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Melting and freezing of Lennard-Jones clusters on a surface

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The properties of clusters containing 13 Lennard-Jones atoms and adsorbed on a substrate were studied using molecular-dynamics simulations. The clusters were found to undergo a transition from one solidlike structure at low temperatures to sets of liquidlike structures at higher temperatures for a wide range of cluster-surface interactions. Coexistence of the solidlike structure with the liquidlike structures was observed over a finite temperature domain, allowing the identification of the transition temperature T_m from plots of the equilibrium energy as a function of temperature. T_m, the analog of the melting temperature of bulk materials, was observed to depend on the cluster-substrate interaction strength ϵ_s. As T_m is approached from the liquid phase in the cluster phase diagram drawn in terms of the parameter ϵ_s, a wetting transition was evident. For weak substrates the cluster desorbed as a whole and the surface remained dry. For strong substrates layered structures built up such that the surface was wet. For intermediate ϵ_s the cluster froze while being adsorbed on the surface, keeping the icosahedral structure at low temperatures. Partial wetting took place.

I. INTRODUCTION

The structure and stability of small clusters of atoms is a very active field of research, both theoretically and experimentally.[1] These aggregates, intermediate between atoms and solids, have very peculiar properties, such as the predominance of argon clusters with icosahedral symmetry rather than being fcc-like,[2] or hollow silicon clusters with pentagonal and square faces rather than being built out of tetrahedral units of diamond symmetry.[3] Electron diffraction on clusters produced in supersonic jets has been used to study the structure of argon clusters[4] with the striking observation that free clusters can exhibit a phase change analogous to the melting and freezing of bulk materials. Computer simulations, both Monte Carlo[5] and molecular dynamics,[6] have been used to describe the thermodynamics properties of free Lennard-Jones clusters. A dispute existed between the results obtained in these calculations as to whether this meltinglike transition was first order[6] or not.[5] The contradictory results have recently been reconciliated[7] by recognizing that the results in the microcanonical[6] and canonical[5] ensembles need not coincide for finite systems.

The theory of clusters adsorbed on surfaces has received less attention, even though *a priori* this is a simpler experimental technique than to produce free clusters. There are phenomena such as nucleation on surfaces and physisorption, heterogeneous catalysis, etc., where the effect of the surface on the clusters become of interest. Electron-microscopy studies are commonly used as an almost unique means of probing the structure of supported clusters.[8] It has been observed that small clusters have lattice-parameter constants different from the bulk.[9] However, even electron microscopy is unable (up to date) to probe into the structure of clusters smaller than 1.5–2.0 nm with approximately 100 atoms. Therefore, theoretical predictions on very small clusters can be very useful in this field. Although the Lennard-Jones potential is really good to model van der Waals systems, it has been used to model the conformation of metals and surfaces.[10] In 1980, Weissman and Cohan[11] presented a molecular-dynamics study for two-dimensional (2D) clusters adsorbed on a surface. In this work, the authors showed that clusters with 7 and 19 atoms were in one stable conformation at low temperatures and changed to a set of high-energy conformations when the temperature was raised. They stated that the effect of weak or strong substrates was qualitatively negligible in describing the meltinglike transition. Recently we reported[12] that Lennard-Jones clusters containing 13 or less atoms acquired mechanically stable 2D conformations only when strong three-body effects were added to the potential and suggested that these interactions could be enhanced when the clusters were adsorbed on a substrate.

In this paper we report a constant-energy molecular-dynamics study of the 13-atom cluster adsorbed onto a planar surface. The purpose of undertaking the study was to understand the phase changes that take place in adsorbed 3D clusters with special emphasis in the melting and wetting transitions.

Section II describes the model and computer-simulation method. Section III gives the body of the results concerning the melting and freezing of clusters, the wetting transition, and the mean-square displacement of atoms and the experiments on clusters in metastable states. The paper ends with the summary given in Sec. IV.

