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SIMULATION STUDIES OF THE 2-D MELTING MECHANISMS

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ABSTRACT

Computer simulations can reveal details of the thermal properties of 2-D systems not observable by other techniques. We report here studies of r^{-6} repulsive systems (256 and 2500 particles) which show the role of dislocations and grain boundaries in the 2-D melting process. Three regions are observed; solid, oriented fluid, and isotropic fluid. The solid is characterized by algebraic decay of g(r), but long range orientational correlations. The oriented fluid has exponential decay for g(r) and algebraic dependence for orientation, while the isotropic fluid phase shows the normal exponential behavior for both properties. The qualitative features of 2-D melting in the systems studied thus are consistent with the Kosterlitz-Thouless-Halperin-Nelson mechanism, although the defect structure in both the oriented and isotropic fluids is rather complex.

Although the melting-freezing transition pair in 3-D is arguably the most important of all phase transitions, we have remarkably little knowledge of the mechanism(s) involved. This ignorance is related to the hard first-order nature of the transition; without a continuous change in order parameter, or at least a significant degree of pretransitional fluctuations, there is no observable signature to test a proposed mechanism. The 2-D melting phenomenon, however, offers more hope: fluctuations are more important in lower dimensions, and there is evidence that, in some cases at least, 2-D melting can be continuous [1].

We report here a combined Monte Carlo (MC) and molecular dynamics (MD) study of melting in a particularly simple system, namely softly repulsive discs interacting pairwise by the potential $V(r_{12}) = \varepsilon(\sigma/r_{12})^6$. The overall density $\rho^* = \rho\sigma^2 = 0.8$ ($\rho \equiv N/A$) was maintained by periodic boundary conditions. Two simplifications of an r^{-n} potential are the impossibility of a gas-liquid transition, and the universal ρ-T phase behavior characterized by a single dimensionless scaling parameter $\phi = \rho^*(\varepsilon/kT)^{2/n}$.

An obvious purpose of these simulations is to test the Kosterlitz-Thouless (K-T) [2], Halperin-Nelson (H-N) [3] theory of dislocation-disclination mediated melting for this potential. Crucial to testing the mechanism rather than just some of its predictions for correlation functions, etc., is determining an unambiguous method for directly observing the defect structure as a function of temperature.

The usual Burgers vector method of dislocation characterization is quite useful for a system with only a few defects, since almost everywhere the underlying lattice structure is apparent. Difficulties appear, however, when the system becomes highly defected.

COMPUTATIONAL DETAILS

All runs reported here were on a 2500 particle system system in a rectangular box of aspect ratio $\sqrt{3}/2$, chosen to accommodate a perfect triangular lattice at low temperature. The standard Metropolis MC method was used. Very long runs were made; in the transition region more than 10^8 moves (4×10^4 per particle) were required, while at least 4×10^7 moves were made away from the transition region. Local equilibrium was tested by examining block averages over 5×10^6 moves. The usual thermodynamic properties were monitored, while the orientational order parameter

$$\psi_6 = N^{-1} \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i) \{\frac{1}{6} \sum_{j=1}^{6} \exp(i6\theta_{ij})\}$$

was used to determine the four point orientational correlation function $g_6(r) \equiv \langle \psi_6(r)\, \psi_6^*(0) \rangle$. Here j labels the 6 nearest neighbors of a given particle, and θ_{ij} is the angle between some fixed axis and the line joining particles i and j.

The defect structure of a 2-D system is conveniently characterized by the coordination numbers (CN) of each atom. An unbiased definition of nearest neighbors is given by the Wigner-Seitz (or Dirichlet Domain) construction, as shown in figure 1. The lines drawn are the perpendicular

