Melting a copper cluster: Critical droplet theory

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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 critical droplet theory and experimental data for Cu, we explain the thermodynamics of the coexistence region. The width of the transition scales as (Number of particles)$^{-1/4}$.

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We simulate the melting of an approximately spherical, 71 Å diameter, 16727 atom cluster of Cu, using molecular dynamics with effective medium theory interactions. 

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 analyze our results in three contexts. First, we observe many of the effects predicted in the theory of equilibrium crystal shapes, including liquid regions on open facets which can either be interpreted as pre-melting or “liquid lenses”. Second, we use critical droplet theory to quantitatively explain the thermodynamics of the transition. By working 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. We show that the broadening we observe in the transition scales as the number of atoms $N^{-1/4}$, which for large $N$ dominates the other studied broadening mechanisms.

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 simulations employ Andersen thermalization for obtaining a given temperature or total energy of the system. The calculations were done on a massively parallel Connection Machine CM-200 computer, using an algorithm where the face-centered cubic computational box was subdivided into a $16^3$ grid. A computational processor is assigned to each grid point computing for the atoms in its associated grid sub-box. The interatomic interactions of the effective-medium theory (which extend roughly to fourth neighbors) are carried out by regular communication of atomic properties inside $5^3$ sub-boxes surrounding each atom, assuring that all non-zero interactions are accounted for correctly, as in the serial-computer algorithm in ref. [2]. These algorithms will be described in a succeeding paper.

In the present study of the solid-liquid phase transition, it is natural to control the total energy parameter and measure the temperature as the average kinetic energy of the atoms. The fluctuation 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 measured fluctuations 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 fcc 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, 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.

Figure 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.

Figure 2 shows the gradual melting of the cluster as the energy is increased. Figure 2a shows pre-melted (110) and (100) facets, with the (110) regions appearing to form liquid
lenses similar to those predicted by Löwen. At slightly higher energies, the melted regions coalesce into a liquid envelope containing a crystalline nucleus. Figure 2b shows the crystalline nucleus near the energy at which it becomes unstable. We also did a simulation series starting from a fully melted liquid cluster with a minuscule central fcc seed. This formed a highly defective cluster with many stacking faults which slightly modified the pre-melting behavior, but left the remainder of the thermodynamics virtually unchanged.

**Figure 2.** Two cross sections of the cluster, at energies (a) -3.065 and (b) -2.990 eV/atom. The cutting planes shown are (a) (100) and (b) (111). The atomic positions are averages over the equilibrated part of the simulation. The liquid atoms are shown in black, the crystalline atoms in white. A histogram of position fluctuations was used to distinguish liquid from crystalline atoms.

The qualitative behavior of the dynamics in this simulation is also of interest. In the case of the highly defective cluster, we observed one of the stacking faults relieve itself during the simulation, when a partial dislocation nucleated and passed through the crystal. The dynamics of defect creation and annihilation will bear further study. For both simulations series, the surface diffusion is rather rapid on the melted surfaces, but moderately slow on the crystalline surfaces on the time scales investigated. Finally, we observe significant critical slowing down of the equilibration 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 figure 2b, they slowed down to several tens of picoseconds (requiring several days of Connection Machine time for full equilibration).

In figure 3a, we plot $E(T)$, the total energy of the cluster versus its temperature $T$. For an infinite system at constant temperature, 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 fluctuations). For the present cluster, this simple jump unfolds. The upper line represents the liquid state. Below around 1315 K the liquid becomes metastable, but the nucleation barrier to form a crystalline nucleus remains insurmountable until much lower temperatures.

The straight portion of the lower curve at low temperatures represents the faceted crystal. The slope of the curve starts to increase well below $T_c$, representing the latent heat of pre–melting for the various facets, starting with the open (110) surface. There have been experimental observations of superheating in metal clusters, which could be due to pinning of the liquid lens boundaries to the facet edges. Superheating has also been observed in simulations for smaller magic–number clusters, but it is likely that this superheating reflects the lack of steps or adsorbed atoms on their facets. We have observed no signs of superheating or latent heat jumps here. It is possible that the pinning barriers are small in our cluster, but may become observable for the much larger experimental clusters.

