.93$), displays two regimes. For the densities lower than $\rho_0^*=0.884$ the significance level shows (within the statistical errors) no systematic dependence on the density. It takes the values larger than 10^{-3}, thus giving no ground to question the usefulness of IGF for solidlike atoms in liquid. The estimate for ρ_0^* was calculated using linear fits to the data. This construction, using 50 configurations, is shown in the inset to Fig. 1. For the

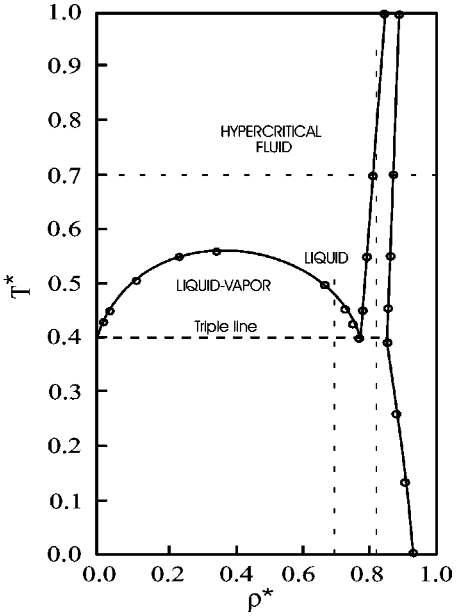

FIG. 2. The paths in the $\rho^* - T^*$ plane along which the freezing of a 2D LJ liquid was studied. The phase diagram is taken from Ref. 11 after Ref. 45.

densities higher than ρ_0^* the significance level decreases dramatically as the density increases, e.g., for the density higher by 4% than ρ_0^*, the significance level drops to 10^{-6}. Small values of α rule out the applicability of IGF; one observes a dramatic crossover from IGF to another ensemble which accounts for the correlations typical for the atoms in solids, in agreement with the scenario discussed in the Introduction. The density $\rho_0^* = 0.884$ is very close to the estimated density at the liquidus line $\rho_l^* \simeq 0.882$. The meaning of this observation is discussed in Sec. V A.

IV. LENNARD-JONES LIQUID

We analyze the freezing of the 2D LJ system along $\rho^* = \mathrm{const}$ and $T^* = \mathrm{const}$ paths in ρ^*-T^* plane, see Fig. 2. Here, $\rho^* = \sigma^2 \rho$, where σ is the length parameter of the LJ potential. For constant-volume freezing studies we have chosen two paths: $\rho^* = 0.694$ and $\rho^* = 0.833$. The former density is smaller and the latter larger than the density of the triple point $\rho_t^* = 0.79$.[45] The constant-temperature studies were made at the temperature $T^* = 0.7$, i.e., well above the critical-point temperature.

The systems of constant density ρ^* were simulated via a standard NVT Monte Carlo method. For thermalization $10^6 - 5\times 10^6$ Monte Carlo steps (MCS's) (1 MCS corresponds to one sweep over all particles) were used and the equilibrium parameters were calculated using $5\times 10^6 - 10^7$ MCS. The results of local-structure analysis were averaged over 20 statistically independent configurations. On the other hand, systems lying along $T^* = \mathrm{const}$ paths were simulated via a standard NVT molecular-dynamics (MD) method,[87] using a velocity Verlet algorithm with a time step $t_0 = 0.064\tau$, where the time unit $\tau = 0.3113$ ps. Long-range corrections for potential energy and pressure were used; the potential cutoff was chosen to be 2.5σ. We have studied $N = 2500$ atoms. The equilibrium characteristics were sampled after 5000 equilibration steps. The local-structure parameters were averaged over 50 configurations.

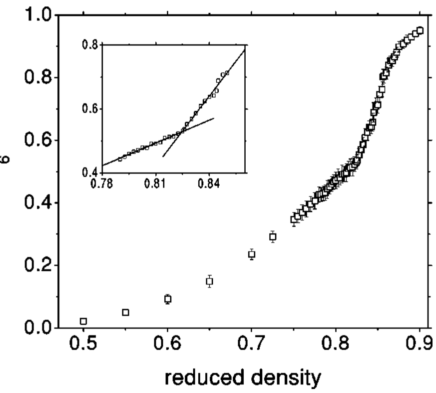

FIG. 3. Plot of the concentration of solidlike atoms c_6 against reduced density ρ^* for a 2D LJ system of 2500 atoms at $T^* = 0.7$. Inset: the same for the density close to the coexistence region.