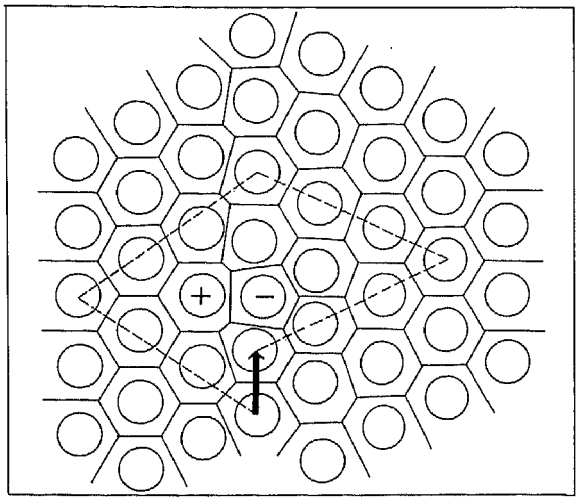

Fig. 1: The Dirichlet domain construction. A 7-5 pair is illustrated, with the path around the dislocation defining the Burgers vector.

bisectors of vectors to neighboring atoms. The smallest polygon around a central particle then uniquely specifies the number of nearest neighbors. For a perfect, T = 0 triangular lattice, all such polygons are regular hexagons, giving CN = 6 for each particle. It is a remarkable property of 2-D, however, that the average coordination number is a conserved variable regardless of the degree of disorder (this is not true in 3-D) [4]. (This statement is true except for a vanishingly small fraction of configurations, of which, unfortunately, the square lattice is one: see the Appendix.)

This conservation principle suggests that the "wrongly" coordinated particles may play a central role as elementary excitations in 2-D disorder. Such is indeed the case. As illustrated in fig. 1, a dislocation of Burgers vector 1 consists of a pair of 7- and 5-coordinated particles, while each non-6 coordinate particle can be viewed as a disclination. Thus a dislocation is a pair of (usually) 7 and 5 coordinate atoms, while a dislocation pair is a 7-5, 7-5 quadrupole. A string of 7-5, 7-5, 7-5... entities is a grain boundary. Vacancies and interstitials can also be identified in terms of clusters of non-6's [5].

RESULTS

A typical configuration of a high temperature ($T^* \equiv k_B T/\varepsilon = 0.15$) solid is shown in fig. 2a. This figure illustrates the great difficulty in identifying the defect structure by eye. However, the Dirichlet domain construction readily reveals the defect structure, as shown in fig. 2b. For clarity, only non-6 coordinate particles are shown, with 7's

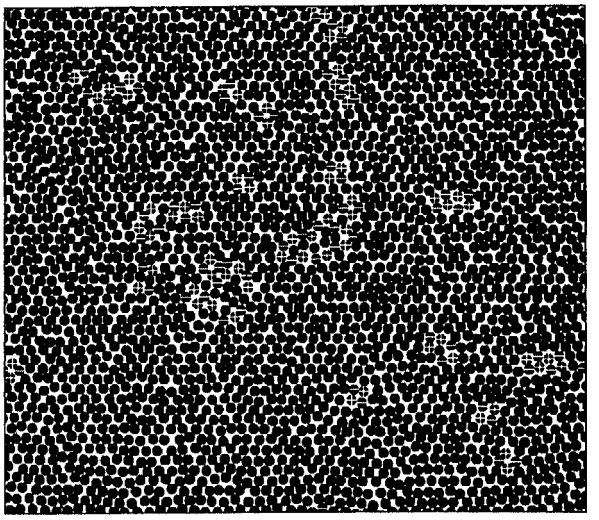

Fig. 2a: Typical configuration for the hot solid at T* = 0.150. Note the misoriented regions within the dislocation loops.

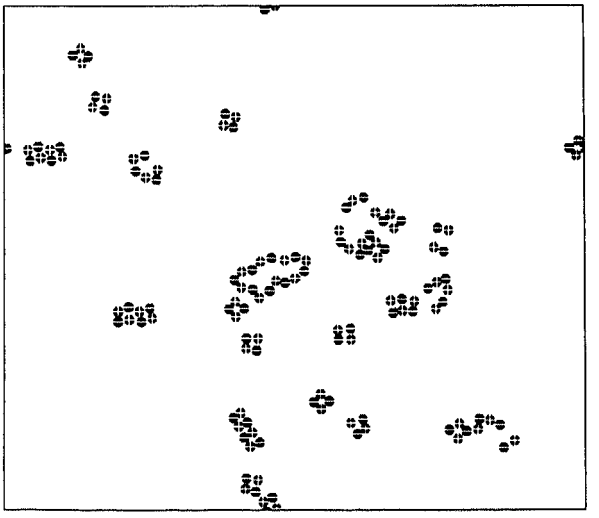

Fig. 2b: Defect structure for the configuration in fig. 2a.

labelled by +, 5's by -, 8's by #, etc. At low temperature (T* = 0.1, Fig. 3) only 7-5, 7-5 quadrupoles (i.e., dislocation pairs) are observed, but at T* = 0.15, just on the edge of the melting transition, more complex structure is apparent, including grain boundary loops and dislocation triplets.