We find that the crystalline nucleus detaches completely from the surface of the cluster below the temperature maximum in the lower curve. At higher energies, the temperature decreases as the energy is increased (as observed in simulations of smaller clusters by Labastie and Whetten). This is a simple consequence of critical droplet theory. The free energy per atom of a cluster with a solid nucleus containing the fraction $\eta$ of the atoms in the cluster is approximately $f(\eta) = -L[(T_c - T)/T_c] \eta + \gamma \eta^{2/3}$. The first term represents the free energy difference between the supercooled liquid and the crystal and $L$ is the latent heat per atom. The second term represents the solid-liquid interface tension and the coefficient $\gamma$ is propor-
tional to a suitable average of the interfacial free energy density over the equilibrium crystal shape. The forces from these two terms balance when \((T_c - T)/T_c = (2/3)(\gamma/L)\eta^{-1/3}\) so the smaller the crystalline nucleus, the larger the undercooling needed to stabilize it. When energy is added to the system, part of the crystal melts, absorbing the energy. The remainder of the crystal has a smaller radius of curvature, and the interface tension demands a larger undercooling: even more of the crystal melts leading to a net decrease in temperature.

**Figure 3.** In (a) is shown the \(E(T)\) energy vs. temperature plot for the copper cluster simulation at constant energy. The black points represent the energies depicted in Fig. 2. In (b) is shown \(E(T)\) as derived from our simple model, Eq. 0.2. Here, the lower solid curve is the (partially) crystalline state, the upper solid curve is the liquid state, the dashed curve represents the unstable critical nucleus. The dotted horizontal line denotes the energy at which the entropies of the liquid and the mixed phases are equal.

A rough estimate of the temperature range over which the transition is broadened can be found by estimating the undercooling at which the crystalline nucleus becomes unstable. Equating the temperature drop from melting a small region to the shift in the undercooling needed to stabilize the now smaller crystalline region yields an instability undercooling \(\Delta T \sim (\gamma^3/L^2 c N T_c)^{1/4} \sim N^{-1/4}\), where here \(c\) represents a weighted average of the specific heats of the bulk liquid and solid. This broadened transition is only visible in constant–energy simulations; as \(N \to \infty\), it is larger than the finite–size effects at constant temperature considered in previous work. \[8\] Using the more complete analysis below, we have tested the size dependence of both the crossover temperature (where the liquid entropy equals that of the cluster) and the instability temperature (where the cluster becomes absolutely unstable): both scale as \(N^{-1/4}\).

We can turn this simple explanation into a quantitative calculation. First, because we work at constant energy, thermodynamics tells us that we must maximize the entropy per atom \(s\) (rather than minimize the free energy \(f\)):

\[
s(\eta, e_s, e_l) = \eta s_s(e_s) + (1 - \eta) s_l(e_l). \tag{0.1}
\]

We here regard the entropy as a function of the solid fraction \(\eta\), the energy per atom in the solid nucleus \(e_s\), and the energy per atom in the liquid region \(e_l\). The entropy in the solid phase \(s_s\) is given as function of energy by \(s_s(e_s) = s_s^c + c_s \log [(e_s - e_s^c)/(T_c c_s) + 1]\) where we make the approximation that the specific heat \(c_s\) is independent of temperature. The superscript \(c\) indicates values at the transition point. The entropy in the liquid phase can be similarly defined, using that the energy difference per atom between the two phases at the critical temperature is given by the latent heat \(L = e_l^c - e_s^c\), and the entropy difference is \(s_l^c - s_s^c = L/T_c\).

