Structural and dynamical heterogeneities in two-dimensional melting

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Abstract – Using molecular-dynamics simulation, we study structural and dynamical heterogeneities at melting in two-dimensional one-component systems with 36000 particles. Between crystal and liquid, we find intermediate hexatic states, where the density fluctuations are enhanced at small wave number $k$ as well as those of the sixfold orientational order parameter. Their structure factors both grow up to the smallest wave number equal to the inverse system length. The intermediate scattering function of the density $S(k,t)$ is found to relax exponentially with decay rate $\Gamma_k \propto k^6$ with $z \sim 2.6$ at small $k$ in the hexatic phase.

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Introduction. – Since a simulation by Alder and Wainwright [1], much attention has been paid to the two-dimensional (2D) melting in simple one component particle systems [2]. However, it has been controversial whether the transition is first order as in three-dimensional melting [1–5] or is continuous as predicted by Halperin and Nelson [6]. They presented a defect-mediated melting mechanism and a “hexatic phase” in a temperature (or density) window between crystal and liquid. In the hexatic phase, the bond-orientation correlation function $g_6(r)$ of a sixfold orientation order parameter $\psi_6(r)$ decays algebraically, indicating a quasi-long-range orientational correlation. Afterwards their prediction has been confirmed in experiments [7–12] and in simulations [13–20]. In the hexatic phase, defects have been observed to proliferate with increasing the temperature $T$ or decreasing the density $n$. As other theories, Chui proposed a melting mechanism mediated by grain boundaries [21], while Saito argued that the 2D melting can be either continuous or first order depending on the specific details of the system [15].

As a marked feature, a number of experiments and simulations [1–3,7–14,22] have observed heterogeneities in the hexagonal structures and in the particle trajectories, developing around the transition. In particular, appreciable dependence on the system size has been encountered in the calculations of the equation of state [1,5,17,20] and the local fluctuations of $\psi_6(r)$ [5,20]. However, the heterogeneities in the 2D melting have not yet been well understood. In this letter, we will visualize them using a disorder variable representing deviations from the hexagonal order [23] and bond breakage used in analyzing glass dynamics [24]. It is also a fundamental issue whether the isothermal compressibility $K_T = (\partial n/\partial p)_T/n$ remains finite or tends to infinity in the hexatic phase. In simulations [17,20], the pressure $p$ was a weakly decreasing function of $n$, apparently suggesting $(\partial p/\partial n)_T < 0$, in the hexatic phase. Hence, we will calculate the structure factor of the density $S(k)$ at small wave number $k$ to see whether the thermodynamic relation $\lim_{n \to 0} S(k) = n^2 T K_T$ holds or not. The intermediate scattering function $S(k,t)$ will then emerge as a new informative quantity.

Numerical method. – Our 2D system is composed of $N = 36000$ particles interacting via a truncated Lennard-Jones potential of the form

$$v(r) = 4\epsilon \left[ (\sigma/r)^{12} - (\sigma/r)^6 \right] - C,$$

which is characterized by the energy $\epsilon$ and the range $\sigma$. For $r > r_{\text{cut}} = 3.2\sigma$, we set $v(r) = 0$ with the constant $C$ ensuring the continuity of $v(r)$ at the cut-off. The system volume $V$ is kept fixed such that $\phi = N \sigma^2 / V = 0.9$. Then the system length is given by $L = V^{1/2} = 200\sigma$. We integrated the equations of motion using the Störmer-Verlet algorithm (a sort of the leap-frog method) under the periodic boundary conditions using the Nosé-Hoover
and hexatic transitions are continuous, taking place at 

\[ T = \frac{2\epsilon}{k_B} \]

for larger \( r \) bounds 1 and 0.36 at \( T = 0 \). The time \( t \) is set equal to 0 at this temperature increase. We continued the simulation until \( t = 2 \times 10^4 \). Hereafter we will measure space, time, and \( T \) in units of \( \sigma, \tau, \) and \( \epsilon/k_B \), respectively.

In 2D dense particle systems, a large fraction of the particles are enclosed by six particles and the local order is represented by the sixfold orientation [6]. We define the orientation angle \( \alpha_j \) in the range \( [-\pi/6, \pi/6] \) for each particle \( j \) at position \( r_j \) using the complex number

\[ \Psi_j = \sum_{k \in \text{bonded}} \exp[6i\theta_{jk}] = |\Psi_j|e^{6i\alpha_j}, \]

where the summation is over particles “bonded” to the particle \( j \). The two particles \( j \) and \( k \) are bonded if \( |r_j - r_k| \leq 1.25\sigma \). \( \theta_{jk} \) is the angle between \( r_j - r_k \) and the \( x \) axis [23,24]. Next we construct another nonnegative-definite variable representing the degree of disorder for each particle \( j \) by [23]

\[ D_j = 2 \sum_{k \in \text{bonded}} [1 - \cos(6(\alpha_j - \alpha_k))]. \]

Here \( D_j \) is nearly zero for a perfect crystal, but is large in the range 5–20 for particles around defects. Thus \( D_j \) is convenient in visualizing the structural inhomogeneity.

