Solid-Liquid Transitions in Argon Clusters

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The solid-liquid transitions in argon clusters of *medium size* ($N>55$) are studied by molecular dynamics simulations on a cluster of 79 atoms. Over an intermediate range of total energy, the cluster exhibits a "dynamical coexistence" of solid and liquid states, in which the cluster fluctuates between solid and liquid states. We propose that for medium-sized clusters, the existence of two types of structures, low-energy solid and high-energy liquid structures, leads to the dynamical coexistence. We predict that the dynamical coexistence is a finite-size effect of a bulk melting transition.

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Being a first-order phase transition, melting is controlled by nonanalyticity in the free energy of a bulk system. Physical quantities which are first derivatives of the free energy, such as internal energy, entropy, and volume, all show discontinuities at the melting point. These discontinuities are direct products of the large size of the bulk system; the thermodynamic limit, in which the system size becomes infinity, introduces the nonanalyticity into the free energy.

What then should we expect of a system of relatively small size? A smooth gradual change from its solid phase to its liquid phase? Is it even sensible to distinguish between solid and liquid phases? Does any precursor exist in a small system to the bulk melting transition? If so, then how does this precursor differ from the bulk transition?

In 1975, Briant and Burton [1] performed molecular dynamics simulations on argon clusters of 2 to 100 atoms, and found relatively sharp first-order-like transitions for some clusters. In 1984, Berry, Jellinek, and Natanson [2] suggested that small clusters should exhibit a coexistence of solid and liquid states within a *finite range* of temperature. This makes small clusters different from bulk systems whose solid and liquid phases coexist only at a *single point* in temperature, the melting point. According to this suggestion, there are three temperature regions before a cluster evaporates: the low-temperature solid region below the coexistence range, the coexistence range, and the high-temperature liquid region above the coexistence range.

A number of molecular dynamics simulations [3] have since shown that only the clusters of particular sizes ($N=7,9,11,13,15,19,25,33,44,55,147$) can exhibit a "dynamical coexistence" of solid and liquid states, in which a cluster fluctuates back and forth between solid and liquid states. Since many of these clusters ($N=7,9,13,15,19,55,147$) have a single stable lowest-energy structure which is separated by an energy gap from higher-energy structures, it has been suggested that the existence of such a structure is necessary for the dynamical coexistence where a cluster hops between this lowest-energy solid state and higher-energy liquid states. For example, clusters with $N=13,55,147$ have markedly stable lowest-energy structures, an icosahedron for $N=13$ and multilayer Mackay icosahedra for $N=55$ and 147, and they all exhibit the coexistence. Furthermore, based on analytical models, Bixon and Jortner [4] concluded that an energy gap between a single lowest-energy structure and higher-energy structures is necessary for the coexistence. It is, however, not clear whether such a single stable structure is always necessary, as some of the clusters ($N=11,25,33,44$), which seem to exhibit the coexistence, do not possess such structures.

The aim of this Letter is to show that a single stable lowest-energy structure is not always necessary for the dynamical coexistence, especially for clusters of *medium size*, say $N>55$ (the significance of $N=55$ will be clear later), and to propose that for medium-sized clusters, the existence of two energetically distinct groups of structures, low-energy solid and high-energy liquid structures, leads to the dynamical coexistence. We will predict that for $N>55$, the dynamical coexistence is a common phenomenon as suggested by Wales and Berry in their attracting-quasiparticle model of melting [5]. We will also predict that the dynamical coexistence is a finite-size effect of the bulk first-order melting transition.

We have performed [6] simulations on a cluster of 79 argon atoms using the constant-energy molecular dynamics method with Verlet's algorithm and a Lennard-Jones potential, $V(r)=4\varepsilon\{(\sigma/r)^{12}-(\sigma/r)^{6}\}$, where $\varepsilon=1.67\times10^{-14}$ erg and $\sigma=3.40$ Å. A time step Δt was taken to be 5×10^{-15} sec. The cluster size, $N=79$, was chosen to be representative of medium size. Starting from a truncated octahedron with the fcc structure, we gradually heated up the cluster by raising its kinetic energy to reach its liquid region, and then slowly cooled it down by reducing its kinetic energy. We have sometimes made long runs up to 750000 time steps for some values of the total energy and found that these long runs were necessary for observing the transitions between solid and liquid states, which do not take place frequently.

