Dislocation Lines as the Precursor of the Melting of Crystalline Solids Observed in Monte Carlo Simulations

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The microscopic mechanism of the melting of a crystal is analyzed by the constant-pressure Monte Carlo simulation of a Lennard-Jones fcc system. Beyond a temperature of the order of 0.8 of the melting temperature, we found that the relevant excitations are lines of defects. Each of these lines has the structure of a random walk of various lengths on an fcc defect lattice. We identify these lines with the dislocation ones proposed in recent phenomenological theories of melting. Near melting we find the appearance of long lines that cross the whole system. We suggest that these long lines are the precursor of the melting process.

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Melting is one of the rare phase transitions that can be observed in real life, outside of laboratories. Being a common-life process, the melting mechanism has been of interest for centuries. However, there is yet no complete understanding of the atomistic dynamics involved in the melting transition. This is due to several difficulties found both in the experimental and theoretical studies of this problem. Let us discuss some of these difficulties.

Upon a phase transition long-range order found in the low temperature phase (LTP) disappears at the transition temperature. In the simplest cases, such as a structural phase transition, order is associated with a geometrical quantity which distinguishes LTP from the high temperature phase (HTP). The dynamical collective structural deformation, namely, phonons, converting LTP into HTP is already present in the higher-symmetry phase. It is therefore natural to assume that the softening of this phonon excitation is the essential mechanism of the phase transition capturing the most important dynamics of the particles near the transition point.

However, at the melting temperature T_m, *both* translational and rotational symmetries of a crystal are destroyed, and it is much more complicated to construct simple models including the relevant excitations on both sides of the transition temperature. Hence, one-phase models have been developed. Starting in the solid phase, the question is what kind of excitation could destroy crystalline order. It is easy to see [1] that phonons alone cannot convert a solid into a liquid; some kind of crystalline defects should be invoked. Kosterlitz and Thouless [2] proposed a fundamental theory of the thermal breakdown of long-range order in two dimensions (2D) by topological defects and related it to transitions in 2D crystals, superfluids, and magnets, the relevant topological defects in the case of melting being crystalline dislocations (which are point defects in 2D). Their theory was greatly extended and detailed by Halperin and Nelson [3] and Young [4] who predicted that the complete transition from solid to liquid takes place in two steps: the dissociation of dislocation pairs drives a crystal into a liquid-crystal phase that retains finite-range orientational order; then a second transition at higher temperature completes the conversion to an isotropic liquid. This complete theory gave detailed predictions of the behavior of the specific heat, the structure factor, and elastic constants, which have been confirmed in numerous experiments and computer simulations.

In three dimensions, the most reliable theories suggest that the defects that break crystalline order are dislocation lines and that these lines proliferate at the melting temperature [5,6]. In addition to big theoretical problems involved in the development of a defects-mediated melting model, experimental evidence showing thermal excitations of such dislocation lines is scarce if not nonexisting [7]. In fact, most of the thermodynamic properties of a crystal could be associated with phonons and their interactions up to temperatures very near the melting point [8]; the premelting temperature zone where the thermal excitations of defect lines should appear seems to be very narrow and difficult to access experimentally.

Numerical simulations of model systems offer an alternative tool to investigate this problem. In fact, from the beginning of the computational era, the problem of melting has been studied by Monte Carlo (MC) and molecular dynamics techniques. The equation of state including the melting points of different materials has been obtained by these techniques, but the mechanism underlying the solid-liquid transition is yet unclear. The essential problem has been to separate the nonvibrational dynamics and to identify a premelting zone where the excitations of

some kind of defects prelude the breakdown of crystalline order.

Here we return to this long-standing problem and try to shed new light on it. By constant-pressure MC simulation carried out for a Lennard-Jones (LJ) fcc crystal we follow the evolution of thermally activated defects. We show that local defects group in clusters which we identify as dislocation lines. These lines are rare at low temperature and do not contribute to the thermodynamic properties of the system. However, as the temperature is increased, we succeed in identifying a crossover temperature (called the premelting temperature, T_{pm}), of the order of $\sim 0.8\, T_{\mathrm{m}}$. For $T > T_{\mathrm{pm}}$ defect lines of all lengths are thermally activated and become the relevant excitation of the system. Moreover, very near the melting point we detect very long defect lines with the maximum available length of our simulated system. We conclude that these system-size-long defect lines are responsible for the melting transition.