In terms of \( \alpha_j \), the sixfold orientation order parameter \( \psi_6(r) \) is defined as [6]

\[ \psi_6(r) = \sum_{j=1}^{N} e^{6i\alpha_j} \delta(r - r_j). \]

In the hexatic phase, the bond-orientational correlation function decays algebraically as

\[ g_6(r) = \langle \psi_6(r)\psi_6(0) \rangle \sim r^{-\eta}, \]

where \( r = |r| \). Theoretically [6], the exponent \( \eta \) depends on \( T \) and \( n = N/V \) in the range 0 < \( \eta \) < 1/4.

**Structural heterogeneity.** – In fig. 1, the curves of \( g_6(r) \) are displayed, which are the long-time averages over the snapshots produced by 5 independent runs in the range \( 10^4 < t < 2 \times 10^4 \). In the hexatic phase at \( T = 1.1, 1.15, \) and 1.2, the exponent \( \eta \) in eq. (6) is 0.03, 0.09, and 0.36, respectively, where 0.03 at \( T = 1.1 \) is very small and 0.36 at \( T = 1.2 \) even exceeds the theoretical upper bound 1/4. However, the curve of \( T = 1.2 \) might decay exponentially for larger \( r \). The hexatic-liquid and crystal-hexatic transitions are continuous, taking place at \( T \approx 1.2 \) and 1.0 respectively. For our system size, it is still difficult to determine the transition temperatures precisely.

For \( T > 1.25 \) the system is in liquid with \( g_6(r) \) decaying exponentially, while for \( T \leq 1.0 \) the system is in crystal without appreciable decay of \( g_6(r) \).

In fig. 2, we display snapshots of \( D_j \) of all the particles in a crystalline phase at \( T = 1.0 \) (a), in hexatic phases at
$T = 1.1$ (b) and $1.2$ (c), and in a liquid phase at $T = 1.3$ (d).

In fig. 3(a), a more expanded snapshot of $D_j$ is given at $T = 1.15$. The average disorder parameter $D \equiv \langle \sum_j D_j/N \rangle$ is $1.07, 1.72, 2.12, 2.55,$ and $3.32$ for $T = 1.0, 1.1, 1.15, 1.2$ and $1.3$ respectively. In the hexatic phases ($1.1 \leq T \leq 1.2$), marked heterogeneity emerges on large scales among crystalline and disordered regions, though there are no sharp boundaries. The patterns are fractal-like, resembling the critical fluctuations near the Ising criticality. Also shown in fig. 3 are (b) the local areal density $\rho_j$ (to be defined below) and (c) the particles with neighbor number being different from six. A common particle configuration was used for these three panels. Here $v_j = \rho_j^{-1}$ is the volume of particle $j$ in the Voronoi cell construction. We treat its inverse $\rho_j$ as the local density at the position of particle $j$. Its variance $V (= \langle (\rho_j - \bar{\rho})^2/N \rangle$ is about $0.05$ with $\bar{\rho} = \sum_j \rho_j/N \approx 0.9$ here. Comparing the two panels we can see that the particles with larger $D_j$ tend to have smaller $\rho_j$. In the literature [7,10,12], defects have been detected around the particles with five or seven neighbors, so we used this Voronoi method to produce fig. 3(c). It exhibits essentially the same heterogeneity as that of $D_j$ (a), though only discrete particles are selected. However, near melting, using $D_j$ is more quantitative and appropriate to characterize the diffuse disordered regions extending on large scales.

The algebraic decay of $g_6(r)$ in eq. (6) arises from the heterogeneity in figs. 2 and 3. Furthermore, fig. 3(b) indicates that small density differences exist among the crystalline and disordered regions. In fig. 4, we thus show the structure factors of the hexagonal order and the density

$$S_6(k) = \int \! dr \, e^{i \mathbf{k} \cdot \mathbf{r}} g_6(r) = \langle |\psi_{6\mathbf{k}}|^2 \rangle, \quad (7)$$

$$S(k) = \int \! dr \, e^{i \mathbf{k} \cdot \mathbf{r}} \langle \delta \hat{n}(\mathbf{r}) \delta \hat{n}(\mathbf{0}) \rangle = \langle |\tilde{n}_k|^2 \rangle, \quad (8)$$

where $\delta \hat{n}(\mathbf{r}) = \sum_j (\delta \hat{n}_j - \hat{n}_j) = n$ is the microscopic density deviation. The $\psi_{6\mathbf{k}}$ and $\tilde{n}_k$ are the Fourier components of $\psi_6(\mathbf{r})$ and $\delta \hat{n}(\mathbf{r})$. These structure factors are the averages over the angle of the wave vector $\mathbf{k} = (k_x, k_y)$.