The fcc structure that we chose as our initial structure

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is actually not the lowest in potential energy, and a structure which contains a multilayer icosahedron ($N=55$) is slightly lower in potential energy [PE(fcc) $= -887.5 \times 10^{-16}$ erg/atom whereas PE(lower) $= -888.7 \times 10^{-16}$ erg/atom]. As we repeated heating and cooling runs starting from this lower-energy structure and found that the results were very similar to those for our original initial structure, we will limit our discussion to the results with our original structure.

Figure 1 shows the temperature of the cluster as a function of time steps for four different values of the total energy inside an interval -720.0×10^{-16} erg/atom $< E < -687.0 \times 10^{-16}$ erg/atom. This energy range is where we have observed the dynamical coexistence, which is indicated by the temperature fluctuations between relatively high and low values. Since the temperature is defined to be proportional to the average kinetic energy and also the total energy is held constant, the higher the temperature is, the lower the corresponding potential energy is. We thus find the cluster switches back and forth between low-potential-energy states and high-potential-energy states. As we will show below, the low-potential-energy states are solid states, whereas the high-potential-energy states are liquid states. Therefore, inside the coexistence range, we have observed five, eight, six, and two passages between solid and liquid states at $E=-687.0\times10^{-16}$, -697.4×10^{-16}, -709.6×10^{-16}, and -720.0×10^{-16} erg/atom (from the top of the figure), respectively. Clearly the frequency of the passages is the highest around the middle of the coexistence range, where the cluster has an equal access to the solid and liquid states in the configurational space.

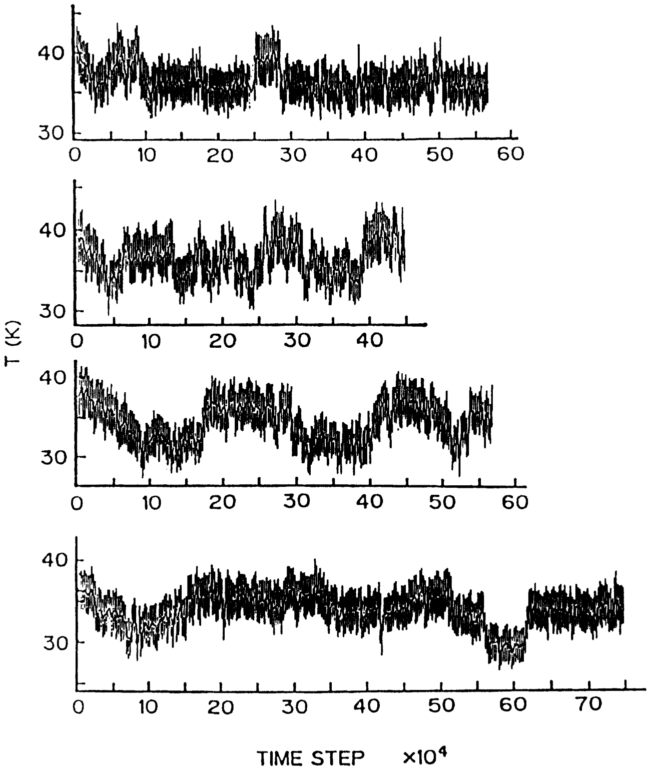

FIG. 1. The temperature of the cluster as a function of time steps inside the coexistence range (at $E=-687.0\times10^{-16}$, -697.4×10^{-16}, -709.6×10^{-16}, and -720.0×10^{-16} erg/atom, from the top).

By examining pair-correlation functions, angular distribution functions, and mean-square displacements, we have confirmed that the low-potential-energy states are solid states, where the atoms are mostly vibrating around their average positions, and that the high-potential-energy states are liquid states, where the atoms go through diffusive motions. What distinguishes the solid states from the liquid states are (1) a peak in their pair-correlation functions at a distance which is $\sqrt{2}$ times the first peak, (2) a peak in their angular distribution functions around 90°, and (3) small constant values for their mean-square displacements (MSD), which are in distinct contrast with monotonically increasing MSDs for the liquid states. (1) and (2) suggest that the solid states contain octahedra spanned by neighboring atoms, and (3) indicates diffusive motions in the liquid states and no such motions in the solid states.