Our simulations have been done on a cubic box of different numbers of particles (between 864 and 6912) interacting via a LJ potential written as $V(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}]$. Here ϵ is taken as the energy unit, and σ is fixed in such a way that the fcc lattice constant is equal to 1 when only nearest-neighbor (NN) interaction is taken into account. We use periodic boundary conditions (PBC) numerically implemented by the minimal image convention method. It has been previously shown that in real systems melting starts at the surface of the sample [9]. As our simulated sample does not contain a free surface the transition temperature may not correspond to the thermodynamic melting point. Nevertheless, we use PBC because this leads to an intrinsic bulk mechanism for melting, and the results are not strongly affected by the finite-size effects.

Let us start with the analysis of the internal energy of the system. In Fig. 1 we show this quantity as a function of temperature. A jump seen at $T_{\mathrm{m}} = 0.56 \pm 0.01$ is associated with melting. For comparison we show our result of a quasiharmonic (QH) calculation on the same system. Both MC and QH calculations are done at zero pressure with a cutoff for the interaction taken at the next-nearest neighbors. We can see that the system behaves as harmonic only at low temperatures. The anharmonicity of the interaction potential produces only a small dilation of the system, but the essential dynamics of the particles is the harmonic oscillations around the lattice sites. This is true almost up to temperatures of $\sim 0.4 T_{\mathrm{m}}$. For higher temperatures, phonons start to interact between themselves, and the anharmonicity becomes relevant. A refinement of the perturbative calculation based on phonons has been recently developed in Ref. [10]. Applying it to a LJ system with only NN interaction the authors of Ref. [10] have shown that this theory can account for the thermodynamics properties of the system up to $\sim 0.8 T_{\mathrm{m}}$. This fact implies that thermally excited defects, if present, do not contribute to the equilibrium properties up to this

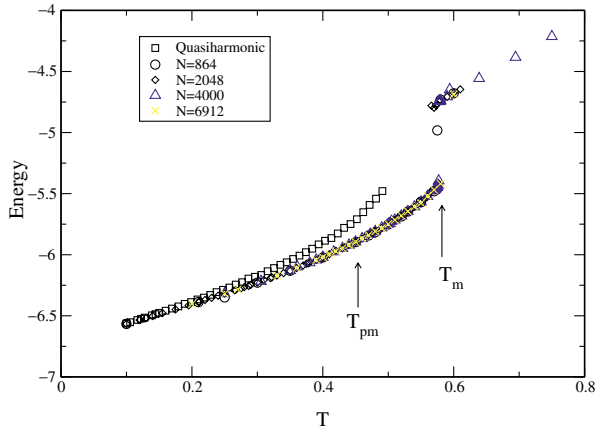

FIG. 1 (color online). Internal energy vs T for the system of $N = 864$, 2048, 4000, and 6912. T_{m} and T_{pm} are the melting and premelting temperatures. See the main text for the explanation.

temperature (which we call T_{pm} in the following). T_{pm} could be identified in Fig. 1 as the temperature where the energy starts to depart from the linear behavior. From T_{pm} some other excitations are created, and we study in detail this process in what follows.

We define a defect as a particle with a coordination number (CN) different from 12 (the number of NN in an ideal fcc lattice). CN is obtained by counting the number of particles around a given one up to a given cutoff called C_{NN}. This cutoff is chosen as the value where the radial distribution function has its first minimum. In Fig. 2 we show the evolution with temperature of the average CN of the whole system. In agreement with our previous discussion, a considerable number of defective atoms appear at T_{pm} where CN starts to decrease from 12. In this figure we also show the important increase of the percentage of defects with respect to the total number of atoms at T_{pm}. As no qualitative changes are observed for system sizes

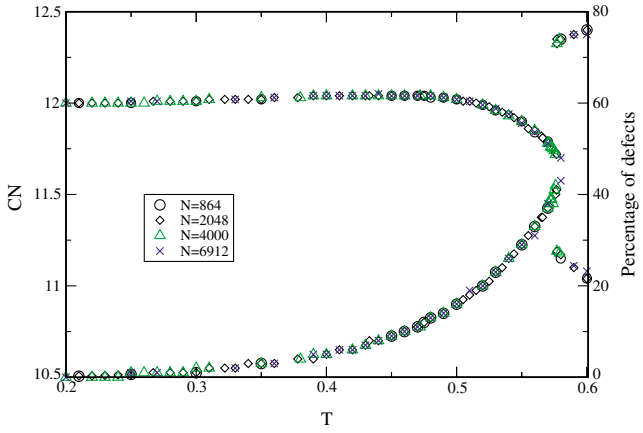

FIG. 2 (color online). The mean coordination number (left scale) and the percentage of defects (right scale) as a function of T for different cluster sizes.

greater than $N = 864$, in the following we show results for the $N = 2048$ system alone.