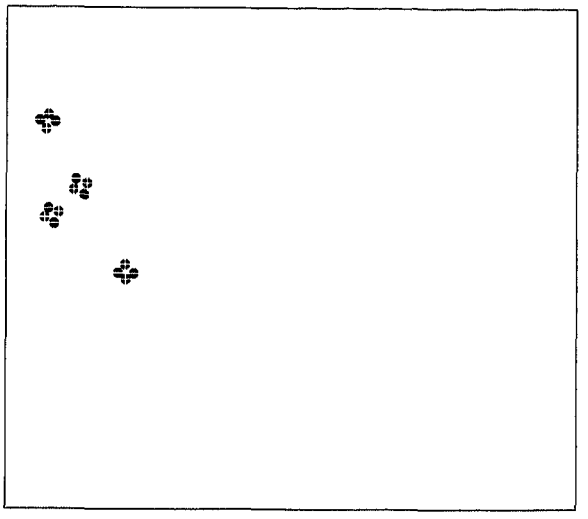

Fig. 3: Defect structure for the moderately hot solid at $T^* = 0.10$. Four dislocation pairs are apparent.

In fig. 4 we display the fraction of defects as a function of T^{-1}. The low temperature behavior yields a dislocation core energy $E_c = 1.5\ \varepsilon \approx 10\ k_B\ T_m$, where T_m is the melting temperature. The defect density changes rapidly in the region $0.15 < T^* < 0.15625$. At $T^* = 0.15$ no free dislocations are apparent, while at $T^* = 0.1525$ a few can be seen in each configuration (fig. 5). MD studies on a smaller (256 particle) but otherwise identical system show that this appearance of free dislocations correlates with a solid-fluid transition. Although some free dislocations are apparent at $T^* = 0.1525$, the majority are in collective loop-like and cluster-like configurations. There is, however, no sign of macroscopic phase separation, although the structural scale is of order a few hundred particles, so smaller systems might lead one to infer a phase separation [6].

The behavior of the correlation functions g(r) and $g_6(r)$ is shown in figs. 6 and 7. For $T^* \leq 0.15$ examination of ln g vs. ln r plots confirms that the envelope of g(r) decays algebraically, as do

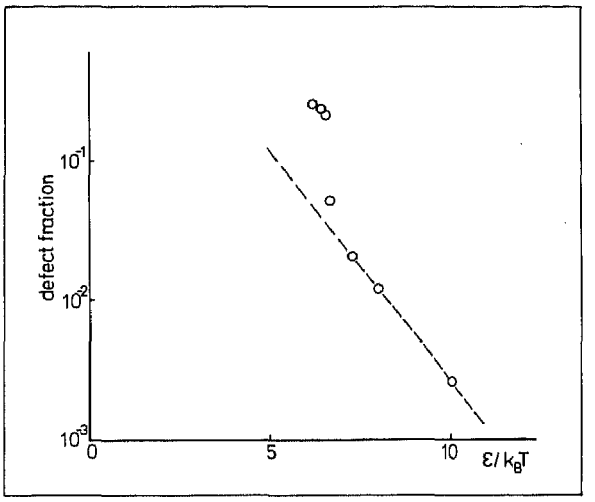

Fig. 4: Ln (defect fraction) vs. T^{*-1}.