A. MD simulation results at $T^* = 0.7$

The plot of the concentration of solidlike atoms c_6 against the density is shown in Fig. 3. As in the case of hard disks,[25] it displays three different regimes. For the density close to, but lower than, $\rho_l^* = 0.825$, a linear regime is present. In a narrow interval $\rho_l^* < \rho^* < \rho_s^* = 0.87$ another linear regime, with a much steeper slope, sets in. At still higher densities the effects of the saturation appear. The values ρ_l^*, ρ_s^* were calculated using linear fits to the three regimes, as shown in the inset to Fig. 3. This procedure is more reliable for estimating ρ_l^* than ρ_s^*. The coexistence interval (0.825,0.87) calculated in this way is in good agreement with the interval (0.82,0.88) found using linear extrapolation of the data presented in the phase diagram in Ref. 7. The concentrations at the boundaries of the two-phase region are $c_6(\rho_l^*) = 0.53$ and $c_6(\rho_s^*) = 0.86$.

The model ensemble of the fluctuations for solidlike atoms in a 2D liquid is characterized by the amplitude ξ_6 [cf. Eq. (3)]; its reliability for this description is given by the significance level α. The plot of the amplitude, see the inset (b) to Fig. 4, shows two regimes of behavior. At low densities, $\rho^* < 0.78$, no systematic dependence on the density is present. When $\rho^* > 0.78$ the amplitude decreases linearly with density. The value of $\rho^* = 0.78$ was calculated from the intersection of the extrapolation of linear parts of the plot. Because of relatively large statistical errors, this result should be treated with some care.

The significance level analysis displays an abrupt breakdown of the IGF, see Fig. 4. The plot shows two linear regimes; a crossover from one to another occurs in close vicinity to the density $\rho_0^* = 0.837$, calculated using linear extrapolation [see the inset (a) to Fig. 4]. At $\rho^* < \rho_0^*$ the significance level is independent of the density (within the statistical errors) and takes the values larger than 10^{-1}, im-

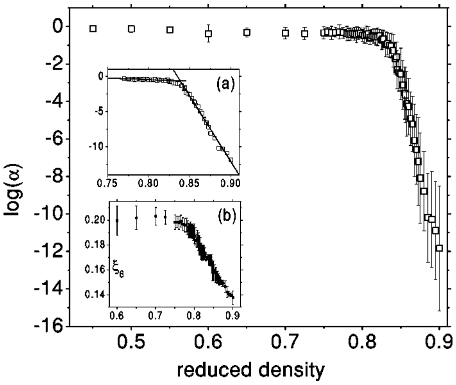

FIG. 4. Plot of the significance level log α against reduced density ρ^* for a 2D LJ system of 2500 atoms at $T^*=0.7$. Inset (a): the same for the density close to the coexistence region. Inset (b): plot of the amplitude of the fluctuations ξ_6 against reduced density ρ^*.

plying that the IGF can be safely used for that part of the phase diagram. On the contrary, α decreases strongly for higher densities. For example, on the solidus line, $\alpha(\rho_s^*=0.87)\simeq 10^{-7}$. For this density the IGF no more reliably describe the fluctuations of the solidlike atoms. Similarly as in the case of hard disks, a crossover to non-IGF takes place.

B. MC simulation results for $\rho^*=0.694$

The snapshots of the configurations of the 3598-atom system (Fig. 5) show three different situations. For temperatures below the triple point $T_t^*=0.4$ the path $\rho^*=0.694$ lies in the gas-solid coexistence region [Fig. 5(a)]. At T_t^* three phases, gas, liquid, and solid, are present [Fig. 5(b)]. Finally, for temperatures slightly higher than T_t^* [Fig. 5(c)] the path lies in the gas-liquid coexistence region. Strictly speaking, the process, which occurs as the temperature decreases below T_t^*, is not freezing but rather a kind of a spinodal decomposition.

At freezing both liquid and solid phases coexist and in our case there is no liquid phase below T_t^*. The thermodynamic properties of the gas phase below and above T_t^* change continuously with temperature. On the contrary, at T_t^* the properties of the corresponding coexisting phases, liquid and solid, undergo (in the thermodynamic limit) discontinuous changes.

For sufficiently large systems, the plot of the average energy per atom (Fig. 6) exhibits a very steep slope in the vicinity of T_t^* and the heat capacity displays a very sharp, δ-like peak localized around T_t^*. Its height increases with the increase of the size of the system. The quasidiscontinuity at T_t^* is also well documented through the plot of the average nearest-neighbor distance $\langle r_{nn}\rangle$ against temperature, see the inset to Fig. 7. Finally, the results of local neighborhood analysis via Voronoi construction are shown in Fig. 7. Surprisingly, the plots are rather smooth which makes a sharp localization of T_t^* rather difficult. One can speculate that it lies in the interval [0.39,0.42]. The fact that this widely used method for studies of local structure fails to reproduce a quasidiscontinuous behavior of the system is a direct manifestation of the relatively weak sensitivity of the local-structure topology in two dimensions against the level of fluctuations.