In the present work we are interested in the correlation between defects and in the study on how these defects group in clusters when the system gets closer to the melting point. We have developed the following algorithm to separate the defects in clusters and analyze their structure. We start with a given defect (let us call it d_1) and search new defects up to the cutoff distance C_{NN}. For each of these defects we repeat the same procedure. We iterate this process up to the completion of a cluster of connected defects. We label this cluster by the name of the first particle, d_1. Then we take a new defect (d_2) disconnected from all of the previous ones and follow the same procedure. At the end of this process we obtain N_{cl} disconnected clusters of defects.

By carefully analyzing the distribution of distances *within* each cluster, we have determined the internal geometry. When the clusters are relatively dilute, our results indicate that the distance between the nearest and next-nearest neighbors in a cluster are $\sqrt{2}/2$ and $\sqrt{3}/2$, respectively. As $\sqrt{3}/2$ is the distance between the vertex and the center of a unit cubic cell, we interpret the internal structure of the clusters as the system of (the parallel lines of) vacancies and interstitials. In every fcc cell inside the cluster one particle shifts from a vertex to the center leaving its perfect-lattice site. The new neighbors of this defective particle, at the centers of the neighboring faces of the cell, relax to stabilize this configuration, so that their separation corresponds to the equilibrium distance of the interaction potential. The resulting configuration is nothing but a vacancy-interstitial pair, which is the building block of the clusters of defects we observe.

At low temperature these clusters are mainly isolated pairs of defects of the type discussed above. When the temperature increases the density of defects increases as well. The creation of a pair of a vacancy and an interstitial in the neighboring cells will be energetically more advantageous than their creation at a longer distance. This simple effect could be the origin of the excitation of chains of defects instead of isolated ones. These chains are the realization of the dislocation lines proposed in phenomenological theories of melting [5,6], as we discuss in more detail below. It is therefore very important to check if these strings of defects appear in our simulation and how they evolve near melting.

We are interested in the behavior near melting of the mean total number of clusters (independent of their lengths) N_{cl}, and also in the dependence of the length L(defined as the maximum distance between two particles within a cluster) of a cluster on the number of particles N within this cluster. In Fig. 3(a) we show N_{cl} as a function of T. The decrease of this quantity at T_{pm} should be compared with the increase of the number of defective particles showed in Fig. 2. These facts indicate that the clusters are becoming bigger and bigger as melting is approached. In Fig. 3(b) we show a plot of log$L$ vs log$N$ for different system sizes at $T = 0.52$, a temperature in the premelting zone. All these curves start with the same linear behavior. This indicates a power-law relationship between L and N, of the form $L \sim N^{\nu}$ with $\nu \sim 0.62$. This value is in agreement with the law expected for a self-avoiding random walk (SAW) of a particle on the nodes of a 3D lattice [11]. Therefore, what we see here is the development of strings of defects located at the sites of an fcc lattice. As far as we know, this is the first evidence that strings of the thermally excited defects are seen in a numerical simulation of a crystalline system.

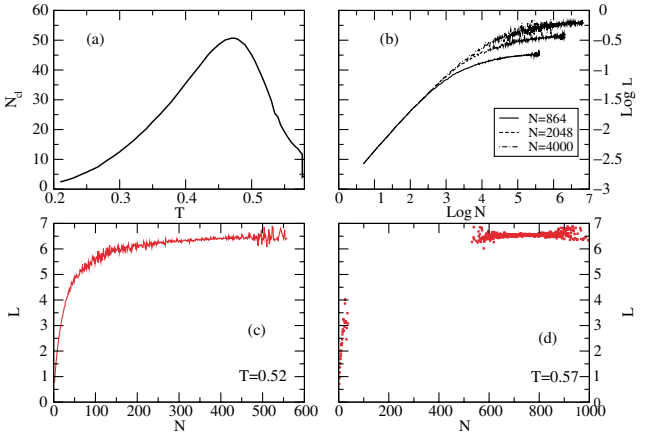

FIG. 3 (color online). (a) The average number of clusters as a function of T for the system of 2048 particles. (b) The logarithm of the length L of a cluster as a function of the logarithm of the number N of constitutive particles of this cluster at $T = 0.52$ for three different system sizes. (c) L vs N at $T = 0.52$ for the system with $8 \times 8 \times 8$ cells. (d) The same for $T = 0.57$.