II. MODEL AND SIMULATION METHOD

The system consists of 13 atoms interacting within the cluster by Lennard-Jones (LJ) potentials with depth ϵ and core σ. The cluster was adsorbed on a plane surface by means of a model potential:[13]

$$V_s = 2.12\epsilon_s \sum_{i=1}^{N} [(\sigma_s/z_{is})^{12} - (\sigma_s/z_{is})^3] , \tag{1}$$

where ϵ_s and σ_s are the parameters measuring the strength of the interaction and the repulsive core cluster-substrate, respectively. The z_{is} are the distances of the N cluster atoms to the surface. As usual, ϵ_s and σ_s can be taken, respectively, as the geometrical and arithmetical means between the LJ ϵ and σ of clusters and of substrate atoms. The ratio σ_s/σ was taken equal to 1. The twelfth power in the repulsive term was chosen as to simulate a very stiff surface. The ratio ϵ_s/ϵ was crucial in determining the characteristics of adsorption phenomena.

Constant-energy molecular dynamics was used in all of our simulations. The Newton equations of motion were solved using the Verlet algorithm[14] with a time step of 0.01τ, where $\tau = (m\sigma^2/\epsilon)^{1/2}$. The free-cluster LJ values of ϵ and $r_0 = 2^{1/6}\sigma$ were adopted as energy and distance units. Quantities reported in these reduced units were noted by an $*$. Also, the reduced temperature is $T^* = k_B T/\epsilon$, where k_B is Boltzmann's constant, and the reduced time is $t^* = t/\tau$.

The simulations were performed at temperatures low enough to prevent evaporation of atoms from the cluster, except for the highest temperatures, where this type of evaporation was important. The process of heating or cooling the adsorbed cluster was always carried out in the presence of a frozen substrate at $T=0$, without possibility of energy transfer from the cluster towards the surface. The center-of-mass momentum was eliminated in the calculations of free clusters, such that the reduced temperature reported for these cases was defined as $T^* = 2\langle E^*_{\text{kin}} \rangle / (3N-3)$, where E^*_{kin} is the kinetic energy of the cluster. However, the adsorbed clusters had overall rotation and center-of-mass translational motion, so the reduced temperature in these cases was defined as $T^* = 2\langle E^*_{\text{kin}} \rangle / 3N$.

The procedure adopted to study the melting transition was the following. First, the heating runs were performed by starting with the 13 atoms adsorbed onto the surface in the icosahedral structure with very low kinetic energy, typically corresponding to $T^* \sim 0.05$. One of the triangular faces of the icosahedron was placed parallel to the surface and the distance from the center of mass to the surface was $1.8r_0$ in all cases. Next, the adsorbed clusters were allowed to evolve for about 500τ at very low temperatures. After equilibration, the clusters were heated by scaling the velocities of the final configuration by a factor 5% larger than 1. This heating process was performed in a steplike manner, allowing in each step of the process for an equilibration time of 20τ and a further run of 50τ to average the calculated quantities. The rate of heating was varied by changing the velocities scaling factor. A typical rate of heating was $\Delta T^*/\Delta t = 1.7 \times 10^{-4}\tau^{-1}$.

For the free cluster, the icosahedral configuration corresponds to the global minimum[12] of the potential energy per atom with value -3.409ϵ. The initial condition of trapping the icosahedral structure onto the surface is consistent with an infinitely fast deposit of the cluster already in its minimum-energy structure. To investigate the behavior of hot clusters upon cooling, a hot cluster was trapped onto the surface as initial condition. The cooling procedure used was similar to the heating procedure, but the velocities were scaled with a factor smaller than 1.

The structural changes accompanying melting and freezing were followed by calculating the pair-correlation function $g(r)$, and the mean coordination number[15] was calculated from it:

$$n_c = \rho_0 \int_0^{r_n} g(r) 4\pi r^2 dr . \tag{2}$$

Here r_n is the distance where $g(r)$ has its first minimum and ρ_0 is the reference density of the system. Atoms at distances smaller than $r_n = 1.3r_0$ were considered nearest neighbors. The coordination number is a structural quantity very appropriate for analyzing the melting transition. For bulk LJ systems, the coordination number presents a sharp discontinuity near the melting temperature when plotted as a function of temperature.

