

## Free energy barrier to melting of single-chain polymer crystallite

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We report Monte Carlo simulations of the melting of a single-polymer crystallite. We find that, unlike most atomic and molecular crystals, such crystallites can be heated appreciably above their melting temperature before they transform to the disordered “coil” state. The surface of the superheated crystallite is found to be disordered. The thickness of the disordered layer increases with super-heating. However, the order–disorder transition is not gradual but sudden. Free-energy calculations reveal the presence of a large free-energy barrier to melting. © 2003 American Institute of Physics. [DOI: 10.1063/1.1553980]

It is easy to supercool liquids but difficult to superheat solids. The reason is that the free surface of a crystallite can melt at a temperature that is well below the bulk melting temperature.<sup>1,2</sup> As a consequence, solids usually melt from the surface inward without significant superheating. There exist experimental studies that show superheating of solids, but in these experiments the crystals are either confined in a nonmelting matrix<sup>3,4</sup> or the experiments reveal superheating of one particular crystal surface only.<sup>5,6</sup>

The melting of a single-chain polymer system is expected to be different. The reason is that all the polymer units are restricted by the strong covalent bonds along the chain. This implies that, when a single polymer partially melts (or dissolves), the molten units cannot escape from the surroundings of the crystallite. Rather, they stay around as a “corona” and can, in this way, affect the remainder of the melting process. The simulations presented below show that these features make the melting of polymer crystallites qualitatively different from that of atomic or molecular crystals.

Lattice models provide a highly simplified picture of freezing and melting. Nevertheless, it has been shown that such models are sufficiently flexible to account for the phenomenon of surface melting in simple “atomic” systems.<sup>7</sup> We used a polymer lattice model described in Ref. 8 to study the melting of a single-chain crystallite. In this model, polymers live on a simple cubic lattice, but the monomer–monomer bonds on the chain can be directed both along main axes of the lattice and along the face and body diagonals:  $6 + 12 + 8 = 26$  directions in all. The polymers can be semi-flexible and have attractive nearest-neighbor interactions. For each bond–bond connection along the chain, all noncollinear bonds are assumed to have the same energetic cost defined as  $E_c$ . The attractive interactions can be anisotropic: Parallel polymer bonds attract more strongly than nonparallel bonds (their difference is defined as  $E_p$ ), or isotropic: the site–site energy change (defined as  $B$ ) when forming one polymer–solvent contact from polymer–polymer and solvent–solvent contacts. By varying  $E_c$ ,  $B$  and  $E_p$ , we can “tune” the “phase-diagram” of a single polymer. A flex-

ible ( $E_c = 0$ ) polymer with a large  $B$  but small  $E_p$  undergoes a coil–globule transition.<sup>9</sup> In contrast, a flexible polymer with a large  $E_p$  but small  $B$  will go directly from the coil state to the crystalline state. In what follows, we consider the simplest case of a crystallizing polymer with 1024 monomers, namely, one where  $E_c$  and  $B$  vanish, but  $E_p$  does not. To minimize the finite-size effect, we used a cubic lattice with a linear size of 256 and periodic boundary conditions. This size was large enough to avoid interactions of the polymer with its periodic image, even in the coil state.

Initially, we prepared the polymer chain in a rectangular crystal with a folding length of 4 units and lateral dimensions of  $16 \times 16$  lattice units. Subsequently, this crystallite was annealed for  $10^6$  MC cycles at a temperature  $T = 2.0E_p/k_B$  in order to reach its equilibrium morphology. Here, one Monte Carlo (MC) cycle corresponds to one trial move per monomer. Having thus prepared an equilibrated single-chain crystal, we slowly heat it. Figure 1 shows the average potential energy  $\langle E/E_p \rangle$  of the single chain as a function of temperature. We choose the potential energy of a fully ordered bulk crystal as our zero of energy. As can be seen in Fig. 1, there is a gradual increase followed with sudden change in  $\langle E/E_p \rangle$  around  $3.125E_p/k_B$ . The sudden change indicates an irreversible abrupt melting of the compact crystallite to an expanded coil. Figure 1 also shows the temperature dependence of the fluctuations in the internal energy. An increase in the energy fluctuations is accompanying with the pretransitional rise of the internal energy. Obviously, the melting is preceded by an appreciable pretransitional effect.