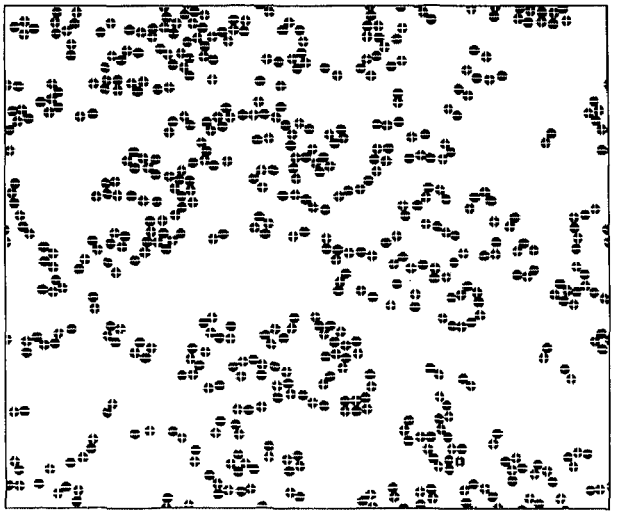

Fig. 5: Defect structure in the oriented fluid at $T^* = 0.1525$. Both free dislocations and many grain boundaries are apparent.

the Bragg peaks $S(\tau_{kh} - q)$. However, for $T^* \geq 0.1525$ g(r) decays exponentially. The orientational correlation function $g_6(r)$ shows sensibly infinite range for $T^* \leq 0.15$, as expected, while at $T^* = 0.1525$ it decays at $r^{-\eta_6}$, with η_6 ($T^* = 0.1525$) ≈ 1.13. At $T^* = 0.15625$ and above $g_6(r)$

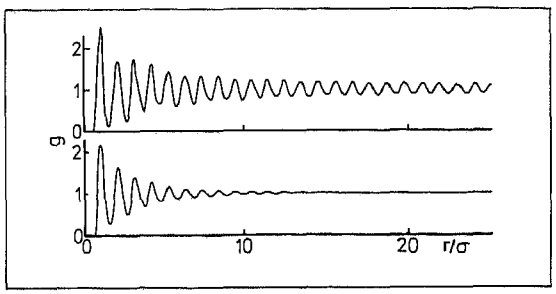

Fig. 6: g(r) vs. r at $T^* = 0.150$ (upper) and 0.1525 (lower). The envelope of the decay of [g(r)-1](0.150) is algebraic, with decay constant $\eta \approx 0.27$. The envelope for $T^* = 0.1525$ is exponential.

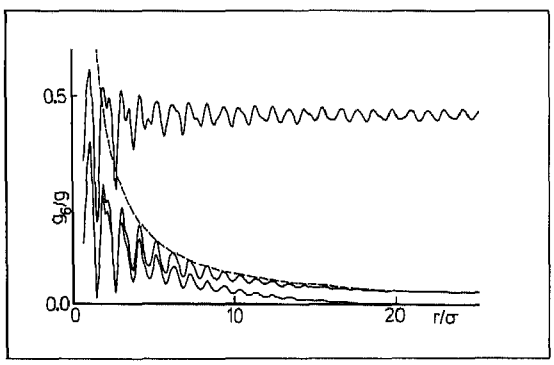

Fig. 7: $g_6(r)/g(r)$ at $T^* = 0.150$ (upper), 0.1525 (middle) and 0.15625 (lower). The dashed line is of the form $r^{-1.13}$. $g_6(r)/g(r)$ represents the orientational order correlation per particle vs. r.

decays exponentially as in a normal isotropic fluid.

According to the K-T theory of melting, T_m is given by the relation $K(T_m^-) = 16\pi$ (≈ 50). Here $K = (k_BT)^{-1} a_o^2 \mu(\mu + \lambda)/(2\mu + \lambda)$ and μ, λ are the Lame coefficients, and a_o is the lattice plane spacing. We find the following values for $K(T^*)$: 101 (0.10); 74 (0.125); 75 (0.137); 56 (0.15); 0 (0.1525). These results are clearly consistent with K-T theory, but the numerical results are preliminary and are probably reliable to only ± 25%. H-N predict that the fluid above this transition should have $g_6(r) \sim r^{-\eta_6(T)}$, with $\eta_6(T_m^+) = 0$, and increasing to $\eta_6(T_i^-) = 1/4$, where T_i is the temperature of decomposition of dislocations into disclinations. We presume that the numerical discrepancy between H-N and the present results is due to the predominance of dislocation loops (grain boundary loops), which provide an additional disorienting mechanism.