The smallest wave number $k_{\text{min}}$ is defined as $\pi(1 + \sqrt{2})/L = 0.035$, where $L = 200$ is the system length. The
structure factors at $k = k_{\text{min}}$ are the averages of the data at $k = 2\pi L^{-1}(\pm 1, \pm 1)$ and $2\pi L^{-1}(\pm \sqrt{2}, \pm \sqrt{2})$. In fig. 4(a), the growth $S(k) \cong A_0 k^{-2+\eta}$ can be seen at small $k$ in the hexatic phase at $T = 1.1, 1.15,$ and $1.2$ in accord with eq. (6), where $A_0 \approx 0.53$ and $\eta \approx 0.09$ at $T = 1.15$. In fig. 4(b), $S(k)$ grows at small $k$ in the hexatic phase, but its amplitude is very small and $S(k_{\text{min}})$ remains smaller than the peak height at $k \sim 2\pi$ by two orders of magnitude (see the inset). In fact, at $T = 1.15$, its curve may be fitted to $S(k) \approx 0.017 + 1.23 \times 10^{-3}/k^{1.55}$ for $k < 1$. The small coefficient ($\sim 10^{-3}$) here arises from small density differences among the crystalline and disordered regions. For our system size, these structure factors do not saturate even at $k = k_{\text{min}}$ in the hexatic phase.

If $S(k)$ saturates to a long wavelength limit $S(0) = \text{lim}_{k \to 0} S(k)$ in the thermodynamic limit $L \to \infty$ at fixed density, the compressibility is given by $K_T = \langle \partial n/\partial p \rangle_T/n = S(0)/n^2 T$. From our simulation only, however, we cannot exclude the possibility of $S(k) \to \infty$ (as $k \to 0$) in the hexatic phase, where $\langle \partial p/\partial n \rangle_T = 0$ ultimately holds in the thermodynamic limit. As in fig. 5, we also performed simulations with 36000 particles by varying the volume $V$, where shown is the pressure $p$ (average of its microscopic expression) vs. the density $n$ at $T = 1.15$. Outside the hexatic region, the long wavelength limit $S(0)$ is attained and the compressibility relation $S(0) = nT/\langle \partial p/\partial n \rangle_T$ surely holds. As in previous work [20], $p$ apparently exhibits a small negative slope and appreciable system-size dependence in the hexatic density range (where the latter is not shown here). Thus we need to use much larger system sizes to settle this issue. In such simulations, the long wavelength fluctuations (with $k < 10^{-2}$) need to be equilibrated on extremely long times.

**Dynamics.** – The dynamics has not yet been well studied at the 2D melting. For the particle displacement $\Delta r_i(t) = r_i(t + t_0) - r_i(t_0)$ in time interval $t$, fig. 6(a) displays the mean square displacement, $\langle (\Delta r(t))^2 \rangle = \sum_i \langle (\Delta r_i(t))^2 \rangle /N$, which is the average over all the particles and over the simulation time. The linear behavior $\langle (\Delta r(t))^2 \rangle \approx 4D_s t$ can be seen at long times for $T \geq 0.6$. The diffusion constant $D_s$ thus obtained increases as $0.181, 1.13, 3.32, 8.23, 60.5$, and $188$ for $T = 0.6, 0.8, 0.9, 1, 1.1,$ and $1.2$, respectively, in units of $10^{-4} \sigma^2 \tau^{-1}$. In crystal ($0.6 \leq T \leq 1.0$), the curves exhibit a plateau followed by the linear growth. Similar two-step behavior is well-known in supercooled liquids [24], but it is here due to motions of defect clusters composed of several particles with finite $D_j$ (see fig. 2(a)). Such clusters were observed in 2D colloidal systems [12]. In the hexatic phase, on the other hand, the plateau disappears and $D_s$ grows abruptly.