III. RESULTS AND DISCUSSION

A. Melting and freezing of clusters

The equilibrium total energy per atom, E^*, as a function of temperature for the free and adsorbed 13- atom cluster rises from a low value characteristic of the solidlike structure to a higher value characteristic of the liquidlike structures. Results of the heating experiments are given in Fig. 1. All of them show that upon heating the energy of the cluster undergoes abrupt changes of value at certain temperatures, whether the cluster was adsorbed or not. This gives an empirical basis for stating the analogy to a first-order phase transition in bulk systems. At low temperatures the cluster is in the lowest potential-energy minimum, which is the icosahedral structure. This is the solidlike phase. At high temperatures the cluster makes excursions over a set of disordered structures (during 50τ the cluster was not seen in the icosahedral structure). This is the liquidlike phase. In the intermediate region, it was observed that the icosahedron and the high-temperature structures were visited back and forth during a long run, i.e., they coexisted over a finite range of temperatures. Therefore, each phase is interpreted as corresponding to a region of configuration space. In Fig. 1, points in the solid branch (low temperatures) and liquid branch (high temperatures) follow very closely two straight lines with different slopes. Points in the transition region are scarce, but show a smooth van der Waals loop because of the finite size of the system.[16] Slow-cooling experiments, starting from the high-energy, high-temperature cluster configurations down to low temperatures, gave no hysteresis loop (not shown in Fig. 1).

The interpretation of phases as sets of structures in the configuration space is classical. Following Honeycutt and Andersen,[7] if the coexistence of two phases is interpreted in terms of the simple model of a chemical equilibrium solid$\rightleftarrows$liquid, then the temperature at any energy in the microcanonical ensemble is given by

$$T_{\mathrm{eq}}(E)=p(E)T_{\mathrm{sol}}(E)+[1-p(E)]T_{\mathrm{liq}}(E)\ , \tag{3}$$

where $p(E)$ and $1-p(E)$ represent the fraction of time spent in the solidlike and liquidlike phases, respectively.

When the solidlike and liquidlike curves were assumed to be linear, we found by a least-squares fit of $\simeq 30$ points in the solid branch and $\simeq 6$ points in the liquid branch that the equations for the free and adsorbed clusters are

$$\begin{aligned} T^*_{\mathrm{sol}} &= a_{\mathrm{sol}}+b_{\mathrm{sol}}E^*\ , \\ T^*_{\mathrm{liq}} &= a_{\mathrm{liq}}+b_{\mathrm{liq}}E^*\ . \end{aligned} \tag{4}$$

We define T^*_1 and T^*_2 as the highest and lowest temperatures of the solid and liquid branches used in the fit of Eq. (4). Then, the melting temperature was taken as half the value of this interval:

$$T_m=\tfrac{1}{2}(T^*_1+T^*_2)\ . \tag{5}$$

Values of a_{sol}, b_{sol}, a_{liq}, b_{liq}, b_{liq}, T^*_1, T^*_2, and T_m are given in Table I for the free and adsorbed clusters. To

