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Surface melting of clusters and implications for bulk matter

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Surface melting on clusters is investigated by a combination of analytic modeling and computer simulation. Homogeneous argonlike clusters bound by Lennard-Jones forces and Cu-like clusters bound by "embedded-atom" potentials are the systems considered. Molecular-dynamics calculations have been carried out for clusters with 40–147 atoms. Well below the bulk melting temperature, the surfaces become very soft, exhibiting well-defined diffusion constants even while the cores remain nearly rigid and solidlike. The simulations, particularly animations, of atomic motion reveal that the surface melting is associated not with amorphous, random surface structures in constant, irregular motion, but rather with large-amplitude, organized, collective motion of most of the surface atoms accompanied by a few detached atoms ("floaters") and holes. At any time, a few of the surface atoms are out of the surface layer, leaving vacancies; these promoted particles wander diffusively, the holes also but less so; the floaters occasionally exchange with atoms in the surface layer. This result is the basis for an analytic, statistical model. The caloric curves, particularly the latent heats, together with the results from an analytical model, show that surface melting of clusters is a "phase change" different from the homogeneous melting of clusters.

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INTRODUCTION

Interest in surface melting has been grown steadily in the last decade [1]. One origin of this subject arose from the question "Why is there no superheated solid?" The answer, at least for solids wet by their own melts, is now believed to be surface melting, which provides liquid nuclei to maintain equilibrium and prevents the solid crystal from maintaining a metastable, superheated state [2]. On the experimental side, ion scattering and low-energy electron diffraction showed the occurrence of surface melting [3], and revealed the number of melted layers as a function of temperature. These experiments were interpreted to show that this number increases abruptly beyond a certain temperature. On the theory side both simulations and modeling by analytic theory have been carried out for various bulk materials [1,4,5]. These studies give various relations between the depth of the liquid surface and temperature. The recent work also elucidates the role of the liquid surface in determining the shape of microcrystals [6]. However, most of the previous reports concentrated on bulk systems; even microcrystals are treated as "infinite." For small systems such as clusters, with three to several hundreds of atoms, although there is much work on the overall melting [7], the information on the surface phenomenon is very limited. Briant and Burton [8] proposed the idea of surface melting for clusters, and Nauchitel and Pertsin [9] showed, by Monte Carlo simulations, that Ar_{55} can exhibit surface melting over a range of temperatures below the lowest temperature of bulk melting.

Surface melting of small systems, seems unsurprisingly to be far less studied and far less understood than surface melting of macroscopic systems. The motivation of our work on this topic is closely related to other work on clusters, a subject that has become integrated into physics, chemistry, and material science [10]. We are interested in clusters as independent species as well as in their role in building bulk matter from the atomic level, atom by atom. For the first reason we want to understand the differences and the similarities of the physical properties of "small" and "large" systems, that is, to characterize any special properties unique to clusters. For the second reason we wish to study the evolution of those physical properties which change either gradually or abruptly as a function of the number of particles in the clusters. One other important motivation is to understand the role of surface melting in sintering, which depends specifically on the diffusion coefficient of material in a mobile surface pool [11]. (Here, we do not treat the competition between mobile surface atoms and mobile atoms close to grain boundaries.)

In this paper we present the results from molecular-dynamics (MD) simulations of Ar_N clusters, $N=40$–147, with magic and nonmagic numbers of atoms, and of the Cu_{55} cluster. We investigated the dynamical properties of the clusters "layer by layer" in order to study the difference between "surface" atoms and "core" atoms. We attempt to define the concept of surface melting of small clusters and to set up an analytic, statistical-mechanical model based on what we have seen in computer simulations, particularly in animations. In the next section the simulation and analytical methods are described. The third section describes the results of the simulations and the analytical model and the final section gives the general inferences we have been able to draw from this work.

METHODS

A. Simulations

The simulation method used mostly in our studies is the simplest conventional, constant-energy molecular-dynamics method implemented with a predictor-corrector algorithm [12]. As in almost every other MD paper, we solve the classical Newtonian equations of motion for a system consisting of N particles. The thermodynamic and dynamical properties of the system are obtained by carrying out various averages assuming the ergodicity of the trajectories. Several calculations were also repeated by the constant-temperature MD method of Nosé [13] in which an extra degree of freedom, with a coordinatelike variable s, is introduced to act as a heat bath exchanging energy with the $3N$ degrees of freedom of the real system by some dynamical process. We fixed N and chose free boundary conditions so that atoms may evaporate from the clusters. This is a natural choice for many conditions occurring in molecular-beam studies of clusters.

The second question is the choice of potential-energy function. Again, we have chosen the very simple Lennard-Jones (LJ) function as the model interatomic interaction for argon clusters. The potential is truncated at a certain distance [14] to save computational time. In some cases the simulations have also been performed with the untruncated potential in order to check the validity of the truncation and understand its consequences.

Other potentials we have used are the potential-energy function for bulk Cu constructed by the embedded-atom method (EAM) [15] and our modified EAM energy function for Cu which was reported in our previous work [16]. Like the Lennard-Jones, the EAM potential is a combination of short-range attraction and still shorter-range repulsion. The modified EAM potential has a larger force constant than does the original EAM potential; we shall see that this difference causes differences in the results for 55-atom copper clusters.

All the atoms of the cluster are initially arranged into a structure based on a core with icosahedral symmetry, the global minimum for the magic-number sizes of homogeneous clusters with pairwise, centrosymmetric forces. For the nonmagic-number clusters, we simply remove some atoms from the clusters with magic numbers. Following this rule, we constructed initial structures for the Ar_N clusters with $N=147$, 140, 130, 120, 110, 100, 55, 54, 50, 45, and 40. The Ar_{56} cluster is prepared by adding one atom to icosahedral Ar_{55}. The dynamics of all these clusters are reported in the next section. Starting from the near-equilibrium geometries we assign every particle an initial displacement in x, y, and z directions randomly and choose the initial linear and angular momentum to be zero to avoid additional complication—although the spinning cluster can be a very interesting subject [17].

The configuration space of the atoms in the clusters is divided into subregions according to the distance from the center of mass which is selected as the origin as usual. The atoms are classified according to radial regions so that we can distinguish a surface atom from a core atom. Some properties, i.e., the mean-square displacement, are calculated for each subregion. At the end of every time step we check whether an atom stays or leaves the subregion to which it belonged at the beginning of that time step. Any jump from one region to another is recorded and the atom is relabeled if it does leave its original subregion.