To follow what is happening before abrupt melting, it is useful to trace the structural change on heating. Therefore, we analyze distribution of local crystalline order as a function of the distance from the center of chain mass. We can quantify the degree of local crystalline order by counting the number of parallel nearest-neighbor bonds around each bond (excluding two adjacent bonds along the chain). In a dense, ordered state, the number of parallel neighbors is equal to 24. In the coil state, it is more than an order of magnitude lower. In Fig. 2, we present the degrees of local crystalline order as

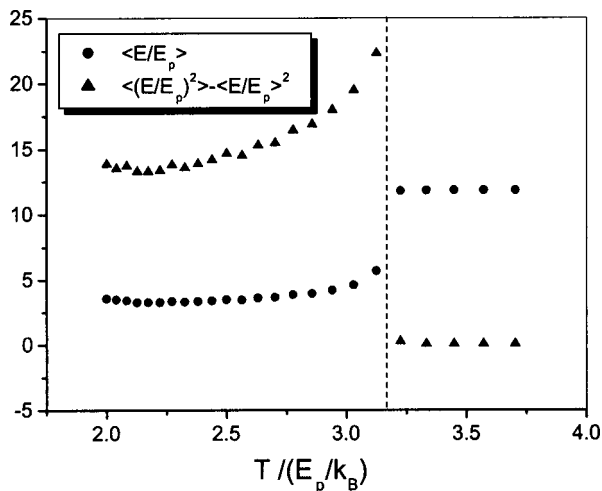


FIG. 1. Stepwise heating curve of the potential energy  $\langle E/E_p \rangle$  (spheres) and its fluctuations (triangles) for a crystallite of a single-chain polymer with 1024 units. The temperature was increased by decreasing  $E_p/(k_B T)$  with a fixed step size of 0.01. The system is allowed to relax during  $10^6$  MC cycles at each temperature and the reported data is averaged over 1000 records with 1000 MC cycles interval for each. The dashed line indicates the approximate temperature where irreversible melting took place.

a function of the distance to the center of chain mass. The figure shows that, as the temperature increases, the crystalline core is surrounded by a “corona” of bonds that occur in a disordered environment typical of a polymer coil. The degree of local crystalline order in the corona (indicated by an arrow in Fig. 2) and its thickness increase with temperature before the point of instability is approached. These results should be associated to the fact that the increase of molten units with temperature enhances the possibility of parallel packing in the corona as well as its outreach. The uncertainty of the tails in Fig. 2 is due to the scarcity in statistics. Within the time scale of  $10^7$  MC cycles, the abrupt melting can be observed at the temperature of  $3.105E_p/k_B$ . Figure 3 shows a snapshot of the crystallite at a temperature of  $3.086E_p/k_B$ , i.e., just below the point of irreversible abrupt melting. The snapshot indeed shows a crystalline core surrounded by a

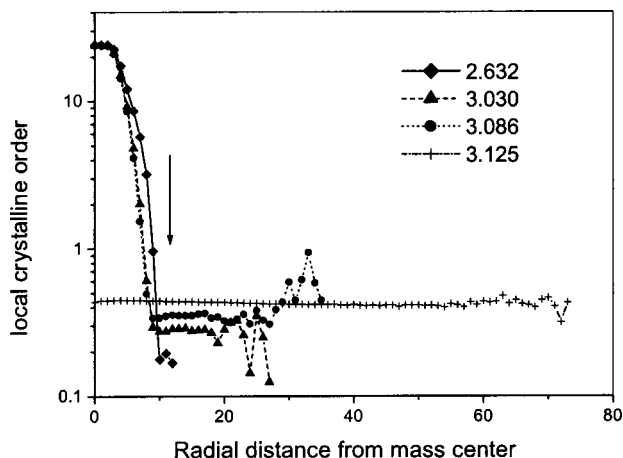


FIG. 2. Radial distributions of the degrees of local crystalline order (see the definition in text) for the single-chain system at several denoted  $k_B T/E_p$  values on heating. The results are averaged over  $5 \times 10^4$  samples, each with 100 MC cycles interval. The lines are drawn as a guide to the eye.