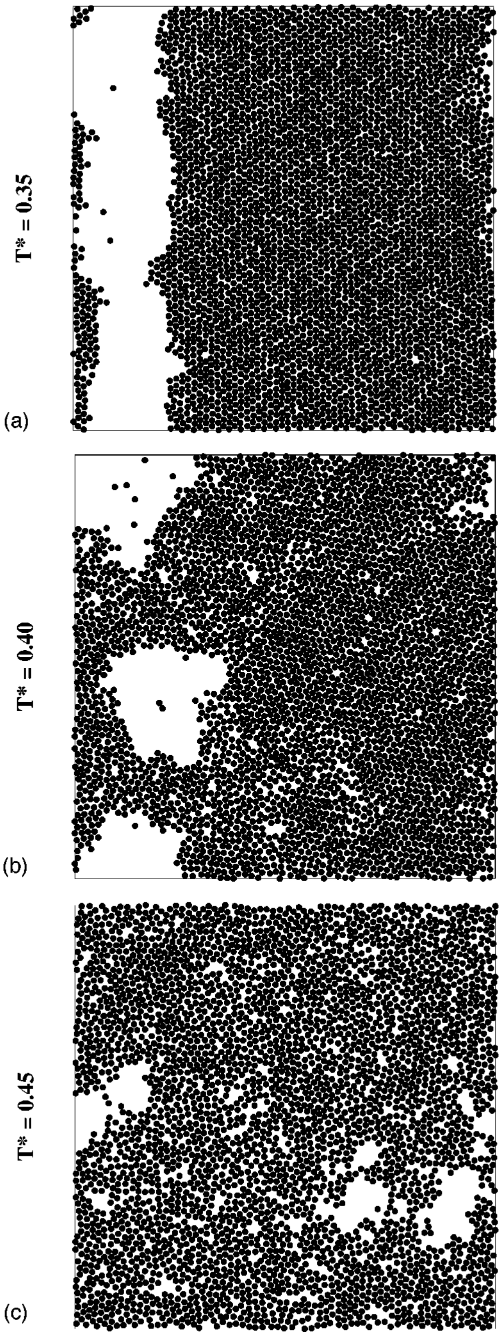

FIG. 5. Snapshots of configuration at $\rho^*=0.694$, for $T^*=0.35$ (a), $T^*=T_t^*=0.4$ (b), and $T^*=0.45$ (c), for the system of 3598 LJ atoms.

Local-structure analysis provides also an important information concerning the character of fluctuations. The concentration c_6 of solidlike atoms is plotted against the temperature in Fig. 8(a) for several system sizes and shows only a weak size dependence. Each of the plots is quasidiscontinuous at T_t^*; the concentration changes from 0.5–0.55 to

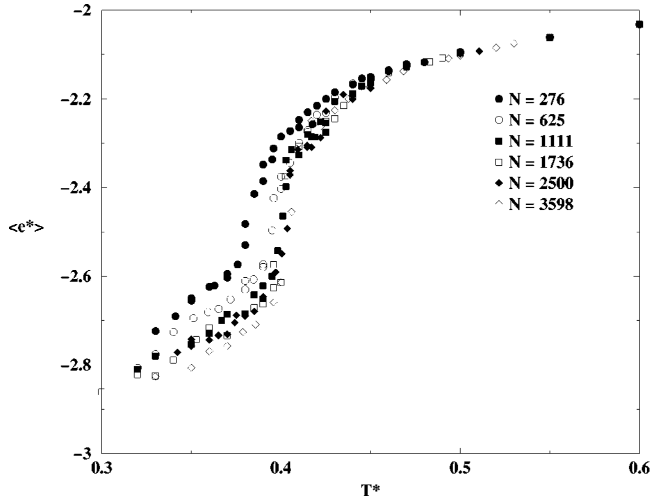

FIG. 6. Average reduced energy $\langle e^* \rangle$ per atom ($e^* = e/\epsilon$) as a function of the temperature for a few sizes of the LJ system at $\rho^* = 0.694$.