Simulations were carried out on various computers, notably Stardent GS-2000 machines. Graphic images were constructed and, for simulated Ar_{147}, an animation of a molecular-dynamics run was generated for one temperature.

B. Analytic model

On the basis of the results of the simulations, and particularly of the animation, an analytic, statistical-mechanical model was developed. According to the commonly accepted diagnostics of mean-square displacement versus time and its slope, essentially the diffusion coefficient, and of snapshots showing the apparently amorphous structure of the surface layer, it was inferred that the surface can be properly described as liquid. Figure 1 shows such a snapshot. Our expectation then, based on naive intuition, was that the molten surface layer would appear as an amorphous shell around a polyhedral core, and that the motions of the atoms of the shell would appear very random and independent-particle-like. Seeing an animation revised that notion totally. Even though most individual snapshots make the structure of the surface appear nearly amorphous, the animation showed that almost all the atoms of the outer shell undergo regular, large-amplitude, anharmonic but collective oscillations about a readily recognized polyhedral structure, and that at almost any instant, a small number of atoms have "popped out" of the surface and migrate as "floaters" above or outside the outer layer of the cluster. While the amplitudes of motion of the atoms still in the outer shell are perhaps three times the amplitudes of the inner-core atoms, they are not free to migrate. The floaters, as we shall call them, are responsible for the diffusive motion and for many of the liquidlike characteristics involving large-amplitude motion. Of course the

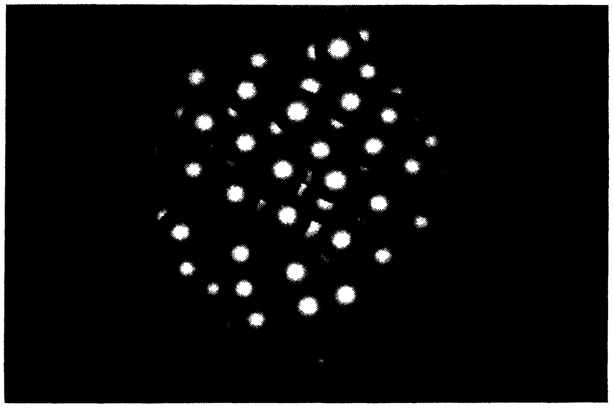

FIG. 1. A snapshot of Ar_{147} with a liquidlike surface and a solidlike core (mean $T=35.8$ K).

floaters exchange from time to time with the outer-shell atoms, so that eventually all the outer-shell atoms participate in diffusive motion.

Based on these results, we constructed an analytic model in which the partition function is a sum over states characterized by the number of floaters that have popped out of the outer shell and move relatively freely on its surface. The free energy is a sum of contributions: the core energy, the outer-shell energy, the energy of the floaters, and the temperature times the sum of the corresponding three entropies. The partition function consists of a sum over all numbers of floaters up to half the number in the outer shell (beyond that it is not clear what the surface layer is); it can be evaluated by summing over all the terms or approximated by evaluating its maximum term.

The partition function is a sum over all the possible numbers of floaters of the corresponding exponentials:

$$Z(T)=\sum_i g_i[(2\pi mkT/h^2)^{3/2}V_0]^i \exp(-E_i/kT) \quad (1)$$

with g_i the degeneracy associated with the choice of i identical floaters removed from the outermost shell, equal to C_i^j, the binomial coefficient for i items selected from j, the number in the outer shell. The energy E_i is the sum of three contributions, the part coming purely from the core atoms interacting with each other, the part due to the atoms in the outer shell interacting with each other and with the core, and the part due to the floaters interacting with each other, with the outer shell and with the core. These terms of course also contain the kinetic energies of the atoms of the core, the outer shell, and the floaters, respectively.

The problem lends itself naturally to a hierarchy of approximations, from the crudest to the most accurate. At the lowest level, the core energy is assumed to be the same for all numbers i of floaters. This level suffices to demonstrate the occurrence of surface melting but cannot exhibit the onset of bulk melting or show, for example, the most probable number of floaters at the temperature at which the bulk can become liquid. Also at the lowest level, the floaters can be treated as independent and free to move throughout a sphere with volume V_0, one atomic diameter larger in radius than the outer shell of the cluster. The atoms of the outer shell oscillate; from simulations, the amplitudes of their motion are typically three times those of the inner-core atoms. This leads to a lowest approximation for the vibrational motions, a Debye harmonic-oscillator model for the core atoms, and another Debye model for the atoms of the outer shell but with a Debye cutoff frequency or temperature $\frac{1}{9}$ of that of the core. Rotations are neglected at this level.

At the next level of approximation, the most important interactions due to the presence of floaters must be treated. These include floater-floater interactions and the effects of the floaters and the vacancies they leave on the vibrational energies of the outer shell. Such interaction in the situation of homogeneous melting was found by Berry and Wales [18] to have a crucial effect on whether or not the width of the temperature interval for coexistence of liquid and solid clusters goes to zero as N goes to infinity. Both can be handled phenomenologically, in terms of parameters measuring their strength. The floater-floater interaction can be left as pair interactions at this stage; the effect of floaters on the outer shell is presumably to lower the vibrational energy levels by leaving vacancies and permitting larger-amplitude in-surface motions than in the maximally occupied outer shell.

Two volumes enter in the models: V_0, the free volume per floater, and the initial volume V_i available for the vibrations of each atom in the outer shell of the cluster. We assume V_0 to be nearly a constant if there is only one floater, i.e., the free volume that a floater can explore is a constant independent of cluster size. As soon as more than one floater has been generated, they share the available space so that V_0 become smaller; on the other hand V_i, the free volume per atom in the outer shell, increases as i increases. At the very extreme, with i equal to half the number N_s in the outer shell, this initial volume becomes comparable to the the floater volume V_0.

Higher levels of approximation can include anharmonicities, explicit core-shell and core-floater interactions, and the creation of defects in the core, which may include promotion of atoms to the outer shell and even to the population of floaters. Higher approximations can also explicitly include barriers to motion of the floaters and exchanges of floaters particularly with atoms in the outer shell.

