CONDENSED MATTER PHYSICS

Melting in Clusters

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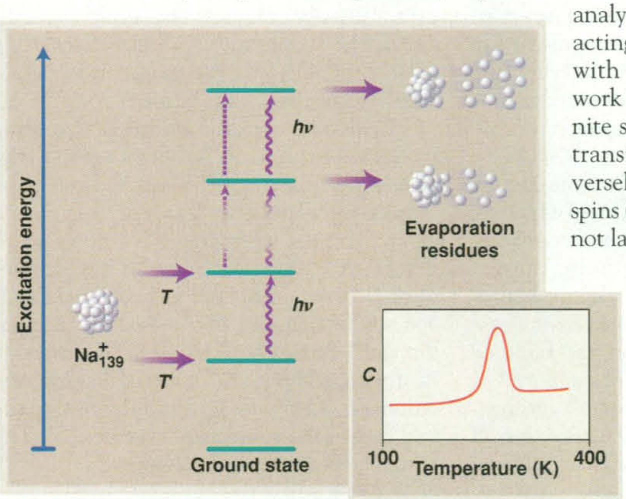
Evidence has been accumulating that nanometer-sized particles can melt at substantially lower temperatures than bulk matter does. A recent experiment (*1*) on free clusters has provided persuasive support for this behavior. The experiment measures the caloric function—that is, the energy as a function of temperature—for clusters of sodium atoms. For singly ionized clusters of 139 atoms, the specific heat function was flat from 100 to 350 K, except for a large bump at about 270 K (see figure inset). The bump is the finite system's precursor of the latent heat of melting in the bulk.

It is remarkable that the caloric function can now be measured in such a controlled way for systems the size of molecules. Producing clusters of a certain temperature is relatively easy, and the clusters can be sorted by size using molecular beam techniques, but how is one to measure their energy? The experimenters' yardstick was the evaporation pattern of the excited clusters, which lose mass by emitting atoms and smaller clusters. The evaporation rate grows exponentially with excitation energy, so the number of atoms evaporated in a given time period is a measure of the energy. However, the evaporation depends on too many factors to be used without calibration in some other way. The researchers overcame this problem by using a clever experimental arrangement to measure energy differences.

They started with a cluster beam characterized by temperature and size. The clusters go through a region exposed to a high-intensity laser beam, which adds energy in the quantum step of $E = h\nu$ for each photon of frequency ν absorbed (h is Planck's constant). The clusters then have some time to evaporate atoms. After this period, the residual distribution of cluster masses is measured. The overall mass distribution will be a superposition of patterns for clusters with energies $E + nh\nu$, where E is the initial energy and n is the number of photons absorbed. The researchers argue that two ensembles of clusters, having starting energies differing by $h\nu$, will have evaporation patterns favoring some of the same masses, because the energy difference could be provided by one more or less photon in the laser irradiation. Thus, if two ensembles at different temperatures have similar evaporation patterns, one can infer that their energies differ by an integer multiple of $h\nu$. In this way, the experimenters inferred the specific heat function

$$C = h\nu/(T - T') \qquad (1)$$

using the periodicity in the appearance of certain evaporation masses as a function of the temperature T. The concept of the experiment is shown in the figure. The latent heat, given by the integrated area of the bump in the specific heat function (inset), is 16 meV per atom, compared with the value of 27 meV per atom for the bulk. These values are close enough to be convincing that the bump is the finite-size precursor of the melting transition. The temperature of the transition was found to be 267 K, about 100 K lower than the bulk melting temperature.



Evaporating atomic clusters. Clusters of given temperature are excited by photon absorption and then evaporate with characteristic patterns. The deduced specific heat function is shown in the inset.

The large temperature shift confirms conclusions reached in more indirect studies, usually performed on much larger clusters embedded in a matrix or otherwise supported by a substrate. For example, Garrigos *et al.* (*2*) deduced a depression of the melting point of lead particles from the variations in the reflectivity of a matrix containing small particles. The phenomenon may be related to surface melting, which has been studied particularly in lead near the critical point. The only previous calorimetric measurement (*3*) used an ensemble of tin particles on a substrate, with cluster sizes of about 10^7 atoms. In free sodium clusters, indirect evidence for the low melting temperature was found earlier (*4*) in a study of magic numbers, which are cluster numbers with unusual properties. The magic numbers disappear in the higher temperature liquid phase.

There have been several theoretical routes to try to understand cluster melting. Kelvin used thermodynamic arguments to assess the relative stability of different phases in small particles. Small solid crystallites in a liquid just at the melting temperature cannot be stable because the surface energy becomes relatively more important for smaller crystallites. However, the particle's surface tension produces a pressure that usually drives the phase boundary to higher temperature. Thus, thermodynamic arguments are ambiguous in a system with only hundreds of atoms. Another approach is to study a model system complicated enough to have a first-order phase transition but simple enough to apply analytic methods. Models of interacting spins have been constructed with these properties, and much work has gone into studying the finite size scaling. One finds that the transition temperature scales inversely as cube root of the number of spins (*5*), suggesting a significant but not large effect. The last approach is the brute-force molecular dynamics simulation of the system. For computational reasons, the systems studied are small, typically 20 atoms or less. A number of these studies, cited by Schmidt *et al.* (*1*), found behavior suggestive of the caloric curve at temperatures far below the bulk melting point. However, it is difficult to make any correspondence between the structural changes in such a small system and the solid-liquid transition. Now that precise experimental data are available, the challenge is to understand what happens to the liquid and solid phases in small particles.

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