0.75–0.80. The plots Figs. 8(b) and 8(c), characterize the changes of ensembles of fluctuations at T_t^*. The amplitude of the fluctuations ξ_6, Fig. 8(b), displays three regimes. For $T^* < T_t^*$ the amplitude is lower than 0.14 and decreases with decreasing temperature. In a close vicinity of T_t^* we find a linear regime, with a very steep slope, which can be interpreted as reminiscent of a discontinuity. ξ_6 undergoes a rapid change from 0.14 to 0.16–0.18. At still higher temperatures a linear dependence sets in. Also here, a systematic size dependence is weak. Figure 8(c) shows the results which demonstrate the dramatic crossover between different ensembles of fluctuations. Because of a strong, systematic dependence of the significance level on the number of atoms N, we plot a rescaled significance level $A_N \log \alpha$ instead of $\log \alpha$. We have used $A_{1111} = 6$, $A_{1736} = 4$, $A_{2500} = 2$, and $A_{3598} = 1$. At the temperatures higher than T_t^* a logarithm of the significance level $\log \alpha$ is practically temperature independent and takes on the values larger than -2. In a very close vicinity of T_t^* an abrupt, quasidiscontinuous drop of $\log \alpha$ occurs. It it then followed by a further decrease at still lower temperatures. Here, two facts are important. First, a quasidiscontinuous behavior is present. Secondly, there is rather systematic dependence of the results on the size of the system. The gap in $\log \alpha$ increases for larger system sizes. The value of the significance level in the lower end of the gap decreases with increasing size of the system: for 1111 atoms it is equal to -2 while for 3598 atoms it is -13. Thus, for the small system (1111 atoms) the decomposition (4) is statistically reliable at $T^* < T_t^*$ close to T_t^*, while in the case of larger systems (2500 and 3598 atoms) it is not. In close vicinity to T_t^*, one observes a qualitative change in the behavior of the significance level. For $T^* > T_t^*$ the Gaussian fluctuations, cf. Eq. (3), serve as a satisfactory approximation to the fluctuations of solidlike atoms in the liquid. On the contrary, those fluctuations yield a nonsatisfactory significance level for $T^* < T_t^*$ and thus have to be rejected. Here, the situation is analogous to the crossover discussed in Secs. III and IV A.

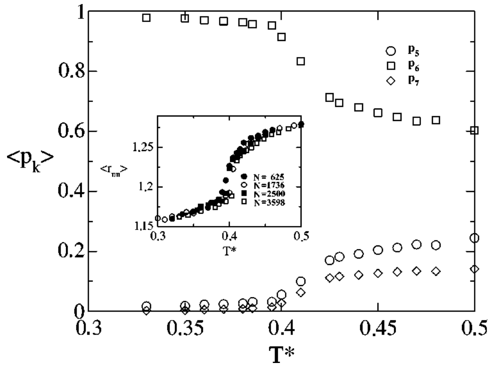

FIG. 7. Plot of the average number $\langle p_k \rangle$ of k = five (circles), six (squares), and seven (diamonds) polygons in Voronoi construction against temperature for the LJ system of 3598 atoms at $\rho^* = 0.694$. Inset: Plot of the average distance $\langle r_{nn} \rangle$ between nearest neighbors against temperature for different sizes of the system at the same density.

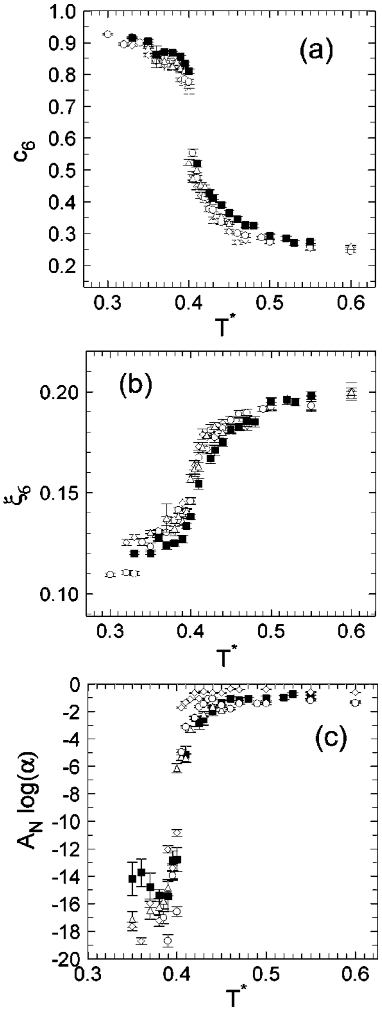

FIG. 8. Local-structure-analysis results for LJ at the density $\rho^* = 0.694$ for a few system sizes N: 1111 (diamonds), 1736 (circles), 2500 (triangles), and 3598 (squares). (a)–(c) show the temperature changes of c_6, ξ_6, and of the rescaled significance level (see text) $A_N \log \alpha$, respectively.