The curves of Fig. 3(b) saturate for large N. They tend to a value of L (identified as L_s) which increases, as expected, when the size of the system increases. In Fig. 3(c) we show the behavior of L vs N for the system of $8 \times 8 \times 8$ unit cells. In this case L_s is equal to $4\sqrt{3}$, that is, half of the diagonal length of the whole system under study. Taking into account that we are using a minimum image convention to measure distance, this is the maximum available distance in our simulated cell. Hence, we conclude that the saturation takes place when the defect lines cannot continue to grow. The thermal creation of new defects cannot increase the length of the cluster due to the finite-size effects.

Let us now demonstrate that the chains of defects studied in this work must in fact be dislocation lines. Consider a plane which is orthogonal to the chain of defects and contains one of the vacancy-interstitial pairs of which the chains are formed. Any symmetric contour around this vacancy-interstitial pair in that plane does not close, a very well-known fact in 2D; its misfit is the Burgers vector of a dislocation formed by this pair of defects. Since the Burgers vector magnitude of a dislocation in 2D is related to the separation of the underlying

defects, the contour misfits in our 3D case will be the same for every plane orthogonal to the array and containing a vacancy-interstitial pair: the lines of vacancies and interstitials are parallel to each other; hence the defect separation is the same for every plane. Thus, the orthogonal contour misfit is an invariant for every chain of defects: it is in fact the (nonzero) Burgers vector of a dislocation formed by this array.

What is the seed of the melting process? Two different scenarios based on the dislocation-line generation could be envisaged. The first one, invoked by most of the existing theories, consider that melting takes place when the crystal is saturated with dislocation loops of all sizes including open dislocation lines crossing the whole system. In fact, the probability to have a loop of length ℓ in a crystal at the critical point is $p(\ell) \sim \ell^{-q}$, where the exponent q depends on the line topology, in other words, the nature of the dislocations as random walks, i.e., Brownian, self-avoiding, etc., and the balance between the loops and open lines [6]. The other possibility, see Ref. [1], is to associate melting with the generation of an arbitrary low density of infinitely long dislocation dipoles. These dipoles are the pairs of dislocations with opposite Burgers vectors. As seen in Fig. 2, the density of the defective atoms is rather high, $\sim$40% at the critical point, which is inconsistent with the density of dislocation dipoles being (arbitrary) low, according to the second scenario. (In fact, this percentage of the defective atoms is consistent with the conclusion of Ref. [6] that about $1/2$ of all atoms are within the dislocation cores at the critical point.) It is therefore plausible to suggest that the first scenario is realized in our simulation, i.e., the proliferation of dislocation loops of all sizes, including the appearance of very long open dislocation lines near T_m.

To gain further support for this scenario, we have analyzed in detail how the clusters of defects are formed at temperatures very near melting.

In Figs. 3(c) and 3(d) we show a plot of L vs N at $T_1 = 0.52$ and $T_2 = 0.57$, respectively, i.e., both in the premelting zone but T_2 near T_m. The most prominent difference between these two figures is that at T_1 the bigger cluster could include any number of particles beyond a critical one. However, at T_2 the bigger clusters appear with a specific number of defects inside it. This seems to indicate that these clusters are the ensemble of lines that cross the whole system. In addition, there is one of these big clusters in each realization of our simulation, and *all* the defective particles belong to this cluster at that temperature [12]. According to our results, such big clusters of defects are the precursor of melting. In fact, we have found that some of the samples that contain these big clusters melt after a long simulation.

The mechanism of the clustering of point defects into dislocation loops in the premelting stage seems to have certain experimental support. Novikov *et al.* [13] suggested that with their concentration growing, thermally generated point defects must cluster into dislocation loops for energetic reasons, and that this effect will be observed in a crystal in the state of premelting. They themselves claim the observation of this effect in lead. Two very recent experiments lend additional support: in Ref. [14] the point defect clustering into dislocation loops was observed in indium during its melting, and in Ref. [15] the formation of defect clusters was observed in silicon close to its melting temperature.

To summarize, we have analyzed the thermal excitation of defects by Monte Carlo simulation. Beyond a crossover temperature, defects group in clusters of all sizes that correspond to dislocation loops. Near the melting temperature, we observe the appearance of very long lines of defects that cross the whole system. We identify these lines with the precursor of the melting transition.

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