Despite the extreme length of our runs we are unable to determine unequivocally whether the melting transition at T_m is continuous or first order. Even after 4×10^4 moves per particle there is still a discrepancy in the energy in coming from higher vs. lower T, and there is still a slow drift in E. As pointed out by Knak Jensen and Mouritsen [7] it is necessary to show that the energy distribution becomes bimodal (first order) or unimodal (continuous) regardless of the direction of approach. What we have shown is that the transition is extremely sluggish, and that even longer runs are required to determine the order. In the region of T_m the energy changes rather rapidly (fig. 8).

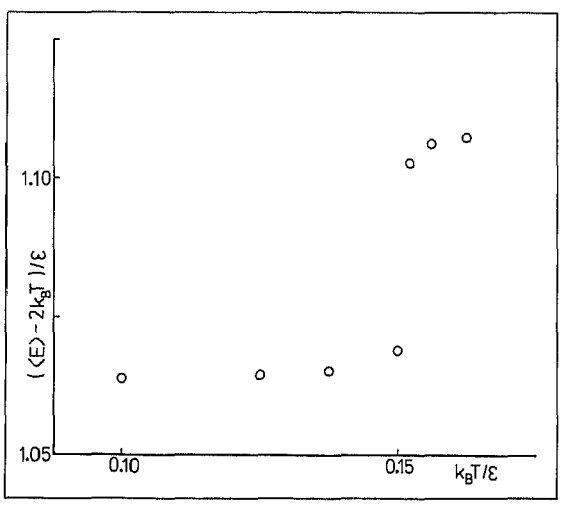

Fig. 8: Temperature dependence of the internal energy.

CONCLUSIONS

By use of the Dirichlet domain construction we have been able to identify the defect structure connected with the melting of a system of soft repulsive discs. The transition from crystal to oriented fluid is both qualitatively and quantitatively given by the K-T theory of dislocation

mediated melting, although we are unable to confirm whether the transition is continuous. However, other defect structures become apparent around this transition; in particular, grain boundary loops are quite significant in both the oriented and isotropic fluids. Above the first transition, the oriented fluid has a large number of clustered defects, including grain boundary loops. The transition to isotropic fluid in the system studied appears to involve microscopic grain boundary structure. Isolated disclinations have only rarely been identified. Where comparable, our results are quite similar to those on the one-component plasma ($V(r) \sim r^{-1}$) [8] and 2-D Lennard-Jones ($V(r) \sim (\sigma/r)^{12} - (\sigma/r)^{6}$) [9], and suggest that dislocations play a major role in 2-D melting for a wide variety of potentials, as originally suggested by Cotterill [10].

APPENDIX

We present here a simple proof that the average coordination number is a conserved variable. As illustrated in Fig. 1 the Dirichlet domain construction defines a connected graph each face of which is a Wigner-Seitz cell containing one particle.

Each vertex of the graph is equidistant from three nearby particles and hence is of degree 3: only in a vanishing fraction of degenerate cases (such as the square lattice) are vertices of higher degree found. Consequently the total number of edges E is related to the number of vertices V by the equation

$$E = 3V/2$$

The conservation law is obtained by applying the Euler formula for a connected graph

$$V - E + N = 2 - 2\gamma$$

which relates the numbers of vertices, edges and faces (particles) to the genus γ of the surface in which the graph may be embedded. In our case, the employment of periodic boundary conditions is topologically equivalent to embedding in a toroidal surface, which is of genus $\gamma = 1$. The above equations then yield

$$E = 3N$$

Since each edge separates two particles the average coordination number is exactly 6.

ACKNOWLEDGEMENTS

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DISCUSSION

B. I. Halperin:

The observation of an exponent of greater than 1/4, for the hexatic phase, is very difficult for me to accept. If one has truly reached thermal equilibrium, and if the distance scale is large enough, then the exponent η is directly related to the Frank constant K_A; if η is greater than 1/4, then the system should be unstable to the formation of disclinations. (Of course, if the core energy is high enough, there would not be many disclinations present in a finite size system.) In any case, I feel that the measured η cannot be simply interpreted as being characteristic of a macroscopic hexatic phase.