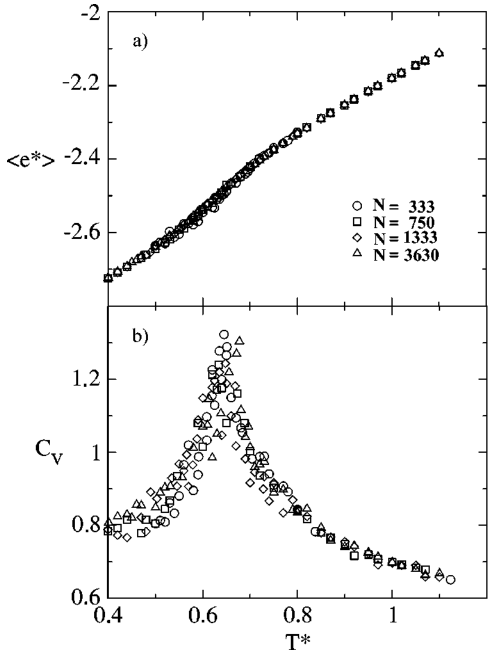

FIG. 9. Plots of average energy $\langle e^* \rangle$ per atom (a) and of the heat capacity at constant volume (b) against the temperature for different LJ system sizes at $\rho^* = 0.833$.

The only difference is due to the fact that the system state changes discontinuously from that corresponding to the liquidus line to the solidus line, as the temperature crosses T_t^*.

C. MC simulation results for $\rho^* = 0.833$

The density $\rho^* = 0.833$ is considerably larger than the triple point density and lies in the solid-liquid coexistence region, at $T^* > T_t^*$, or in the solid-gas coexistence region, at $T^* < T_t^*$. Figures 9(a) and 9(b) present the temperature changes of the average energy and the heat capacity (per atom), respectively. Contrary to the case of $\rho^* = 0.694$, we do not find any systematic dependence of those quantities on the system size. The energy changes smoothly with temperature and offers no ground for identifying the freezing point. Heat capacity displays a broad maximum centered around $T^* = 0.65$. Standard structural characteristics give a slightly higher temperature of the freezing point. The plot of the average nearest-neighbor distance, $\langle r_{nn} \rangle$ (see the inset to Fig. 10), possesses a well-developed linear piecewise character. The extrapolation of those two parts of the linear regions leads to the intersection point, which is located at $T^* = 0.7$. A similar situation holds for the results of Voronoi analysis (Fig. 10). The two linear parts change their slopes at the temperature close to $T^* = 0.7$.

Local-structure analysis yields interesting results. The plots of the concentration c_6 against the temperature for $N = 750$, 1333, and 3630, shown in Fig. 11(a), display two linear regimes of different slopes. The change of the slope increases slightly with the system size. The linearly extrapolated plots intersect at T_l^* located in the interval [0.72,0.75] and the corresponding concentrations $c_6(T_l^*) \in [0.52, 0.55]$. At the temperatures below the intersection point we do not find any saturation effects, which evidently take place at temperatures lower than those used in our simulations.

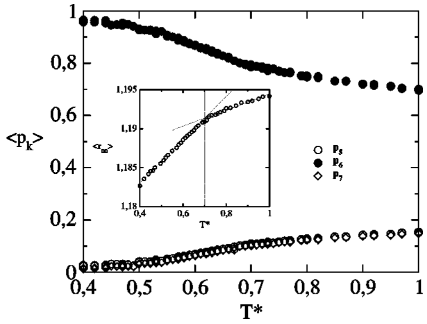

FIG. 10. Plot of the average number of $\langle p_k \rangle$, $k =$ five (empty circles), six (filled circles), and seven (diamonds) polygons in Voronoi construction against temperature for a LJ system with $N = 3630$ at $\rho^* = 0.833$. Inset: Plot of the average distance $\langle r_{nn} \rangle$ between nearest neighbors against temperature for the same density and number of atoms.

Figures 11(b) and 11(c) characterize the crossover between the ensembles of the fluctuations. The plot of the amplitude of the fluctuations $\xi_6(T^*)$, Fig. 11(b), displays three linear regimes. The slopes at high ($T^* > T_{l,\xi}^*$) and low ($T^* < T_{s,\xi}^*$) temperatures are nearly equal and are both smaller than the slope at $T_{s,\xi}^* < T^* < T_{l,\xi}^*$. The change of the slopes makes possible a reliable identification of the temperature $T_{l,\xi}^*$, which lies in the interval [0.7,0.75].

