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Melting a Copper Cluster: Critical-Droplet Theory.

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Abstract. – We simulate the melting of a 71 Å diameter cluster of Cu. At low temperatures the crystal exhibits facets. With increasing temperatures the open facets pre-melt, the melted regions coalesce into a liquid envelope containing a crystalline nucleus, and the nucleus finally goes unstable to the supercooled liquid. Using the critical-droplet theory and experimental data for Cu, we explain the thermodynamics of the coexistence region.

We simulate the melting of an approximately spherical, 71 Å diameter, 16727 atom cluster of Cu, using molecular dynamics with effective-medium theory interactions [1,2]. By using a realistic interaction potential we are not only able to make specific experimental predictions, but we are also able to compare our results to analytical calculations using experimentally determined latent heats, specific heats, surface tensions, etc. We analyse our results in three contexts. First, we observe many of the effects predicted in the theory of equilibrium crystal shapes [3], including liquid regions on open facets which can either be interpreted as pre-melting [4] or «liquid lenses» [5,6]. Second, we use the critical-droplet theory [7] to quantitatively explain the thermodynamics of the transition. By simulating the cluster at fixed energy (rather than fixed temperature) the first-order transition unfolds, revealing an interesting partially melted region in which adding more energy to the cluster *reduces* its mean temperature (the system has a negative specific heat). Third, we make contact to the formal theory of finite-size effects in first-order phase transitions.

The molecular-dynamics simulations of the properties of this Cu cluster are carried out using the Verlet algorithm for time integration of the equation of motion. The calculations were done on a massively parallel Connection Machine CM-200 computer, using an algorithm where the face-centred cubic computational box was subdivided into a 16^3 grid with a computational processor per grid point. The interatomic interactions of the effective-medium theory (which extend roughly to fourth neighbours) are computed inside 5^3 sub-boxes surrounding each atom.

In the present study of the solid-liquid phase transition, it is natural to control the total

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energy parameter and measure the temperature as the average kinetic energy of the atoms. The fluctuation $\langle(\Delta T)^2\rangle$ of the equilibrium temperature T at constant energy can be shown to be $k_B T^2[2/(3Nk_B) - 1/C]$, where N is the number of atoms, and C denotes the specific heat of the cluster as a whole. The fluctuations in the simulation agree well with this formula except near the instability point where the critical slowing-down (see below) makes sufficient statistics impractical to collect.

The Cu cluster was initially a spherically truncated f.c.c. crystal, heated to 1282 K in order to melt about 3 layers of surface atoms. This cluster was both cooled and heated, respectively, at a sufficiently slow rate to maintain thermal equilibrium. Figure 1 shows the facet distribution developing after the cooling. The relative areas of these facets in equilibrium depend on their relative surface energies through the Wulff construction [3], and are therefore quite sensitive to the model of interatomic interactions. The effective-medium theory has been shown to describe the various Cu surface energies with good accuracy [8].

Figure 2 shows the gradual melting of the cluster as the energy is increased. Figure 2*a*) shows pre-melted (110) and (100) facets, with the (110) regions appearing to form liquid lenses similar to those predicted by Löwen [5]. At slightly higher energies, the melted regions coalesce into a liquid envelope containing a crystalline nucleus. Figure 2*b*) shows the crystalline nucleus near the energy at which it becomes unstable. For smaller clusters, Ercolessi *et al.* [9] previously found liquidlike precursors prior to complete melting, and coexistence was also reported in ref. [10].

The surface diffusion is rather rapid on the melted surfaces, but moderately slow on the crystalline surfaces on the time scales investigated. Also, we observe significant critical slowing-down of the equilibrium between crystal and liquid near the instability point. Deep in the liquid and crystalline regions of temperature, the equilibration time scales were essentially zero; at the energy shown in fig. 2*b*), they slowed down to several tens of picoseconds (requiring several days of Connection Machine time for full equilibration).

In fig. 3*a*), we plot $E(T)$, the total energy of the cluster, *vs.* its temperature T. For an infinite system at constant T, this plot would consist of two straight lines and an abrupt vertical jump at T_c (ignoring the exponentially small, experimentally unobservable effects of droplet fluc-