The free energy can be approximated as the logarithm of the maximum term of the series (1), especially if one term dominates the series. In that case, the Helmholtz free energy is a sum of an internal energy E_i and an entropy contribution TS_i, in which the energy contains the core energy, the outer shell energy, and the floater energy based on the most probable number of floaters i, and the entropy term contains the corresponding three contributions to the entropy. It is convenient to refer the energies and entropies to the energy and entropy of the cluster with no floaters and to write just the differences:

$$\Delta F_i=\Delta E_i-T\Delta S_i \ , \quad (2)$$

where

$$\Delta E_i=n_i\epsilon-\sum_j C_j^i \varepsilon^{(2)} \ . \quad (3)$$

In the first term, n_i is the net number of bonds broken when i floaters are made from the no-floater structure; it is assumed in lowest order that each floater has three bonds to the atoms of the outer shell. The second term is the vacancy-vacancy interaction in the outer shell. This is an upper limit of course unless floater-floater bonds are included, but these, as stated previously, are included only in the next order. The number of bonds in the no-floater state depends on the number of atoms in the cluster, and is estimated from an icosahedral geometry for clusters of the sizes we consider here. The entropy change

$$\Delta S_i=\ln g_i+\ln(V_0/v_0) \ , \quad (4)$$

where v_0 is the volume of a single atomic site in the outer shell, essentially $4\pi/3$ times the cube of the zero-point vibrational amplitude. Other terms that could be included would account for the changes in the surface vibrational modes which would soften under the influence of floaters and vacancies.

The procedure is then to find the minimum or minima in ΔF as a function of i, from the behavior of either the sum (1) or of the individual values of ΔF_i with respect to i. For finite systems, the occurrence of a minimum for some nonzero i implies that, so long as the dynamics permit such a state to persist long enough to be observed, the state with i floaters is a stable state. The state with no floaters is solidlike; this state is clearly the only stable state at low enough temperatures because the entropic terms are negligible at low temperatures and the entirely solid cluster has the largest number of bonds and therefore the lowest energy.

At issue is whether the entropic contributions can stabilize a surface with the characteristics shown by the simulations to correspond to the melted surface—or, more precisely, (a) what the necessary and sufficient conditions are for a state with a melted surface to be stable at temperatures below the temperature at which the entire cluster may become liquid, and (b) how the presence and nature of the melted-surface "state" depends on the number of floaters. If the number of floaters increases markedly with temperature, the transition from a cluster with a melted surface to a liquid cluster may be gradual; if the most probable number of floaters in a molten-surface cluster remains small up to the temperature at which the entire cluster may turn liquid, then the melting of the entire cluster can be expected to be well defined. Furthermore, if the most probable number of floaters is small, the latent heat associated with the formation of the melted surface may be too small to be discernable, and the transition may look as if it had no associated latent heat. All of these are matters that can be probed with the analytic model just described.

With our floater model, we tested three sets of estimated parameters for 55-, 147-, and 309-atom argon clusters. We calculated the free energy $F(i)$ as a function of vacancy number i. At large i we insert some model functions in Eq. (4). One of the functions is chosen to be the inverse of tangent i which is used to model the decrease in the final volume of the floater. It has maximum slope at i equal to half of the number of surface atoms, N_s, and at small i its contribution can be neglected compared to the noncorrected term in the equation. The second correction is the change of the free volume V_i due to creation of the floater. Again, at small i, the correction is insignificant but as i reaches $N_s/2$ the initial volume of the floater almost reaches the fraction of the volume that a floater would occupy in the surface shell; i.e., just before an atom leaves the surface shell and becomes a floater in the next shell, it already behaves partly like a floater. These two correction terms we arbitrarily added to Eq. (4) should be understood as part of our model, which in fact gives a reasonable shape to the $F(i)$ curve at large i. We focus here only on the qualitative behavior of the function. At the low i values which turn out to be of greatest interest to us, the original model is almost uninfluenced by this additional contribution.

RESULTS

A. Simulations

The results of the relevant numerical simulations are, first and foremost, (1) the layer-by-layer mean-square displacements as functions of time, for clusters of the various sizes and for several temperatures, and (2) the slopes of the straight-line portions of these mean-square displacements, which are six times the corresponding diffusion coefficients. (The intercepts of these lines are at present of less interest than the slopes.) The intercepts and the time intervals prior to the straight-line behavior reflect short-time relaxation, how long and how far the atoms move before the diffusive, large-amplitude motion hides the rapid, small-amplitude motion. Another quantity is the permutation index, the mean distance, after ca. 100 000 time steps, of atoms that began as nearest neighbors. This quantity probes the extent to which the cluster explores its configuration space, and in particular the extent to which it reaches all its geometrically equivalent permutational isomers. This quantity has been introduced especially to distinguish soft solid from liquid [19].

Figure 2 shows a set of typical, layer-by-layer mean-square displacements for a simulated cluster of 55 copper atoms, based on the embedded-atom potential modified to fit both the minima for Cu_6 given by a density-functional (discrete-variable or DVM) method. Figure 3 shows a similar set of curves for argon clusters of several sizes. These have all been selected to fall in the energy range within which the outer layer is liquid and the core is solid. Many previous simulations have shown no (or very little) diffusion for solid clusters and diffusion of all the atoms for liquid clusters [7].

Figure 4 shows how the mean-square displacements of separate shells change with temperature. These curves are made for single long runs and are based on averages over 100 initial points and 1000 steps of trajectory. Preliminary values of the temperature dependence of the diffusion coefficients, shown in Fig. 5, appear irregular because of the small number of initial conditions used for

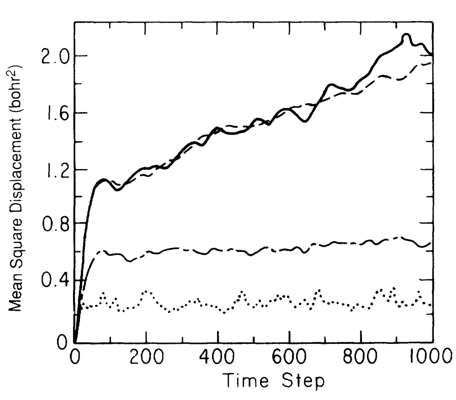

FIG. 2. Layer-by-layer mean-square displacements of Cu_{55} at $T = 620$ K. Bottom to top: innermost particle, first layer; the second layer and third layer have essentially the same mean-square displacements.