Both c_6 and ξ_6 exhibit only weak size dependence effects. On the contrary, the analysis of the significance level α yields, as in the previously studied cases, strong N dependence. In Fig. 11(c) we show the plots of $A_N \log \alpha$ with $A_{750} = 9$, $A_{1333} = 4$, and $A_{3630} = 1$. At high temperatures [$T^* > T_0^*$, cf. Fig. 11(c)] $\log \alpha(T^*)$ is practically N independent and assumes the values higher than -3, which indicates that the model IGF are acceptable. For $T^* < T_0^*$ the significance level decreases strongly with decreasing temperature. The crossover between those regimes is quite well defined and takes place at the temperature $0.72 < T_0^* < 0.74$. Note a good coincidence of the estimated temperatures T_l^*, $T_{l,\xi}^*$, and T_0^*, which corresponds to the onset of physical processes related to the changes of the fluid local structure. The slopes of the linear plots for $T^* < T_0^*$ are strongly N dependent. Even at temperatures much lower than T_0^* (e.g., at $T^* = 0.5$) the significance levels for smaller systems ($N = 750$ and 1333) are not low enough to invalidate the IGF. On the contrary, for the system containing 3630 atoms, the significance level drops to the values smaller than 10^{-6} at the temperature equal to 0.9 T_0^*, indicating clearly, as in the cases previously studied, a crossover to non-IGF.

V. DISCUSSION

The main goal of this paper was to analyze the local-structural properties of two-dimensional hard disks and Lennard-Jones fluids in connection with freezing, using the probabilistic-based method of local-structure recognition. The results clarify and systematize some of the structural

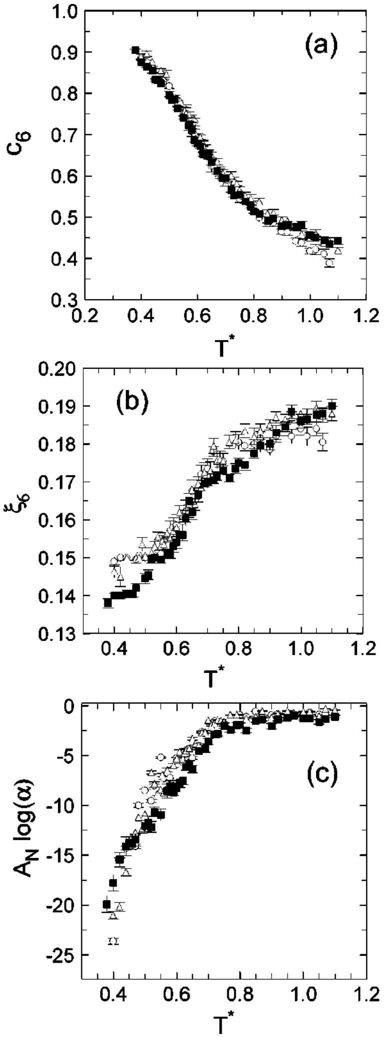

FIG. 11. Local-structure-analysis results for LJ at the density $\rho^* = 0.833$ for a few system sizes N: 750 (circles), 1333 (triangles), and 3630 (squares). (a)–(c) show the temperature changes of c_6, ξ_6, and of the rescaled significance level (see text) $A_N \log \alpha$, respectively.

aspects of the behavior of 2D liquids close to as well as within the two-phase coexistence region. They include, in the methodological part, (i) an attempt to identify the structural processes that accompany freezing in two dimensions and (ii) a quantification of the concept of a sudden crossover between different ensembles of fluctuations of atoms in the liquid and the solid states (more precisely, of the solidlike component of the local structure in both phases). This, in turn, offers an intuitively attractive interpretation of the liquidus line. We have found some universal behavior related to the onset of freezing, which in consequence leads to the formulation of local-structure-based and Lindemann-like freezing criteria in two dimensions. On the other hand, our studies offer some practical applications. Having, as physical bases, clearly defined concepts, our method offers an interesting approach to the analysis of phase diagrams in computer simulations. One of its advantages is that satisfactory results can be obtained from a small number of the configurations recorded during the simulation run. In the case of a sufficiently large system size ($N \simeq 2000$ or more) reliable results can be obtained from the analysis of a single configuration. A more detailed discussion of those topics is presented below.

