Inherent Structures and Two-Stage Melting in Two Dimensions

Frank L. Somer, Jr.,[1,2] G. S. Canright,[1,2] Theodore Kaplan,[3] Kun Chen,[2] and Mark Mostoller[2]
[1]*Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996-1200*
[2]*Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831*
[3]*Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831*
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A large-scale study of the "inherent structures" (IS) associated with equilibrium two-dimensional Lennard-Jones systems is presented. The results validate, for simple 2D fluids, an essential premise of inherent-structures theory: there are consistent, *qualitative* differences between the IS associated with distinct equilibrium phases. The hexatic IS show free dislocations plus some nonpercolating grain boundaries. The liquid IS always contain percolating grain boundaries, but no evidence of free disclinations. Our results are consistent with the dislocation-unbinding scenario for the hexatic phase, but leave open the question of the microscopic melting mechanism leading to the isotropic liquid. [S0031-9007(97)04274-9]

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Some years ago, Stillinger and Weber [1] developed a theory of liquids based on the partitioning of the configuration space into potential-energy basins, defined by steepest-descent paths to the nearest local minimum of the potential energy. These minima were coined "inherent structures" (IS), and the theory takes all other configurations to be vibrational excitations of them. A fundamental notion of the *inherent-structures theory* (IST) is that singularities in thermodynamic functions may be traced to singularities in the probability distribution of potential-energy basins; hence the inherent structures associated with different equilibrium phases should differ qualitatively, in consistently reproducible ways. Support for this claim has been found for some three-dimensional systems [2], but in two dimensions (2D), there are only limited results [3,4]. In principle, however, it would seem that 2D offers an ideal testing ground for IST, since here even simple liquids are thought to have *three* condensed phases. In this work, we test and validate, for simple 2D fluids, this fundamental idea of IST, working with particle numbers 1–2 orders of magnitude larger than those in previous 2D work [34], and finding three "phases" of IS, with dramatic qualitative differences among them.

The existence of three condensed phases in 2D was predicted by Halperin and Nelson (HN) [5], following work by Kosterlitz and Thouless [6], Nelson [7], and Young [8], who predicted a continuous melting transition for the solid phase in 2D. The union of these ideas is commonly called the "KTHNY theory" of 2D melting. In this theory, the solid phase melts via the unbinding of dislocations. The resulting phase is not an isotropic liquid, but rather a *hexatic* phase with some residual bond-orientational order [5]. An isotropic liquid is obtained via the unbinding (at higher T) of the *disclinations,* of which the dislocations are "composed" [5]. (For a detailed review of the KTHNY theory and the defects involved, see Strandburg [9].) Confirmation of the existence of the hexatic phase in simulations [10] has been elusive, presumably because of limitations in system size. Recently, large-scale simulations on Lennard-Jones systems [11,12] have provided some compelling evidence for the hexatic phase, though the thermodynamic stability of the latter is still in question [11]. Clear identification of the free dislocations predicted by KTHNY has been extremely difficult in such simulations, however, due to the presence of many "virtual dislocations," which are manifestations of vibrational excitations of the system. An obvious way to overcome this difficulty would be to remove the vibrational excitations. This is evidently equivalent to minimizing (locally) the potential energy—that is, to finding the inherent structure. The latter will then reveal the topological defects present in equilibrium, *if* those defects are mechanically stable.

We are thus led to the question: what is known about the mechanical stability of free defects (dislocations and disclinations) in these fluids? We consider first free dislocations, which are expected to appear in the hexatic phase. The KTHNY theory sums over all possible positions of these defects. Elasticity theory is used to obtain the strain fields for each such position; and the latter theory uses the assumption of mechanical equilibrium *of the medium* (the "equations of equilibrium") [13]. Thus, the positions of the defects themselves are assumed stable with respect to *elastic* deformations of the medium. However, they may or may not be stable with respect to topology-changing ("tearing") motion. The continuum theory has nothing to say on this question (except that it *assumes* such moves do not occur); rather, one must look to the underlying microscopic structure. Here we find the well-known Peierls-Nabarro potential [13] which can trap the dislocations. Hence, we find reason to expect that the IS obtained from the hexatic (and liquid) phase will exhibit the free dislocations predicted by KTHNY.