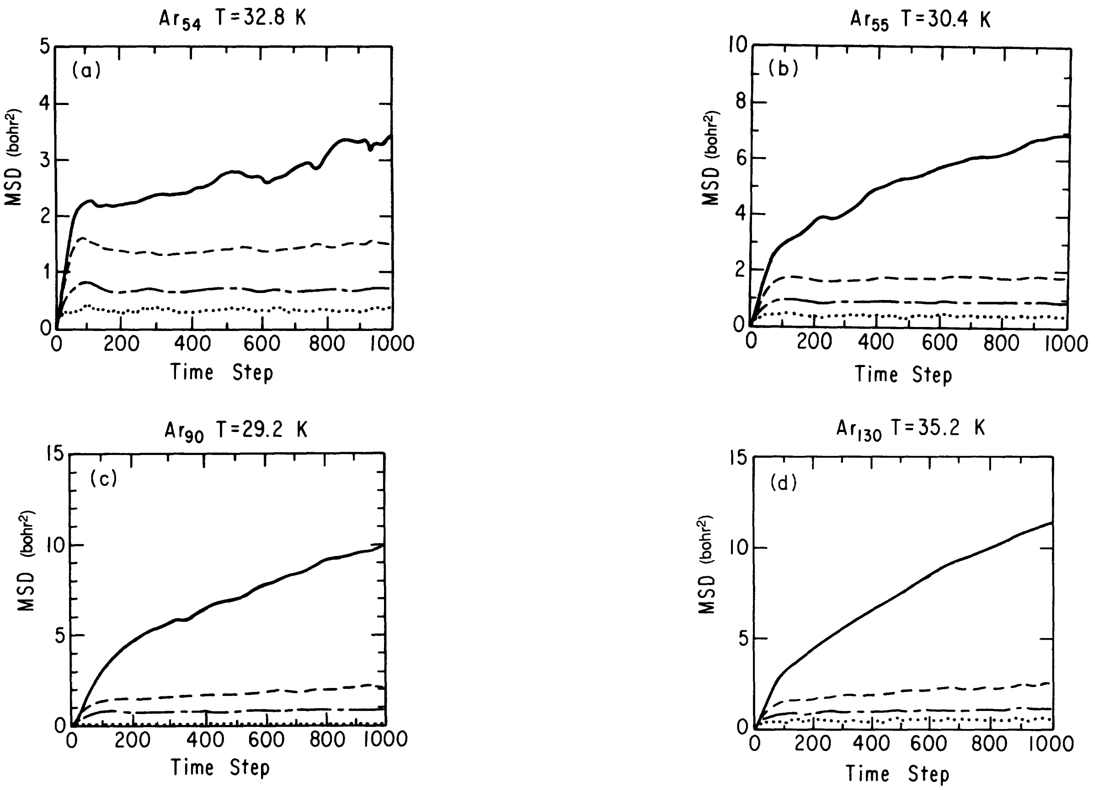

FIG. 3. Layer-by-layer mean-square displacements of atoms in various argon clusters. Top to bottom: outermost, then successive layers moving inward.

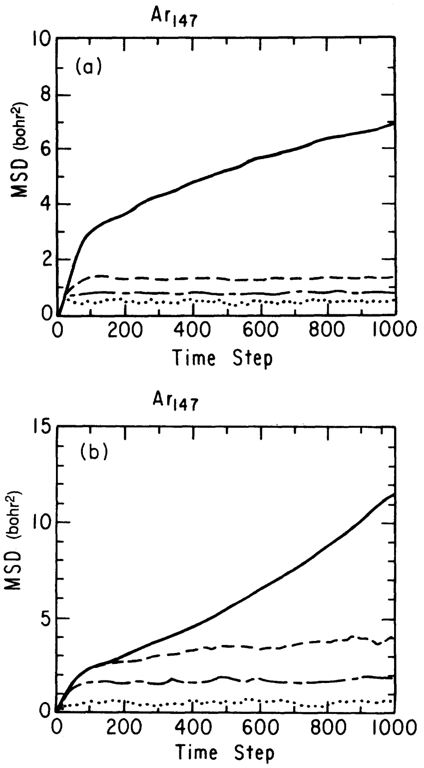

FIG. 4. Layer-by-layer mean-square displacements of atoms in Ar_{147} at two temperatures. The curves, top to bottom outermost, then successive layers moving inward. Upper panel, 38.0, liquid surface on solid; lower, 37.2 K, showing the effect of a single atom evaporating.

some of the temperatures; the true diffusion coefficient is expected to increase monotonically with temperature, of course. The diffusion coefficients obtained from MD simulations for all sizes of clusters at all the temperatures thus far investigated are collected in Table I for argon. For comparison, the reported self-diffusion coefficient D for liquid argon at 85 K is 1.84×10^{-5} cm^{2}s^{-1} and the value one would infer from that at 38 K is 1.23×10^{-5} cm^{2}s^{-1}.

The temperature ranges within which clusters may have liquid surfaces and solid cores have not been established with great precision but these have been inferred in a few instances. This can be done most reliably by examining the mean-square displacement curves for successive temperatures. It can also be done less precisely but more quickly in some cases by examination of the caloric curve of mean temperature versus energy. If the latent heat associated with melting of the surface is not negligible then its effect is to displace the melted-surface portion of the curve toward high energies relative to the solid portion. If the heat capacity of the melted surface differs significantly from that of the solid outer shell, then the slope of the melted-surface portion has a slope different from that of the all-solid portion. Thus far, only small effects of this type have been found. One example is shown in Fig. 6. This is consistent with the finding from simulations that only a few floaters are enough to permit the surface to melt. A challenging question yet to be answered is this: As the number of atoms in the cluster increases, how many floaters per surface atom are necessary or sufficient to give rise to surface melting?

In order to answer this question, we measured the mean density of atoms in the clusters as a function of the distance from the center of the mass. Figure 7 shows the density at several temperatures. At low T, the peaks are relative sharp; within a certain temperature region, those peaks are broadened and there is a "tail" at distances beyond the last peak; this is due to the population of floaters. Above the homogeneous melting temperature, in the liquid region, we can see that there is overall expansion in cluster size, and the radial distribution is much smoother than for the solid. This density function provides us with a measure of the mean number of the floaters.