J. P. McTague:

I have no estimate of the disclination core energy so I cannot estimate whether we are in the asymptotic region, other than to note that our results are similar for 256 and 2500 particle systems, and that similarly large values of η are found for Lennard-Jones systems, where the intermediate phase is stable over a considerably wider temperature region.

The question of thermal equilibrium is always a thorny one near a transition. We have made exceedingly long runs by simulation standards, but the equivalent times are still very short on a laboratory scale. The results in Lennard-Jones systems near the middle of the intermediate phase should not be subject to as much uncertainty.

D. R. Nelson:

I would like to suggest that you clean up your 5-7 pictures further by blocking the system out, and computing the net "charge" and "dipole moment" within each cell. The net dipole moment rotated by 90° could be interpreted as a cell Burger's vector, and the net "charge" as a cell disclination charge.

J. P. McTague:

This is in progress at present.

E. K. Riedel:

Do you find a Kosterlitz-Thouless like melting transition for all densities?

J. P. McTague:

Yes, there is only one parameter in the theory. However, for u > 6 the transition may be first order. Already for u = 6 the hexatic phase region is very narrow.

D. S. Fisher:
(a)
What is the energy of vacancy and interstitials?

(b)

Grain boundaries can form as metastable structures if the time scale is not long enough for dislocations to climb. This seems to be a worry as far as equilibrium is concerned.

J. P. McTague:

The energy of a vacancy should be about 3 E, while T_m is about 0.15 E, so it is a very high energy excitation for this system. Interstitials should also have a high energy.

A. Holz:

From your slides I had the impression that below the melting transition there exists essentially closed bound pairs of dislocations and above melting there still exist lots of closed bound pairs, grain boundaries and only a few free dislocations. Is it possible that the fluidity of the sample is caused by other mechanisms, say grain boundary sliding? In addition what is the influence of the boundary by means of mirror faces on the generation of free dislocations?

J. P. McTague:

The grain boundary loops can soften the shear modulus but not to zero, so finite sized loops can not influence the k = 0 flow, but will influence the short time, short distance motion.

The periodic boundary conditions do not appear to be affecting the generation of free dislocations in any essential way in the large systems (2500 particles) but probably do play a role in the small systems at low temperatures.

J. G. Dash:

The limited number of particles in your computer simulation might be too small for reliable comparisons with theory, but it could be quite adequate for comparison with experiment. In most of the current studies the typical sizes of uniform domains in the monolayer films on graphite are on the order of ∿100 Å, and these sizes can contain no more than about 10^3 molecules. One qualification could be important, however. In most of the determinations of experimental domain sizes the films have been in registered phases, and it may well be that the characteristic sizes of incommensurate phases are considerably greater. The differences may in fact be relevant to the tendency that registered films seem to undergo less sharp "melting" transitions.

J. P. McTague:

With regard to Griffith's question about whether the correlation functions observed in the intermediate phase could be modeled by a sum of small crystallite and liquid correlation functions, the answer for g(r) is no, since a good exponential is seen ($g(r) \sim \exp(-r/\xi)$, with ξ of order a few atomic diameters.

D. J. Thouless:

Vacancies and interstitials are very important in equilibrating dislocations. Have you studied the vacancies in your systems?

J. P. McTague:

Vacancies and interstitials are not as easily identified in our defect constructions as are dislocation pairs. However, some interstitials are observable as tight loops of 3 7-5's surrounding a single 6 - coordinate atom.

A. N. Berker:

The Kosterlitz-Thouless-Halperin-Nelson-Young mechanism for melting involves a low-temperature phase of bound dislocation pairs, the average separation between two dislocations forming a pair increasing with temperature and becoming infinite at the transition. The number of dislocations remains small. However, slides from your simulations show small pair separations up to melting and a substantial increase in the number of dislocations at melting. Can't this be interpreted as a preemption by a standard first-order transition?

J. P. McTague:

Although the average distance of separation within a dislocation pair does increase slightly with

temperature, it does not go continuously to infinity. At the transition there is a discontinuity in the screening factor which causes a spontaneous creation of unbound pairs.

With regard to the order of the transition, as stated in the text, we can make no statement from the Monte Carlo data concerning the events at the transition. We can state that, away from this region, dislocations and dislocation pairs play a significant role.