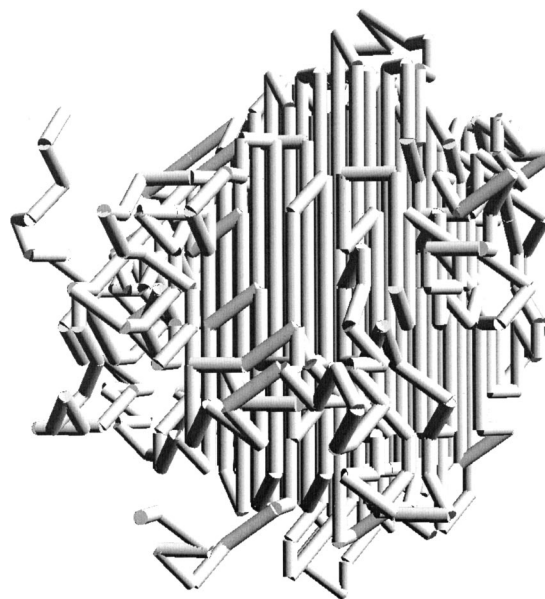


FIG. 3. Snapshot of the crystalline state of a single chain containing 1024 units at a temperature of  $3.086E_p/k_B$ , i.e., just below the abrupt melting temperature. Only the bonds connecting chain units are drawn as cylinders.

dilute “gas” of coil bonds. It should be stressed that these bonds belong to many different loops. Hence, the surface disordering is not limited to the chain ends.

The stability of this partial melting implies a free energy barrier for further melting. In our simulations, we directly calculated the free-energy change on melting. To this end, we computed the probability distribution  $P(n)$  to find  $n$  molten units in the system. Here, each molten unit is defined as the bond with fewer than five parallel neighbors. The Landau free energy of a state with this value of  $n$  is given by  $F(n) = -k_B T \ln P(n)$ . To improve the statistical accuracy of the calculation for those values of  $n$  where  $P(n)$  is small, we used umbrella sampling.<sup>10,11</sup> The results of this calculation are shown in Fig. 4. In this figure, we see two minima of the free energy change: one corresponds to the crystallite with a

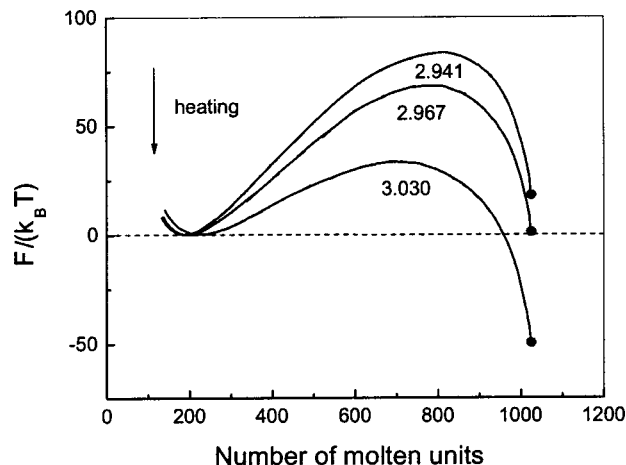


FIG. 4. Free energy curves on the number of molten polymer units for the melting of a single-chain crystallite at a series of temperatures. The free energies were calculated using umbrella sampling with 15 overlapping windows. Since our estimation is not for absolute free energy, the curves are shifted longitudinally to meet the minima of crystalline states at zero line.

disordered surface, the other to the disordered coil. On the crystalline side, there are about 100 molten units belonging to the bonds on the hairpin folds located at the crystallite surface. Nevertheless, the change of molten units is mainly attributed to melting and crystallization at the surface of crystallite. Increasing the temperature, the minimum of crystalline state gradually shifts to a larger number of molten units, reflecting the reversible equilibrium between melting and crystallization on the free surface of the single-chain crystallite.

Figure 4 allows us to determine the temperature at which coil and crystalline states are in equilibrium. We find that at the equilibrium temperature of  $2.967E_p/k_B$ , there is a high free-energy barrier (about  $70k_B T$ ) separating the crystalline and the coil states. As the temperature is increased, the disordered state becomes more stable, but the barrier for “explosive” melting remains higher than the thermal energy, up to a reduced superheating of 4.7%, where the free energy barrier becomes lower than the thermal energy, resulting to the final sudden melting. Here clearly, the abrupt melting is not initiated “from within”<sup>12</sup> but rather from the global instability.

The high free energy barrier at this equilibrium melting point demonstrates a typical first-order phase transition in

this small system. This simple homopolymer reproduces some of the aspects of protein folding. If we identify the crystalline state with the native state, and the coil state with the denatured state, then the present model has a pronounced barrier for both folding and unfolding. Correspondingly, the pretransition of melting can be associated to those intermediate states called “molten globule state.”<sup>9</sup>

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