As one more diagnostic in addition to the diffusion constant, we calculated the permutation index, the mean-square distance between two atoms initially adjacent to each other. Figure 8 is a plot of this quantity versus total energy for Ar_{147} with the untruncated LJ potential. The solid squares are the data corresponding to states with melted surfaces; the points to the left represent solid clusters, and the rightmost point is just at the energy at which the cluster first may become liquidlike. Increasing the energy further produces a large jump not shown in the figure. In the solidlike region there is one small peak with the same height as the first in the molten surface range. We can see, by looking at its zero diffusion constant and its atomic motion, that this is due to one or two "localized floaters" which, instead of traveling around the outside of the surface, stay for long intervals very near the places from which they "pop up." We believe that such points are a kind of noise that can be reduced by averaging over several dynamical runs.

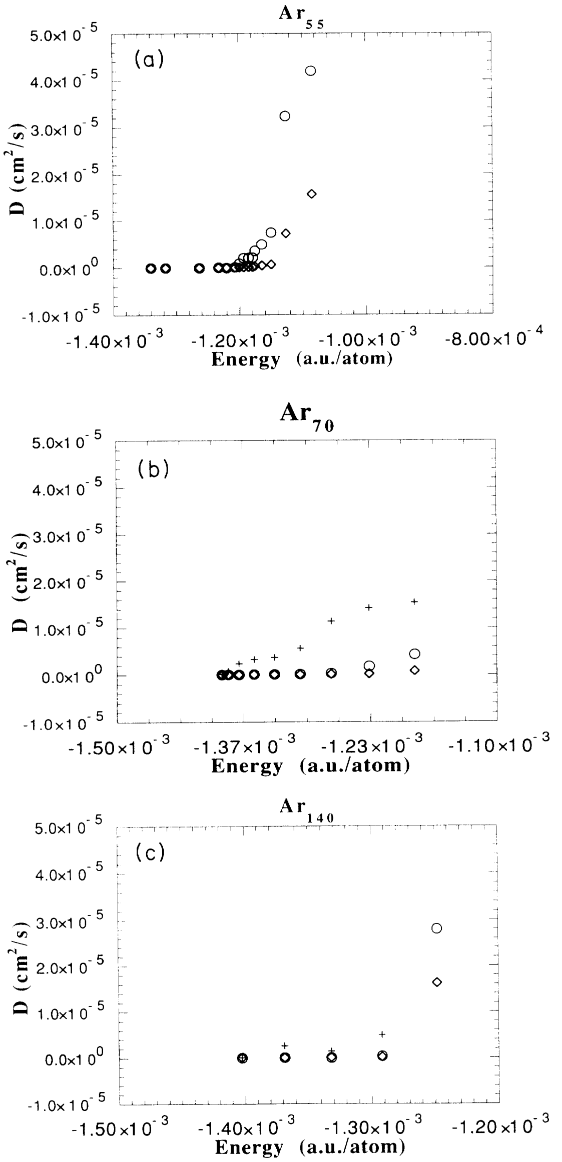

FIG. 5. The diffusion coefficients for the layers of Ar_{55} as functions of total cluster energy. Top to bottom: outermost, then successive layers moving inward.

B. Analytical model

Figure 9 is a set of curves of $F(i)$ at different temperatures for Ar_{147}. From the shapes of these curves one can see that at low temperatures, the no-floater state is the most stable. Then, when temperature increases to a certain value the no-floater state is no longer stable. This is perhaps the most significant difference between surface melting and bulk melting for finite-size clusters since the latter is characterized by solid-liquid coexistence and a double-minimum free energy. Surface melting of clusters, as shown in Fig. 9, does not exhibit a two-phase coexistent region but only has one minimum throughout the all-temperature range in which the cluster exists. The shift of the free-energy minimum from one floater to three or four floaters is rather gradual. The most probable number of floaters does not increase very rapidly with temperature. Both features of the model are consistent with the simulation results. In the simulations of Ar_{147} no state with more than four floaters was observed below the temperature at which homogeneous melting occurs, while for Ar_{55} the system does not sustain more than two floaters at temperatures below the temperature of homogeneous melting. The surface melting temperature increases with N, the number of total atoms in the cluster, due to the increase of energy needed to create a floater-vacancy pair from the surface shell, under the constraint that the free volume of the floater, V_0, be independent of N. As N increases further the energy per atom at which surface melting occurs converges to a constant and the surface melting temperature is then expected to converge to a limiting value too.

In the case of nonmagic number clusters, our model is basically still consistent with the simulations and, equally important, with intuition. For the clusters having a few atoms less than a closed shell, e.g., Ar_{146}, Ar_{143}, etc., we simply lower the cohesive energy and increase the initial volume a little so that for the surface the melting temperature will be lower for these clusters, as the simulations show. For clusters that have a few more atoms than a closed shell, e.g., Ar_{56}, Ar_{59}, etc., the situation is a little bit more complicated since we first want to argue about how to define the surface layer. At temperatures or energies below those at which the closed surface shell starts to be diffusive, the "extra atoms" are very mobile above

TABLE I. Typical diffusion coefficients D for argon clusters, Ar_N, at various temperatures.

N	$-E$ (10^2 hartrees)	$\langle T \rangle$ (K)	Shell	D(10^5 cm^2 s^{-1})
45	0.129	10.2	1	0.003
			2	0.003
			3	0.002
	0.128	11.7	1	0.002
			2	0.020
			3	0.025
	0.125	14.6	1	0.011
			2	0.019
			3	0.033
50	0.124	17.0	1	0.008
			2	0.033
			3	0.073
	0.123	18.2	1	0.020
			2	0.031
			3	0.080
54	1.209	28.2	1	0.001
			2	0.001
			3	0.008
outmost 11 atoms				0.014
	1.172	30.3	1	0.001
			2	0.003
			3	0.039
outmost 11 atoms				0.104
	1.195	29.5	1	0.002
			2	0.008
			3	0.043
outmost 11 atoms				0.101
55	1.202	29.6	1	0.001
			2	0.001
			3	0.001
outmost 12 atoms				0.001
	1.208	29.4	1	0.002
			2	0.017
			3	0.023
	1.180	30.3	1	0.000
			2	0.003
			3	0.035
outmost 12 atoms				0.135
	1.167	30.7	1	0.001
			2	0.008
			3	0.083
outmost 12 atoms				0.150
	1.157	28.3	1	0.003
			2	0.063
			3	0.125
overall average				0.109
56	1.216	27.1	1	0.000
			2	0.005
			3	0.057

TABLE I. (*Continued*).