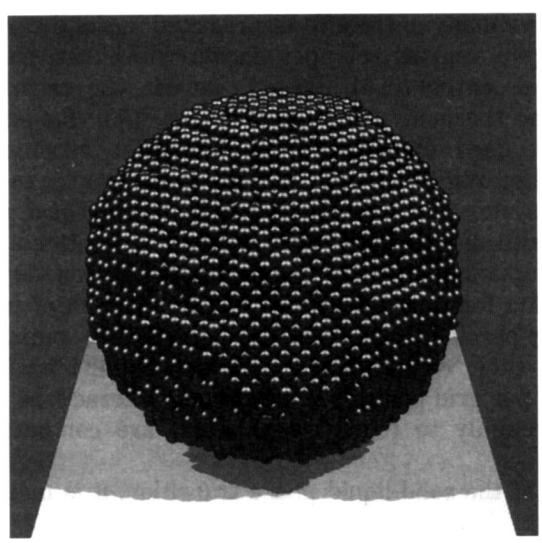
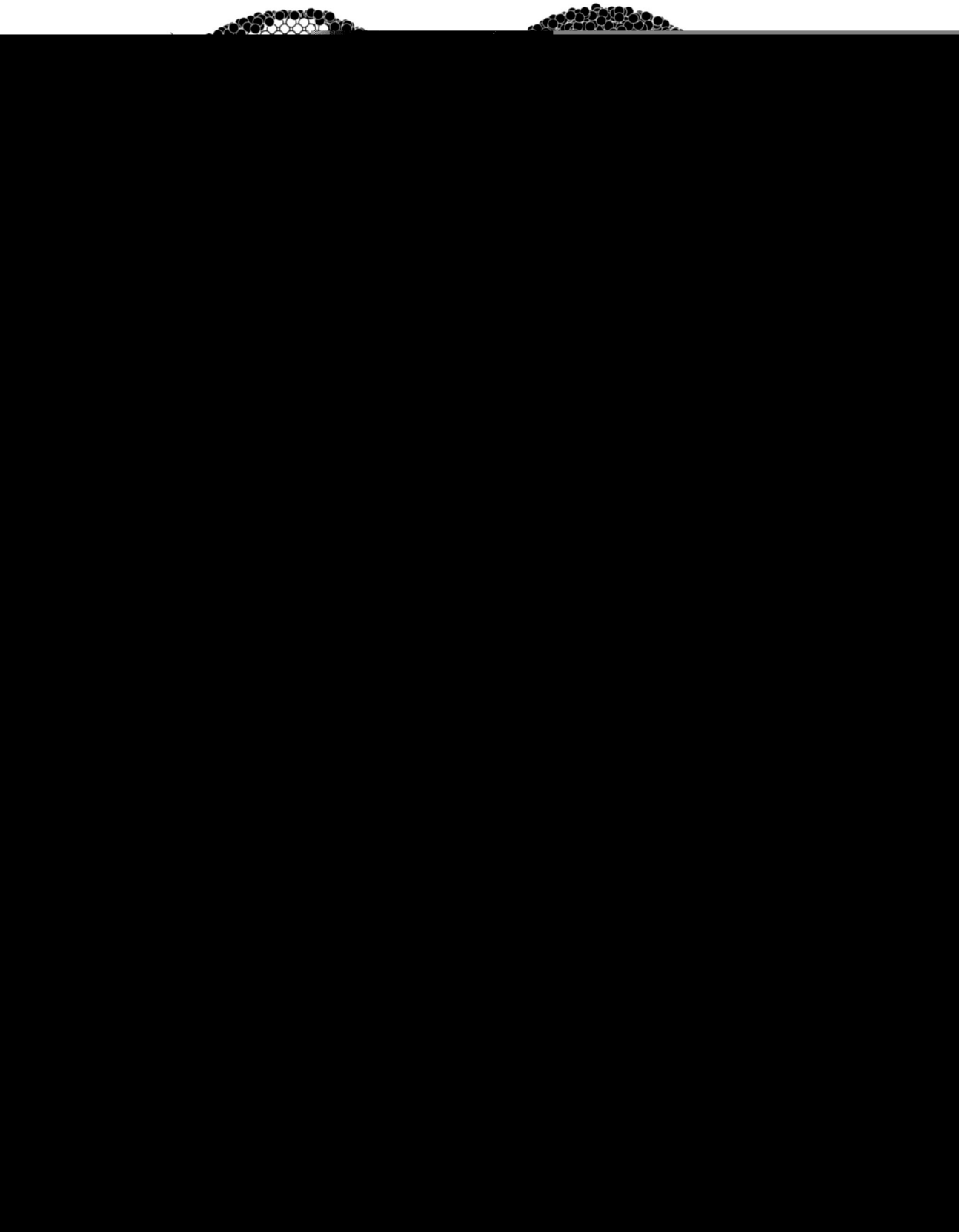


Fig. 1. – The faceted copper cluster at low temperature (522 K), with prominent (111) and (100) facets, clear areas of (110) facets, and terraces on the (111) facets.



supercooled and metastable, as is the mixed phase above this energy. Near e_{cross}, the system is in principle in a mixed state, where the crystalline nucleus appears and disappears with thermal fluctuations. This mixing will smear the jump over an energy range $\sim cT_c^2/(L\gamma)$, which is small for our system (~ 0.003 meV/atom). The *time* needed to see a fluctuation is huge, however. The intersection of the dotted line with the middle, dashed curve represents a transition state with a smaller, crystalline nucleus of the same energy and consisting of approximately 1100 atoms. However, this critical nucleus has an entropy lower by about $170k_B$, which is thus the entropy barrier between the two metastable states. The nucleation rate of the crystal from the supercooled liquid is consequently some microscopic prefactor times e^{-170}. We conclude that the nucleation rate is negligible both in simulations and experimentally down to temperatures much lower than T_c.

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