First of all, however, let us briefly comment on the art of simulation of melting/freezing. Following accepted standards in the literature (see, e.g., Ref. 28), we just span certain ranges of temperatures or densities. It has been correctly pointed out[88,89] that such a way of simulations may, in some cases, lead to serious discrepancies of results because of possible overheating of simulated systems, originated by a slow nucleation in computer experiments. To overcome this difficulty, a promising two-phase method was invented.[88,89] It has lead to a critical revision of simulation data, see, e.g., in Refs. 90–94. Overheating may take place, however, in three dimensions, where the melting/freezing is a strongly first-order PT (phase transition) and metastable states exist. In two dimensions the situation is quite different. Melting/freezing of hard disks takes place either via two continuous transitions or is a very weak first-order transition.[28] In the first case there are no hysteresis effects (overheating, supercooling) at all, in the second they are very small. We believe that this is also true for a 2D LJ system, as a result of very specific and general behavior of 2D systems discussed in the Introduction. For those reasons we think our simulations are sound. Moreover, most of our results correspond to a close vicinity of liquidus line (or the line of transition from the liquid to hexatic phase), where the two-phase method cannot be directly used because of a specific ordering of atoms in a 2D liquid. Namely, close to this line the liquid is in a high degree locally ordered in a solidlike fashion.

A. Reliability of the localization of liquidus line via LSA

The coexistence region was localized using the plot of the concentration c_6 of solidlike atoms. Since we are mainly interested in the onset and early stages of freezing, we discuss the low-density or high-temperature boundary, i.e., the liquidus line. The results are in fair agreement with other constant-volume simulations. For hard disks, LSA (Ref. 25) yields $\rho_l^* = 0.882$, and this should be compared with the value of 0.880 reported in Refs. 12 and 21 and of 0.887 given in Ref. 19. The relative difference of the LSA result and other estimations of ρ_l^* is smaller than 6×10^{-3}. For the Lennard-Jones liquid at $T^* = 0.7$, the relative difference between the LSA result, $\rho_l^* = 0.825$, and the value, $\rho_l^* = 0.82$, estimated from the phase diagram[7] again yields the relative accuracy of 6×10^{-3}. Those numbers show that LSA localizes correctly the liquidus line. This important observation allows us to make conclusions related to the physical nature of the onset of freezing.

B. Ensembles of fluctuations: crossover. Onset of freezing

The main methodological result of this paper is the quantification of the concept of a crossover between liquidlike and solidlike ensembles of the fluctuations of the atoms constituting the solidlike component of local structure in liquids close to and in the two-phase region. The crossover manifests itself in a dramatic change of the statistical parameter (significance level), which determines the degree of relevance of independent Gaussian fluctuations in the description of the solidlike atoms in the system. The crossover occurs at a well-defined density ρ_0^* or temperature T_0^*. Two regimes of totally different behavior were found. In the first one, corresponding either to constant temperature and densities below ρ_0^*, or to constant density and temperatures above T_0^*, the significance level is density independent and takes large values $(10^{-1}-10^{-3})$. Moreover, no systematic size dependence within that regime was found. The two above observations lead us to the conclusion that the independent Gaussian ensemble offers a good choice for the description of the simulation data. In the second regime ($T^*=\text{const}$, $\rho^*>\rho_0^*$ or $\rho^*=\text{const}, T^*<T_0^*$) the significance level decreases strongly with increasing density or with decreasing temperature. The slope of the plot of $\log\alpha$ shows a very strong size dependence. For large systems, the significance level decreases from large $(10^{-1}-10^{-2})$ to small $(<10^{-6})$ values already in close vicinity to ρ_0^* or T_0^*. We conclude that the IGF no longer offer a reasonable approximation to the fluctuations of the solidlike atoms. Here, the size dependence plays the decisive role: the increase of the system size increases the statistics, which in turn requires more realistic ensembles to model the fluctuations of patterns of local structure. We believe that the failure of IGF is mainly due to the assumed statistical independence of fluctuations of the atoms and not to the chosen Gaussian distribution (see a short discussion on 3D ensembles in Ref. 85).

The points ρ_0^* and T_0^*, where the crossover occurs, lie close to the liquidus line. The distance to this line, relative to the width of the coexistence region, is given by the ratio $d_\rho\equiv(\rho_0^*-\rho_l^*)/(\rho_s^*-\rho_l^*)$, or $d_T\equiv(T_l^*-T_0^*)/(T_l^*-T_s^*)$. For hard disks $d_\rho=0.07$, while for 2D LJ liquid at $\rho^*=0.833$ and for three different system sizes reported above, $d_T<0.04$ [we have used a very rough estimation $T_s^*\simeq 0.5$, taken from the plot in Fig. 11(c)]. For 2D LJ liquid at $T^*=0.7$ d_ρ is higher: $0.2<d_\rho<0.25$. Note that all the results discussed here were obtained using linear extrapolation which depends on the number of points analyzed and hence should be treated with some care. In general, we find a clear tendency: the points where the ensemble crossover occurs lie close to the liquidus line. This line, where (according to thermodynamics) the coexistence regime sets in (or the liquid-hexatic transition occurs), acquires a much more interesting physical interpretation. Namely, it is a line at (or close to) which a "truly-" solidlike behavior starts in the following sense. On the liquid side of this line, but close to it, the liquid has a large concentration, around 50%, of the solidlike atoms (see Sec. V C) and in the two-phase region this concentration just continues to increase. In other words, it is not the liquidus line where the solidlike local structures start to appear in abundance. What changes in the system properties are the fluctuations, from uncorrelated, typical for gases, to highly correlated, typical for 2D solids. We conclude that a 2D liquid close to its liquidus line has both solidlike features (a large concentration of local solidlike structures) and gaslike features (fluctuations). The onset of freezing is accompanied by disappearance of gaslike features in the local solidlike component of a liquid. Those statements quantify similar, mostly qualitative concepts formulated earlier.[55,53,54]