N	$-E$ (10^2 hartrees)	$\langle T \rangle$ (K)	Shell	D(10^5 cm^{2}s^{-1})
outmost single atom				0.435
90	1.331	24.6	1	0.002
			2	0.002
			3	0.001
			4	0.133
	1.244 25	29.2	1	0.005
			2	0.006
			3	0.022
			4	0.273
110	1.265	30.9	1	0.000
			2	0.017
			3	0.013
			4	0.034
		31.9	1	0.006
			2	0.009
			3	0.024
			4	0.356
120	1.292	31.1	1	0.005
			2	0.005
			3	0.010
			4	0.180
	1.269	32.0	1	0.006
			2	0.008
			3	0.109
			4	0.297
130	1.305	32.8	1	0.004
			2	0.003
			3	0.002
			4	0.152
	1.248	35.2	1	0.006
			2	0.013
			3	0.045
			4	0.406
140	1.367	31.0	1	0.000
			2	0.001
			3	0.001
			4	0.003
	1.314	34.6	1	0.003
			2	0.002
			3	0.002
			4	0.061
	1.263	34.9	1	0.007
			2	0.047
			3	0.162
			4	1.176
147	1.288	37.3	1	0.000
			2	0.001
			3	0.002
			4	0.003

TABLE I. (*Continued*).

N	$-E$ (10^2 hartrees)	$\langle T\rangle$ (K)	Shell	D(10^5 cm^{2}s^{-1})
	1.277	38.0	1	0.001
			2	0.000
			3	0.000
			4	0.143
	1.266	38.8	1	0.001
			2	0.002
			3	0.021
			4	0.340
	1.266	37.2	1	0.006
			2	0.012
			3	0.066
			4	0.495

some size-specific temperature. As the number of the extra atoms increases, more careful consideration should be taken in order to define the surface layer first. However, those necessary corrections such as the effective energy to generate a floater can always be made with our model.

For Ar_{147} we also tried to include the change in free energy caused by changes with i, in the vibration spectrum. We included that correction by constructing an i-dependent Einstein model which describes the relation between i and the amplitude and the frequency of the vibrational motion, assuming all the atoms vibrate with one frequency. We found that soft-mode vibrations of the remaining surface atoms do not contribute significantly to the free energy in our floater model, at least in the case of magic-number clusters and nearly magic-number clusters.

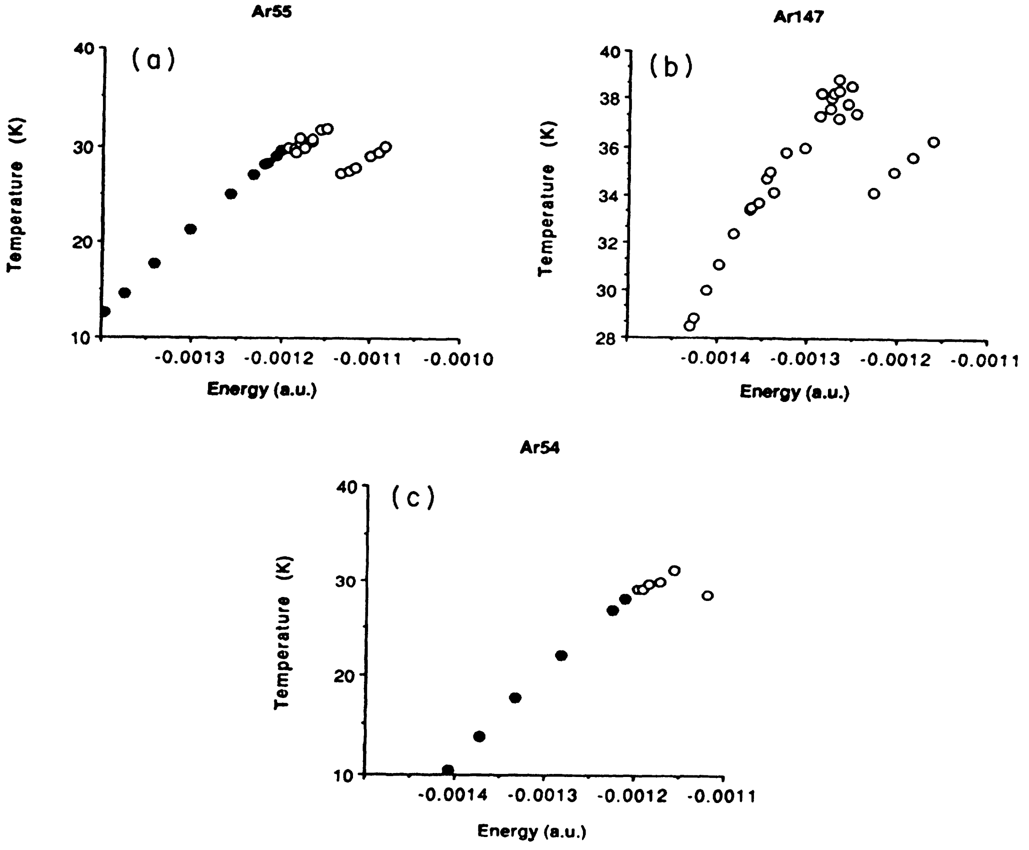

FIG. 6. Caloric curves of three argon clusters, mean temperature vs total energy: (a) Ar_{55} (closed-shell icosahedron), (b) Ar_{147} (closed-shell icosahedron), (c) Ar_{54} (open shell).