To examine the particle-configuration changes, we introduce the bond breakage [24]. For each particle configuration at a time $t_0(\sim 10^4)$ after long annealing, a pair of particles $i$ and $j$ is considered to be bonded if $r_{ij}(t_0) = |r_i(t_0) - r_j(t_0)| \leq A_1$, where we set $A_1 = 1.2$ (around the peak distance of the pair correlation function). After a
time interval \( t \), the bond is regarded to be broken if \( r_{ij}(t_0 + t) \geq A_2 \), where we set \( A_2 = 1.6 \). In fig. 6(b), we plot the number of the surviving bonds \( N_b(t) \) vs. \( t \) for various \( T \). It is equal to the initial bond number \( N_b(0) \) \(( \approx 8.4 \times 10^4) \) minus the number of the broken bonds. It may fairly be fitted to the exponential form \( e^{-t/\tau_b} \). The bond life time \( \tau_b \) is determined by \( N_b(\tau_b) = N_b(0)/e \). Then \( \tau_b = 91, 8.1, 1, 0.3 \), and 0.09 for \( T = 0.6, 0.8, 1 \), and 1.2, respectively, in units of \( 10^3 \tau \). Here we notice that the product \( D_\lambda \tau_b \) is between 1 and 2, where \( D_\lambda \) is the diffusion constant determined in fig. 6(a).

Thus

\[
D_\lambda \sim \tau_b^{-1},
\]

which demonstrates that the particle motions are caused by the configuration changes in our jammed states. We should furthermore examine how this observation can be related to the experiments [9,12].

We examine how the dynamic heterogeneity evolves in time. In fig. 7, we pick up the particles with broken bonds in three consecutive time intervals and mark them in ultramarine, magenta, and black in this order. Here we set (a) \( \Delta t = 800 \) at \( T = 0.8 \), (b) \( \Delta t = 100 \) at \( T = 1.0 \), and (c) \( \Delta t = 10 \) at \( T = 1.2 \). Colors: ultramarine \((\ell = 1)\), magenta \((\ell = 2)\), and black \((\ell = 3)\) in the chronological order. Corresponding snapshots of \( D_j \) of (a) and (b) at \( \ell = 3 \) are shown in figs. 2(b) and (c).

The mobility of the particles is strongly correlated to the disorder variable \( D_j \) visualized in fig. 2(c). The dynamic heterogeneity can be seen over a rather broad temperature range around the melting, where the time scale changes dramatically [9,12–14,22,23].

Since the large-scale density fluctuations are enhanced as in fig. 4(b), we are interested in their relaxation. As shown in fig. 8, we calculated the intermediate scattering function

\[
S(k,t) = \int dr \ e^{ik \cdot r} \langle \delta n(r,t) \delta n(0,0) \rangle
\]

in the hexatic phase at \( T = 1.15 \) where the initial value \( S(k) \) is enhanced as in fig. 4(b). In an early stage it undergoes an oscillatory decay arising from the acoustic propagation. We find that it then decays exponentially as

\[
S(k,t) \approx S(k) A_k e^{-\Gamma_k t}
\]
for small $k \ll 1$. The amplitude $A_k$ approaches unity and the decay rate behaves as $\Gamma_k \sim k^{z-2}$ with $z \sim 2.6$ for small $k$. The dotted lines in fig. 8 represent this exponential form, which are excellently fitted to the numerical data. This slow decay arises from the evolution of large-scale density heterogeneities produced by the structural fluctuations. In the hexatic phase, the diffusion constant depends on the wave number as $D_k \propto k^{z-2}$ if it is introduced by $D_k = \Gamma_k/k^2$. This is analogous to the thermal diffusion constant at the gas-liquid criticality, where $z = 3$ in three dimensions [25]. However, we cannot explain this exponential relaxation in the hexatic phase at present. In passing, we also calculated exponential relaxation in the hexatic phase at present.

We make further comments. i) In our simulation, mesoscopic coexistence of the ordered and disordered regions is realized dynamically in the hexatic phase. There are no sharp boundaries between the two regions and the free energy penalty due to the structural inhomogeneity should be very small. These structural fluctuations resemble the critical fluctuations in Ising systems. It remains puzzling whether or not the long wavelength limit of $S(k)$ tends to a finite constant in the thermodynamic limit. If so, it follows a finite compressibility. ii) Growth (shrinkage) of the disordered regions gives rise to an increase (a decrease) in the pressure $p$ at fixed volume. We should perform constant-pressure simulations also to examine whether or not the hexatic phase exists depends on the boundary condition. iii) In binary mixtures the size dispersity serves to pin the particle motions and the relaxation times are much longer than in one-component systems. iv) Shear flow has been applied to glassy and polycrystal states [24,26]. We plan to examine nonlinear rheology in the crystalline and hexatic phases in two dimensions.

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