By monitoring the numbers of the tetrahedra and octahedra spanned by neighboring atoms, we have found that the solid states contain more octahedra and less tetrahedra than the liquid states. We have also studied graphically how these tetrahedra are connected with each other as well as how the octahedra are connected with each other. We first list up all the possible tetrahedra and octahedra, and if two tetrahedra or two octahedra share a face, then we draw a solid line between their centers of mass. Similarly, if two tetrahedra or two octahedra share an edge (or a vertex), then we draw a dotted (or broken) line between their centers of mass. Let us call these graphical representations of cluster structures tetrahedral or octahedral connectivity diagrams. If we find a dodecahedron in a tetrahedral (or octahedral) connectivity diagram, then the cluster contains an icosahedron ($N=13$) (or a multilayer Mackay icosahedron with $N=55$).

Figure 2(a) shows that when the cluster is in a solid state (at 180000 steps) during the simulation at $E = -709.6\times10^{-16}$ erg/atom (inside the coexistence range), the cluster contains a multilayer icosahedron surrounded by an icosahedron (at top left) and some incomplete pieces of icosahedra. This structure persists up to 300000 steps, and then transforms into another solid structure [7] which includes a piece of the hcp structure [Fig. 2(b)]. When it is in a liquid state (at 330000 steps) [Fig. 2(c)], the cluster contains only broken pieces of icosahedra and no multilayer icosahedron. All the solid states found in our simulations contain a multilayer icosahedron surrounded by some complete or incomplete icosahedra except that we have sometimes found structures containing the hcp structure, whereas the liquid

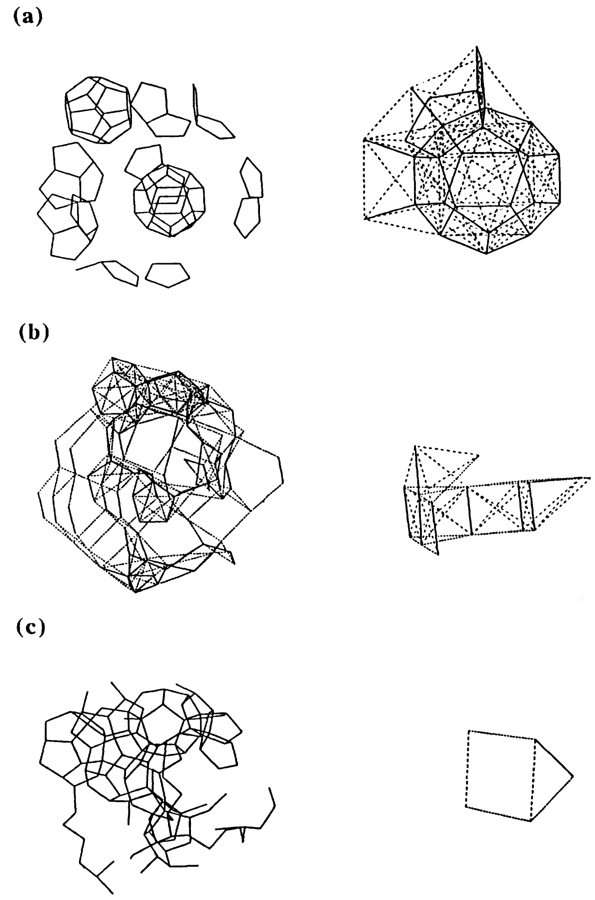

FIG. 2. The tetrahedral (right) and octahedral connectivity diagrams for the structures inside the coexistence range (at $E=-709.6\times10^{-16}$ erg/atom). (a) A solid structure at 180000 time steps. (b) A solid structure at 300000 time steps. (c) A liquid structure at 330000 time steps.

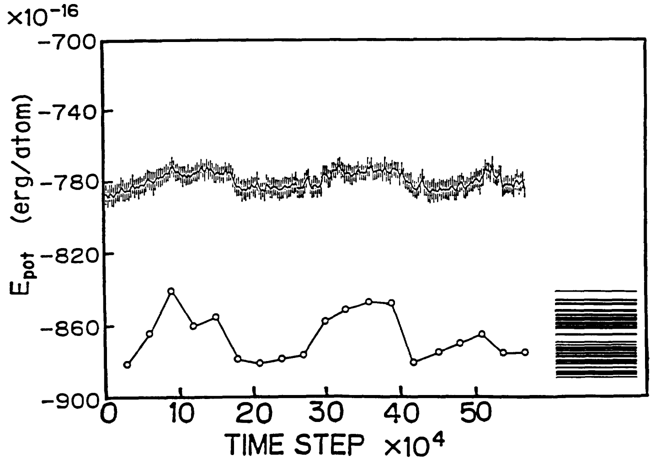

FIG. 3. The potential energy before and after (open circles) the quenching as a function of time steps for $E=-709.6\times10^{-16}$ erg/atom together with the energy-level diagram (at far right).

states always consist of broken pieces of icosahedra. This is why we find more octahedra in the solid states, because a multilayer icosahedron consists of both tetrahedra and octahedra. This structural difference between the solid and liquid states is analogous to that between bulk solid and liquid phases in a sense that the solid states are structurally *more ordered* than the liquid states.