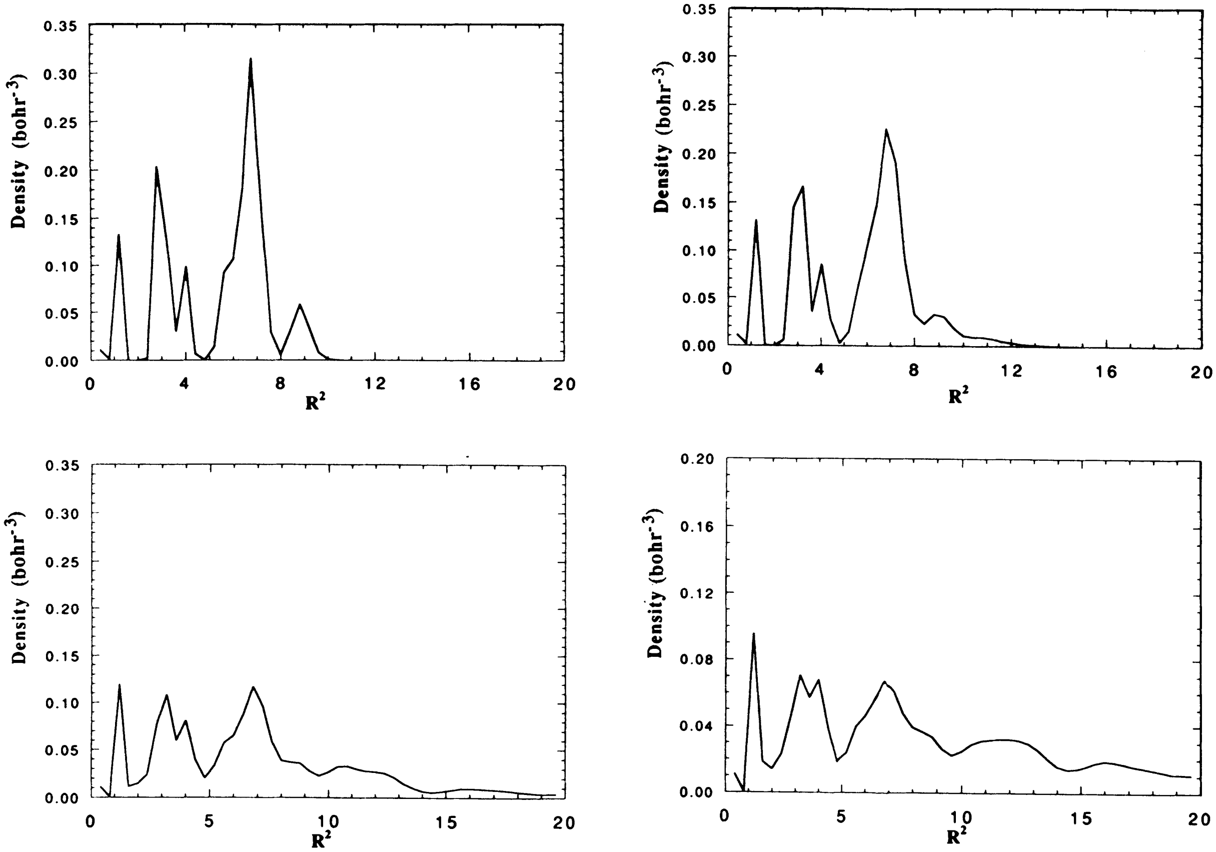

FIG. 7. Calculated density of atoms in the cluster as a function of the distance from the center of mass at several different temperatures; upper left, ca. 10 K, solid; upper right, ca. 38 K, solid; lower left, 38 K, liquid; lower right, 40 K, liquid.

DISCUSSION

Using molecular-dynamics methods we have investigated a wide range of cluster sizes of argon clusters and 55-atom copper clusters. To summarize and discuss our results, it is necessary to go back to the list of questions we asked before and during this work. Those questions are of two kinds: (i) How should we define and what are the criteria for surface melting of clusters? (ii) What is the mechanism for the surface-melting phenomenon we have observed and what are its physical characteristics? Our studies on this subject have answered some of those questions. For a cluster with a given surface structure, as the temperature reaches a value well below that at which the entire cluster may melt, the surface atoms become much more "active" than the core atoms. Under slight perturbation some of the surface atoms break the bonds with their neighbors and become floaters, staying above the normal cluster surface. These floaters contribute significantly to the surface diffusion constant. The vacancies left in the surface layer of the cluster induce (together with floaters) the soft surface modes and large-amplitude vibrations and hence also contribute to the surface diffusion constant. Within 10 000 time steps, the floaters exchange positions with other atoms on the surface. Thus the surface melting of the clusters investigated in this paper is characterized by nonzero diffusion constant, floater motion, soft surface vibrations, and floater-surface atom interchange. It produces a change in slope in the caloric curve of the cluster but not a visible latent heat. The curves of free energy versus the number of floaters show only single minima, in contrast to the double minima exhibited for homogeneous melting and freezing of many small clusters.

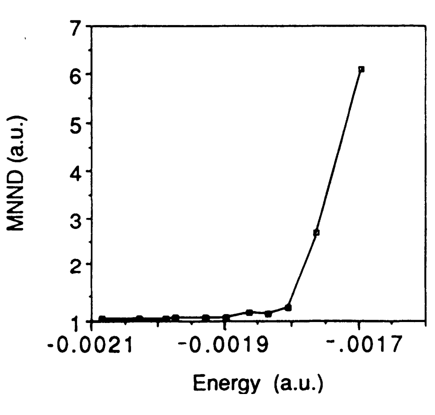

FIG. 8. Mean-square distance after 100 000 steps, of initially nearest-neighbor atoms as a function of total cluster energy, for an Ar_{147} cluster.

The results in Table I show that the temperatures corresponding to surface and bulk melting are quite sensitive to the outer-shell structure. Generally, these tempera-