Next, we consider free disclinations. Halperin and Nelson [5] viewed these defects as scalar singularities of a bond-orientation field, analogous to vortices in an XY magnet. The logarithmic interaction then comes, analogously to the case of dislocations, from the assumption [6] that the spin fields (the "medium") are relaxed to a local minimum of the coupling energy, with the vortex positions held fixed. And, again, we face the question of the stability of the given vortex configuration with respect to ("tearing") motion of the vortices themselves. Here, however, we have much less microscopic evidence that such objects may be pinned by some analog of the Peierls potential. Thus, we cannot *a priori* say what kind of IS might arise from an equilibrium configuration which includes a nonzero density of free disclinations. Let us then consider our IS results, examined in the light of these stability arguments.

As mentioned above, in IST, equilibrium configurations are connected to their corresponding inherent structures by steepest-descent paths. In practice, however, steepest-descent minimization is not computationally feasible [2] for the very large system sizes used in the present study. Instead, we use a highly damped molecular-dynamics approach (herein, referred to as "quenching") at very low temperature. The low temperature (plus damping) ensures that the system trajectory nearly follows the steepest-descent path in configuration space (again see [2]); also, we insist that the chosen energy function (U for constant-V quenches, or $U + pV$ for constant-p quenches) strictly decreases until a local minimum is reached. It is likely that our small deviation from steepest-descent minimization produces a scatter in our results much like that expected from sampling at different times; hence it should not have any significant effect on the results.

With the (metastable [11]) equilibrium hexatic phase as the starting point, our quenching procedure results in structures like that shown in Fig. 1. The free dislocations are clearly evident. [In contrast, in quenching from a crystal, just below the transition temperature, we find that essentially all of the dislocations have "canceling" (equal and opposite Burgers vector) dislocations within one or two lattice spacings.] Also evident is a tendency for the dislocations to arrange themselves into small-angle grain boundaries [14], as well as a few large-angle grain boundaries which are identifiable as chains of very closely spaced dislocations. While networks of large-angle grain boundaries are capable of destroying the quasi-long-range orientational order characteristic of the hexatic phase, those present in our hexatic quenches are relatively small and isolated, so that this order is preserved. This is confirmed in Fig. 2, where we show log-log plots of the orientational correlation function [$g_6(r)$] for a typical hexatic "MD snapshot" and its associated quenched structure. The linearity of the equilibrium plot, indicative of the power-law decay [$g_6(r) \sim r^{-\eta_6}$] associated with the hexatic phase, is maintained on quenching.

Quenching from the equilibrium liquid, we obtain structures such as that shown in Fig. 3. Rather than the free disclinations that might be expected from the HN disclination-unbinding mechanism, the only additional defects, as compared to the hexatic phase, are percolating networks of large-angle grain boundaries. In principle, this result allows for two competing scenarios. First, it is possible that our equilibrium liquid contains no free disclinations. In this case, our IS suggest (compare Figs. 1 and 3) that the system is melting via a grain-boundary mechanism [15], rather than by the HN disclination-unbinding mechanism. We have attempted to test for the presence of free disclinations in the equilibrium liquid by way of a procedure described by Halperin [16], using the disclination "charge-charge" correlation function, but the results, thus far, are too noisy to allow any definite conclusion. This leaves open the second possibility—that there *are* free disclinations at equilibrium, but that these are unstable, and somehow transformed into a system of grain boundaries on quenching. The viability of this idea is demonstrated in Fig. 4. Here, starting with a configuration whose only defects are four widely spaced disclinations (two positive and two negative), our quenching procedure results in a roughly square grain-boundary network whose nodes correspond closely to the positions of the original disclinations. This would suggest a strong correlation between the average separation of disclinations in an equilibrium configuration, and the average grain