To study the connection between the dynamical coexistence and a single stable lowest-energy structure, we have applied the steepest-descent quenching method pioneered by Stillinger and Weber [8]. We chose various states from a simulation inside the coexistence range, and rapidly cooled the cluster to obtain a zero-temperature inherent structure. The potential energy of these inherent structures as a function of time steps is shown in Fig. 3 together with the potential energy prior to the quenching. Figure 3 also includes the "energy-level" diagram (at far right) which shows the potential energies of inherent structures for various structures generated in our simulations. The energy-level diagram shows that our cluster does not possess a single lowest-energy structure isolated by a large energy gap. The energy levels are instead clumped into two groups: the lower group derived from the solid states and the upper group from the liquid states. Our cluster thus has two energetically separate groups of structures: the low-energy solid and high-energy liquid structures. The absence of an energy gap is easy to understand because every solid state is built around a multilayer icosahedron whose surface provides atoms with various positions which are very close in energy.

The energy difference between the two groups is mainly due to the structural difference between the solid and liquid states, because a presence of a multilayer icosahedron inside a solid state leads to a substantial lowering of the potential energy; the *multilayer icosahedral order* is responsible for this energy difference. This energy difference is actually playing a role similar to that of the large energy gap for those clusters with a single stable lowest-energy structure. Both of them ensure the stability of solid states by energetically separating them from liquid states. Because of this "phase stability" for solid states, it is sensible to distinguish between a low-energy solid phase and a high-energy liquid phase even for clusters of medium size.

We thus conclude that a single stable lowest-energy structure is not necessary for the dynamical coexistence in clusters of *medium size* as long as they contain a multilayer icosahedron, i.e., $N>55$. We propose that for medium-sized clusters, the existence of two energetically separate groups of structures, low-energy solid structures with multilayer icosahedral order and high-energy disordered liquid structures, leads to the dynamical coexistence. Since the existence of two such groups of structures should be common among medium-sized clusters, we predict the dynamical coexistence to be a common phenomenon for these clusters.

We can provide a further support for the above criterion proposed for the dynamical coexistence for medium-sized clusters by generalizing a model considered by Bixon and Jortner. Instead of assuming a single lowest-energy structure separated from higher-energy structures by an energy gap, we can construct a model where we have degenerate lowest-energy structures separated from higher-energy structures by an energy gap. It is straightforward to work on this model which mimics medium-sized clusters and to show the coexistence for this model.

Solid and liquid states in a medium-sized cluster thus exhibit various features similar to those of bulk solid and liquid states except that the solid structures for medium-sized clusters are not based on a crystalline order. The dynamical coexistence is then nothing but a finite-size effect of a bulk first-order melting transition. This view is consistent with the conclusion reached by Labastie and Whetten [9] in their Monte Carlo study of the clusters of $N=13,55,147$.

To better understand the dynamical coexistence, we have studied the thermal expansion of the cluster by calculating the mean distance of the atoms from the center of the cluster. This quantity provides a measure for the spatial size of the cluster, and attains larger values for the liquid states than for the solid states. Our results [6] show that the solid states expand more rapidly within the coexistence range than in the solid region, which implies that the solid states become increasingly unstable inside the coexistence range. By comparing the two potential-energy curves in Fig. 3, we also see that the thermal expansion not only raises the potential energy of both the solid and liquid structures but also reduces the energy difference between the solid and liquid states.

As a final remark, let us draw a dynamical picture of the solid-liquid transitions in medium-sized argon clusters. As the total energy is increased, the kinetic energy of the cluster increases leading to a rise in temperature. Because of increasingly larger amplitudes of atomic thermal vibrations, the cluster expands. This thermal expansion, in turn, raises the potential energy of solid states and brings it closer to the potential energy of liquid states. As the energy difference between solid and liquid states becomes smaller, the cluster begins to find pathways in the configurational space between solid and liquid states; the cluster starts to fluctuate between solid and liquid states: the dynamical coexistence. On further heating, solid states finally become unstable and the cluster stays as a liquid.

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