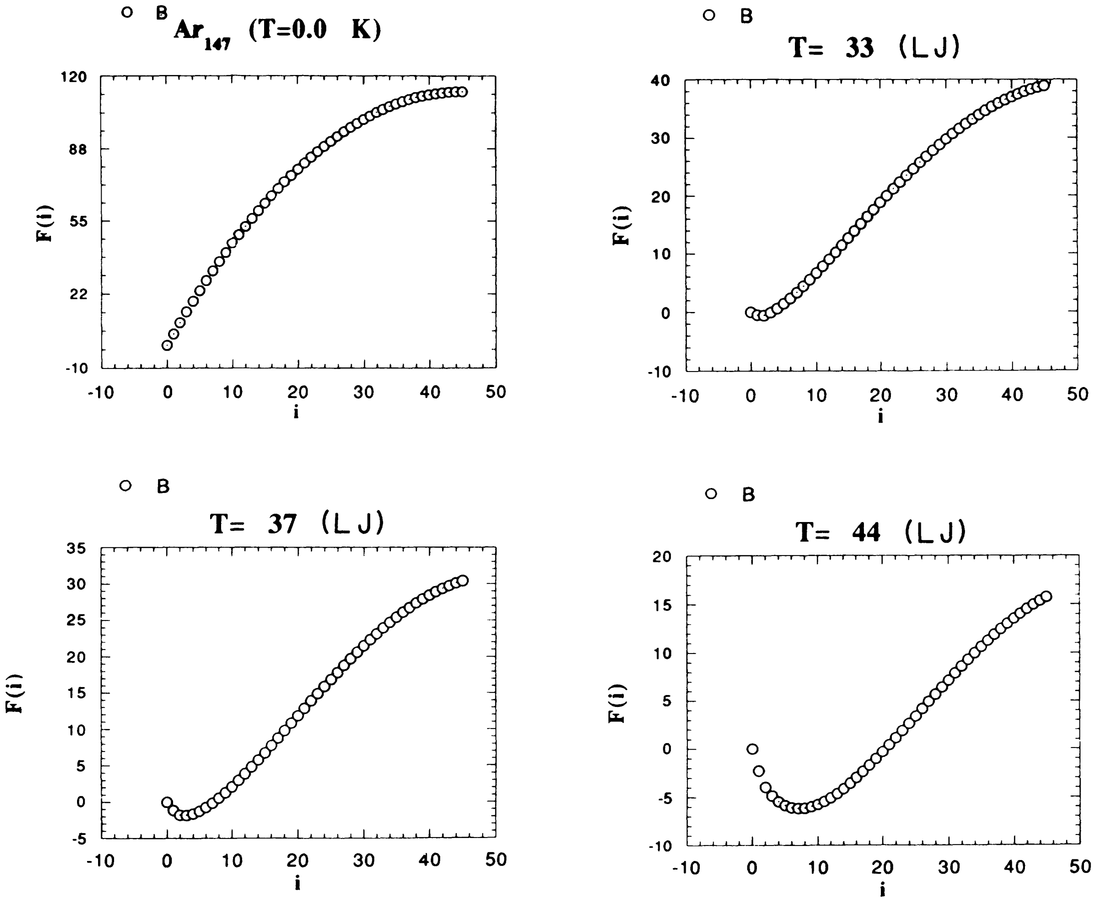

FIG. 9. Free-energy change as a function of i, the number of floaters, for Ar_{147} at different temperatures. The zero of Helmholtz free energy is set at zero floaters in each case. Units are "temperature," i.e., $k_B T$ in kelvins.

tures increase as the cluster size increases, but not monotonically. They drop gradually as the number of vacancies developed from a closed-shell structure increases and drop rapidly upon adding extra atoms to a closed-shell structure. For argon clusters of 54 and 55 atoms, the diffusion constant D of the surface shell is typically less than one-fifth of the liquid value; however, if we only average the outmost 11 or 12 atoms the value goes up to about half of the diffusion constant of liquid argon. In the case of the 147-atom argon cluster and smaller clusters generated from Ar_{147}, the surface diffusion coefficient (averaged over the entire outer shell) is about half the liquid self-diffusion coefficient. It is also noticeable that some surface atoms in large Ar clusters evaporate at temperatures below that of the overall cluster melting and therefore the apparent D value of the surface layer becomes larger than that of liquid argon. The use of the untruncated LJ potential can reduce this evaporation significantly.

From the simulations we understand that a modified EAM potential (short range) and an untruncated LJ potential also yield surface melting on 55- and 147-atom clusters. In contrast, an unmodified EAM potential (that potential developed for bulk copper) does not indicate such a state due to its small force constant. Replacing the truncated LJ potential with the long-range, untruncated LJ potential narrows the energy range of surface melting as expected since the truncation of a potential typically increases the number of geometrically distinct minima on the potential-energy surface [20].

The surface melting of clusters studied here seems sharply distinguishable from bulk melting because it appears associated with very small latent heat and with no persistent local stability of the homogeneously solidlike cluster. The latent heat result may well be quantitative rather than a qualitative matter. The latent heat expected for surface melting based on the generation of vacancies and floaters is approximately the number of floaters times the change in the number of bonds associated with each floater. If the most probable number of floaters for Ar_{147} is only two or three, then we can expect generally to find only about one floater per 30 or 40 surface atoms. Each of these has roughly 5 or 6 fewer bonds as a floater than as an atom in the outer shell, so the expected latent heat of surface melting is only about $\frac{1}{5}$ to $\frac{1}{8}$ of the energy of a bond, per atom, or about $\frac{1}{30}$ to $\frac{1}{40}$ of the total binding energy of the surface layer (taking into account the factor of $\frac{1}{2}$ to avoid double counting). Typical latent heats of fusion for nonmetallic bulk matter are of order $\frac{1}{16}$ to $\frac{1}{3}$ the binding energy of the corresponding solids. The corresponding latent heats of fusion for clusters are some-what lower but so are the binding energies or heats of vaporization. Hence it would not be surprising if typical latents heat of surface melting were too small to be detected unless special efforts were made to isolate such a quantity. However, even if the latent heat of surface melting of a cluster is nonzero but small, surface melting of cluster seems more akin to a second-order than a first-order transition of bulk matter in the sense that the solid surface loses even its local stability, in sharp contrast to the *homogeneous* melting and freezing of small clusters.

The occurrence of a single minimum for all i in the free energy of molten-surface clusters has one other important implication for bulk matter. In contrast to homogeneous melting, the single minimum implies that surface melting has no metastable analog to superheating or undercooling of bulk matter. Like the solid range, there is always only *one locally* stable state for a cluster in the molten-surface energy or temperature range, in contrast to the energy or temperature region in which the homogeneous liquid and the solid may both be locally stable [18]. Thus surface melting due to floaters is like a second-order transition but with a small latent heat.

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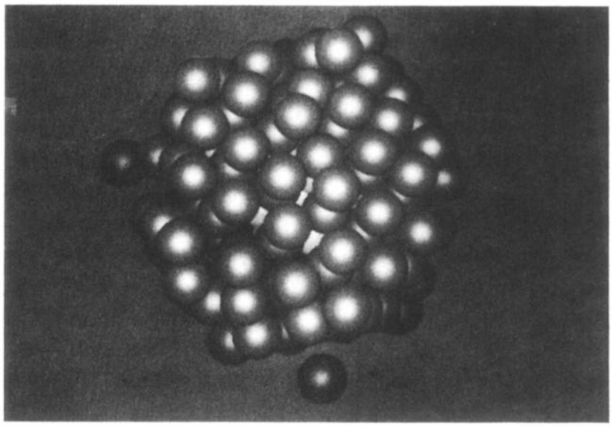

FIG. 1. A snapshot of Ar_{147} with a liquidlike surface and a solidlike core (mean $T = 35.8$ K).