Finally, let us comment on some aspects of the energy distribution in the coexistence region. In standard thermodynamics, a point in a two-phase region represents a mixture of different phases with weights given by the lever rule.[52] In our case the system has local structure and the situation is more complicated. A dramatic decrease of the significance level for large systems suggests that a solidlike ensemble sets in rapidly, and not in a smoother way as suggested by the lever rule. This new ensemble governs the distribution of energy between the solidlike degrees of freedom in the system. The total-energy relations in the system are thus determined by a solidlike behavior of local solidlike component and by a non-solid-like behavior of the remaining part of the system. Those two regimes result in a complex behavior. In particular, there is no reason to expect *a priori* that an overall mean-square fluctuation of the energy, which is proportional to the heat capacity, displays some anomaly at the very onset of freezing. This conclusion is supported by the observation made in Sec. IV C, where the maximum of the heat capacity appeared at $T^*\simeq 0.65$, well below the temperatures $T_l^*=0.72-0.75$.

C. Lindemann-like and concentration-based criteria of onset of freezing in two dimensions

The onset of the freezing displays some universal features related to the amplitude of the fluctuations ξ_6 and the concentration c_6 of solidlike atoms. In this respect the case of $\rho^*=0.693$ is of particular importance because (i) there is no uncertainty accompanying the localization of the liquidus and solidus lines at T_t^* and (ii) c_6 and ξ_6 undergo a (quasi-) discontinuous change at this temperature. Thus, the values of c_6 and ξ_6 on both sides of the gap provide "unbiased" estimates $c_6^{(l)}$, $\xi_6^{(l)}$ and $c_6^{(s)}$, $\xi_6^{(s)}$ of solidlike atom concentrations and amplitudes of fluctuations on liquidus and solidus lines, respectively. We find $\xi_6^{(l)}=0.17-0.18$, $\xi_6^{(s)}=0.14$, $c_6^{(l)}=0.50-0.55$, and $c_6^{(s)}=0.75-0.80$. If there is some universality in local structures for various 2D liquids, then the corresponding values of $c_6^{(l)}$ and $\xi_6^{(l)}$ should fall into those intervals.

We find, for the liquids analyzed here, that the concentrations of solidlike atoms, on the liquidus line, lie in a narrow interval: $c_6^{(l)}=0.56$ (hard disks), 0.53 (LJ, $T^*=0.7$), and 0.52–0.55 (LJ, $\rho^*=0.833$). The statistical error is, as a rule, smaller than ± 0.01. Those results suggest a universal criterion of the onset of freezing in two dimensions:

$$c_6^{(l)}\in[0.50,0.56]. \tag{6}$$

The thumbrule criterion $c_6^{(l)}=0.50$ was first formulated in Ref. 83 using heuristic lever-rule arguments.

The result (6) offers a very interesting interpretation of freezing in two dimensions as a percolation process in view of the fact that on a regular triangular lattice the site percolation threshold is exactly 0.5.[95] According to a simple scenario[96] percolating structures propagate a shear stress through the system, giving rise to a solidlike response of the system to an external static (or low-frequency) strain. Further discussion of this topic goes beyond the scope of this paper.

The level of fluctuations also shows an universal behavior. We find $\xi_6^{(l)}=0.17$ (hard disks), 0.175 (LJ, $T^*=0.7$), and 0.17–0.18 (LJ, $\rho^*=0.833$). This suggests a Lindemann-like freezing criterion in two dimensions: $\xi_6^{(l)}\in[0.17,0.18]$ at the onset of freezing. Since an average fluctuation per atom is given by $\sqrt{(\Delta\vec{r})^2}=\xi_6/\sqrt{2}$ (Sec. II), the Lindemann-like freezing criterion finally takes the form

$$\sqrt{(\Delta\vec{r})^2}\in[0.12,0.13]. \qquad (7)$$

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