The energy per atom \(e\) we write as

\[
e(\eta, e_s, e_l) = \eta e_s + (1 - \eta) e_l + \frac{4\pi}{N}[R^2 \gamma_{lv} + R_s^2 (\gamma_{sl} + \Delta \gamma \exp(-2(R - R_s)/\xi))], \tag{0.2}
\]

with \(\Delta \gamma = \gamma_{sv} - \gamma_{sl} - \gamma_{lv}\), where \(\gamma_{sv}, \gamma_{sl},\) and \(\gamma_{lv}\) denote the free energy densities of the solid–vapor, solid–liquid, and liquid–vapor interfaces, respectively. The radius of the cluster \(R\) and the radius of the solid nucleus \(R_s\) can be expressed in terms of the densities and the
solid fraction $\eta$. The last term in Eq. 0.2 represents the interaction between the solid–liquid and the liquid–vapor interfaces and gives rise to premelting of a surface if $\Delta \gamma$ is positive. As usual, [13] the ambiguity of where to place the liquid–solid interfacial position is reflected in the breakup of the surface free energy into entropy and energy: we use the convention that attributes the free energy cost entirely to energy.

The experimental values of most of the parameters entering Eqs. 0.1 and 0.2 are known. [16,17] There is substantial uncertainty in only two: The solid-vapor and solid-liquid interfacial energies. The value for the solid–liquid interfacial energy $\gamma_{sl}$ we take as [17] 263 mJ/m$^2$. However, values as low as 177 mJ/m$^2$ have been found. [18] The value for the solid–vapor interfacial energy $\gamma_{sv}$ is poorly known. Here, we take the value from ref. [17]. A change in this parameter of only 1 percent will change the $\Delta \gamma$ by a factor of 2. This parameter controls the onset of pre–melting, and hence the shape of $E(T)$. With the present model (ignoring anisotropy as well as faceting and disorder on edges and vertices) and the given experimental values, we do not expect to reproduce in detail the pre–melting observed in the simulations. The exponential decay of the interaction between the solid–liquid and liquid–vapor interfaces follows from a Ginzburg–Landau analysis [17] of pre–melting of flat surfaces. The correlation length $\xi$ can be estimated from the solid–liquid interfacial free energy density using the Hansen–Verlet melting rule. [17]

Maximizing the entropy, Eq. 0.1, with respect to $e_s$ and $e_l$ at fixed energy $e$, Eq. 0.2 gives rise to the natural condition that the solid and liquid parts of the cluster must have the same temperature, and a further maximization with respect to the solid fraction $\eta$ leads to the $E(T)$ curves shown in figure 3b. At constant temperature, the transitions are vertical on this plot: there are two metastable states separated by the critical nucleus. The pre–melted crystal becomes unstable when the $E(T)$ curve has a vertical tangent. At constant energy, on the other hand, the crystalline nucleus surrounded by liquid becomes unstable when the tangent is horizontal.

Comparing figures 3a and 3b, we find that the molecular dynamics simulations using effective–medium theory potentials are in surprisingly good agreement with our simple model that uses only experimental data for the specific heats, the latent heat, and the effects of surface tension. However, there is a fairly substantial temperature shift between the figures. The experimental transition temperature for bulk copper is 1356.2 K: the interfacial tensions depress the transition in the model cluster to about 1190 K as seen in figure 3b. On the other hand, the transition is seen at 1335 K in the simulations. This could in part be due to the large uncertainty in the experimental value for the crystal–liquid surface tension used in our simple model, but it is also conceivable that the effective–medium theory [1,2] transition temperature could be off by the necessary 145 K. Simulations for a range of cluster sizes could pinpoint these properties.

We have shown that simple critical droplet theory, developed to study nucleation rates, provides a complete explanation for our copper cluster melting problem as studied through molecular dynamics simulations. We conclude by using the theory to calculate the nucleation rate for constant total energy. The dotted horizontal line in figure 3b shows the energy $e_{cross}$ at which the entropy of the liquid state equals that of the mixed state, which at this point has about 7200 atoms in the crystalline nucleus. Below $e_{cross}$ the liquid droplet is 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. The time needed to see a fluctuation, though, is huge. 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 until temperatures much lower than $T_c$.

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