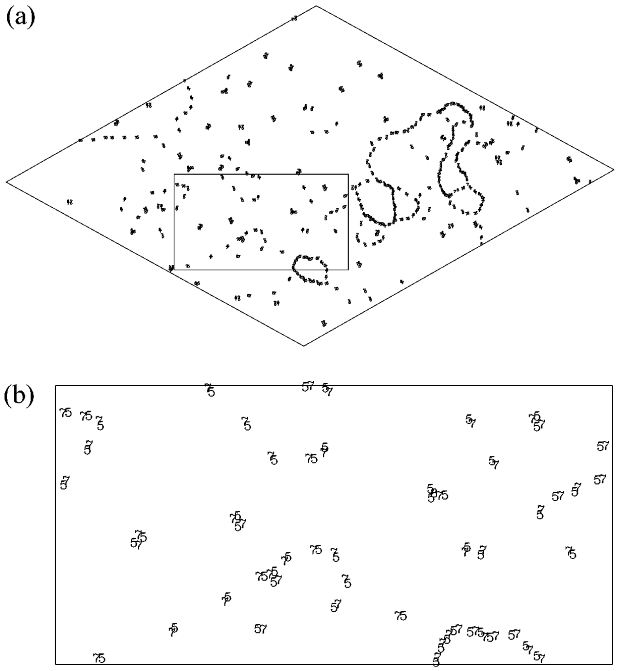

FIG. 1. (a) Inherent (mechanically stable, or "quenched") structure for 36 862 particles with periodic boundary conditions, obtained by relaxing a configuration from a hexatic phase in (metastable) equilibrium. The relaxation is done at constant pressure $p = 20$, from an equilibrium snapshot at $T_s = 2.154$ [units, interaction potential, and constant-(p, T) MD algorithm, are as in Ref. [11]]. Only those atoms which are not sixfold coordinated are marked. (b) Enlargement of the boxed-in section of (a). Free dislocations appear as isolated 5–7 pairs.

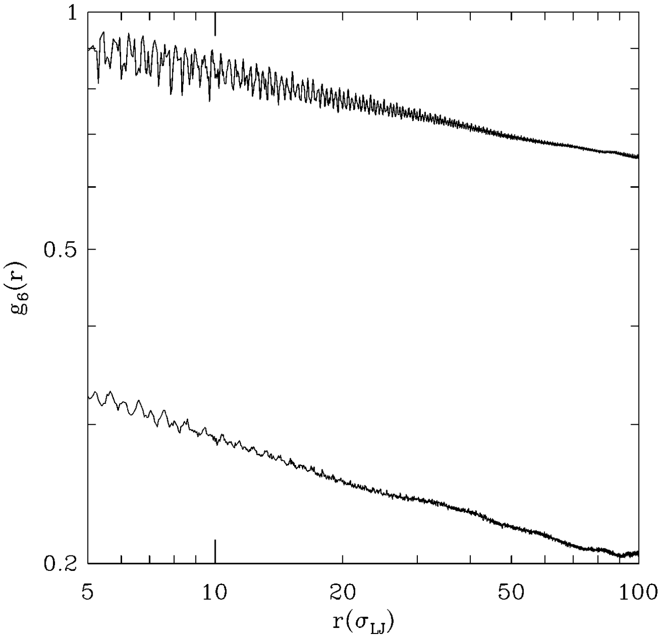

FIG. 2. Orientational correlation function $g_6(r)$ for the quenched (upper curve) and equilibrium (lower) hexatic phase. In each case a power-law behavior holds at large r. The decay is slower for the quenched structure because the disorder arising from torsional vibrations has been removed.

size in the corresponding quenched structure. The fact that the equilibrium and quenched configurations have nearly identical correlation lengths (Fig. 5) thus appears consistent with the presence of free disclinations in the equilibrium liquid—without, however, providing decisive evidence for their existence.

Our large-scale numerical experiments have decisively established that quenched (inherent) structures clearly and *qualitatively* distinguish among the different phases of condensed matter in 2D—a fundamental premise of IST—and that there are *three* such distinct "phases" of inherent structures. In the process, we have provided strong, microscopic evidence for the existence of the hexatic phase, by extracting the telltale free dislocations from amidst the vibrational "clutter" of the equilibrium phase. This evidence is distinct from, and complementary to, the previously accumulated evidence for this phase, which has been based mostly on correlation functions. While the fact that our isotropic-liquid quenches contain *percolating large-angle grain boundaries*, rather than free

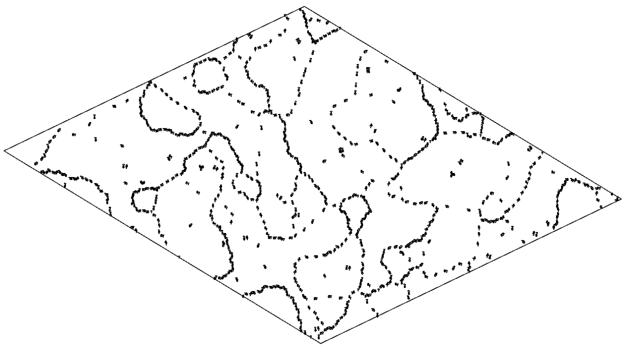

FIG. 3. Inherent structure obtained by relaxing an equilibrium liquid configuration. The parameters are as in Fig. 1, except $T_s = 2.17$. The grain boundaries, isolated in Fig. 1, span the sample here, and in all other liquid quenches we have done. There is no evidence for free disclinations (which would appear here as isolated 5's and 7's).

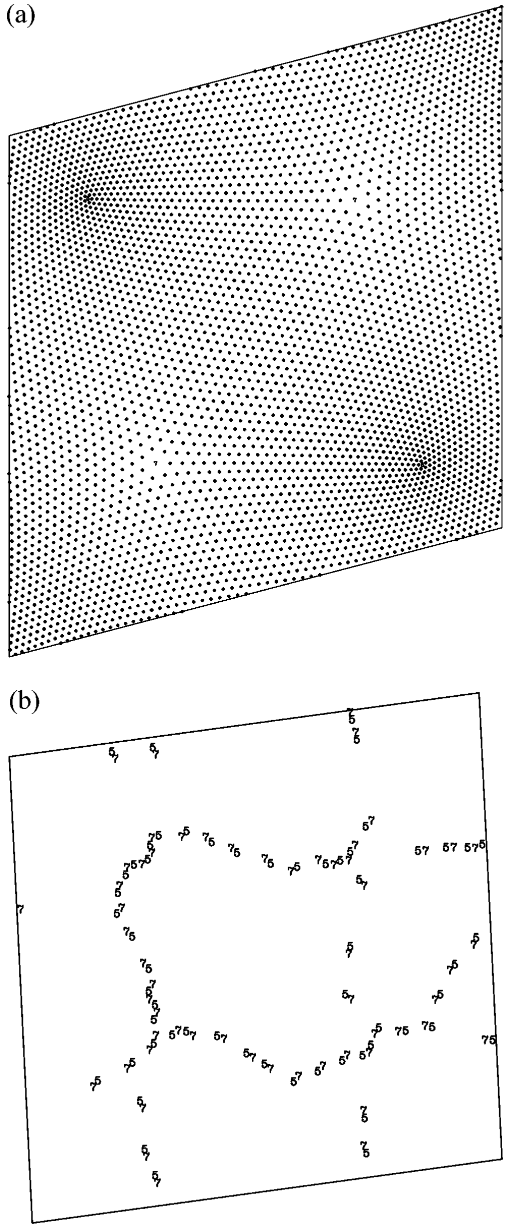

FIG. 4. (a) An artificial starting configuration for 4096 particles, constructed with four widely spaced disclinations of zero net scalar and vector charge. Again we use periodic boundary conditions. (b) The relaxed structure for (a) (defects only). The free disclinations have vanished; what remains is a network of grain boundaries which closely marks the original positions of the disclinations.

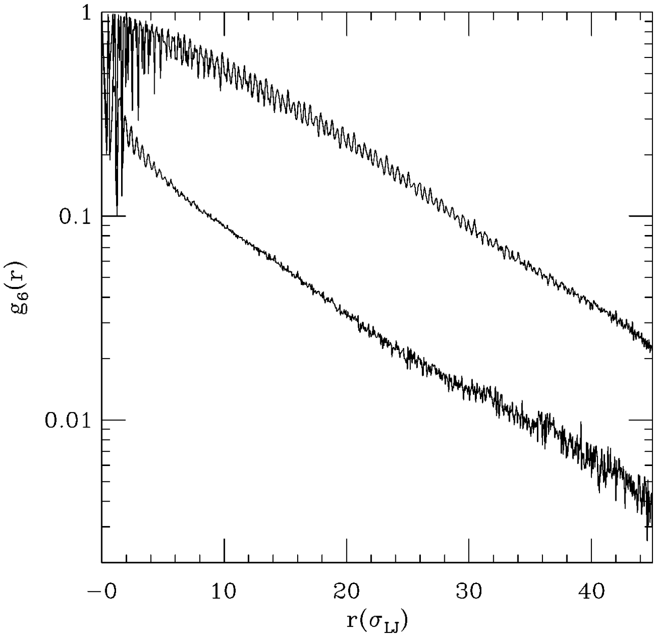

FIG. 5. $g_6(r)$ for the quenched (upper curve) and equilibrium (lower) liquid phase. The correlation length is practically the same in each case; in the quenched (inherent) structure, it is roughly equal to the grain size.

disclinations, is suggestive of grain-boundary melting, our demonstration that free disclinations can "quench to grain boundaries" leaves open the question of the mechanism by which the transition to the isotropic liquid occurs. This should certainly be the subject of future study. Another avenue for future study presents itself when we realize that our quenched structures are also (structural) *glasses*—that is, mechanically stable configurations with frozen-in disorder. The consistency of our results for various quenches [17] from each equilibrium phase, along with the large system size studied, suggests strongly that (barring the existence of heretofore unknown equilibrium phases) we have found *every* type of glass (except for a set of vanishing probability of occurrence) for single-component 2D simple fluids. This realization is relevant for studies of 2D glasses—a subject which, to date, has received primarily theoretical attention [18] (but see [19] for experimental *two*-component "glasses").

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