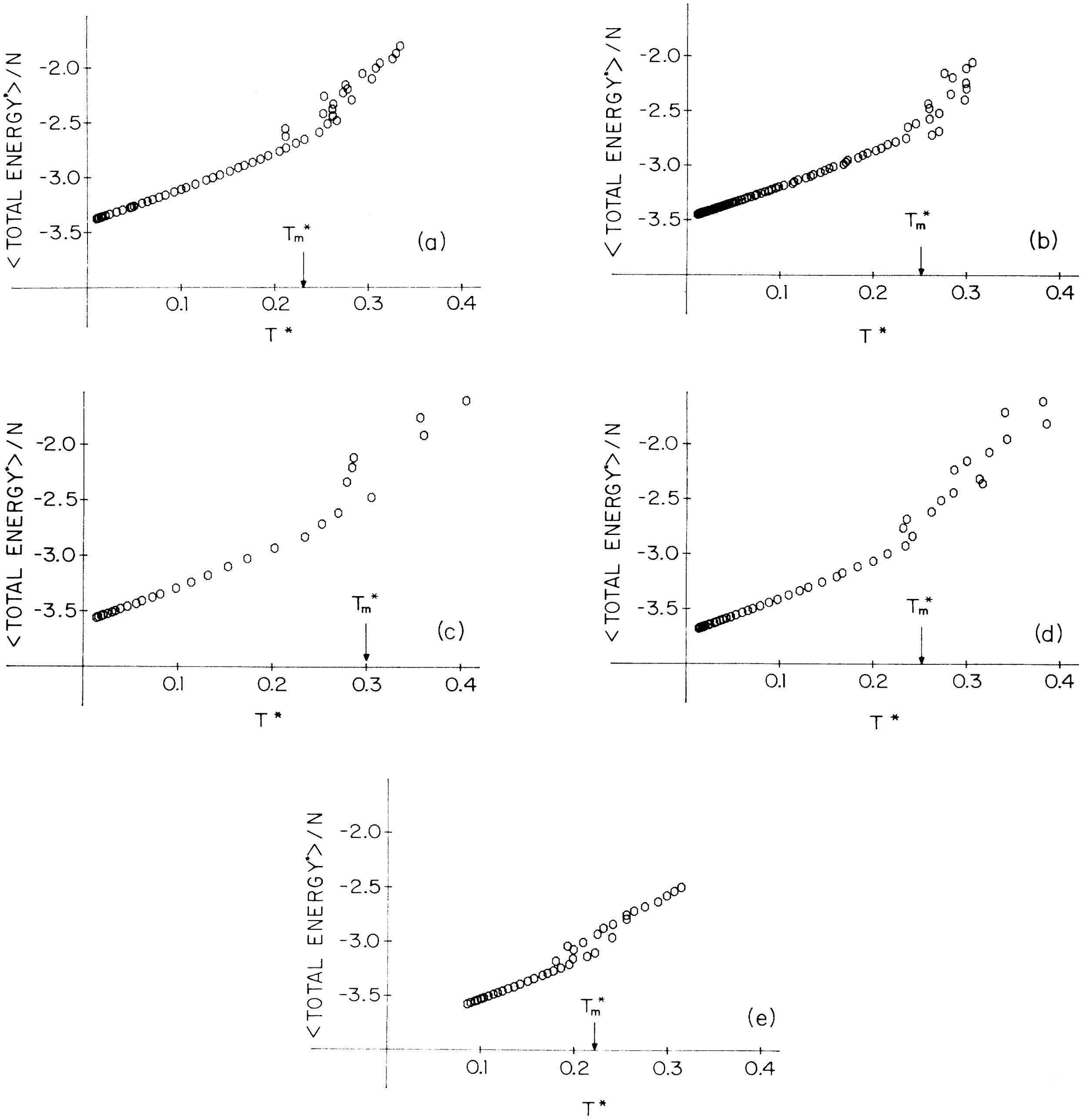

FIG. 1. Total energy per atom as a function of reduced temperature. (a) Free cluster; (b)–(e) correspond to supported clusters with substrate strengths of 0.2, 0.5, 0.8, and 1.1, respectively.

TABLE I. Values of the constants entering in Eqs. (4) and (5) in reduced units.

ϵ_s^*	0.0	0.2	0.5	0.8	1.1
Equation (4)					
a_{sol}	1.1150	1.1394	1.0875	1.1341	1.1494
	1.0745[a]				
b_{sol}	0.3262	0.3257	0.3006	0.3036	0.2967
	0.3143[a]				
$E_{\text{sol}}(T=0)$	-3.4090	-3.4982	-3.6183	-3.7351	-3.8734
a_{liq}	0.6227	0.6689	0.7503	0.5961	0.7729
	0.6162[a]				
b_{liq}	0.1554	0.1662	0.2134	0.1290	0.1844
	0.1527[a]				
$E_{\text{liq}}(T=0)$	-4.0077	-4.0245	-3.5153	-4.6220	-4.1913
Equation (5)					
T_1^*	0.20	0.23	0.25	0.22	0.18
	0.19[a]				
T_2^*	0.30	0.28	0.35	0.29	0.27
	0.29[a]				
T_m^*	0.250	0.255	0.300	0.255	0.225
	0.240[a]				

[a] Corrected values to account for the rotational degrees of freedom.

compare data among free and adsorbed clusters. where the temperature was defined differently as indicated in the preceding section, it is possible to replace NE^* by $NE^*-3T^*/2$ in Eq. (4) for the free cluster. In this way the three degrees of freedom lacking in the free cluster are taken into account.

The comparison of Fig. 1(a) with molecular-dynamics data of Jellinek *et al.*[6] is perfect within the numerical error of our fitting procedure in both the solid branch and the liquid branch. Honeycutt and Andersen[7] considered a value of -3.5ϵ for the energy at $T=0$, different from the global minimum value of -3.41ϵ. This situation, added to the fact that they could not obtain data on the liquid branch, yielded a poorer comparison to their results equivalent to Eq. (4). Qualitatively, their results and ours agree well in the two-phase coexistence region. Data in this region were not reported by Jellinek *et al.*

B. Structural analysis and surface-wetting behavior

The set of structures that the cluster could reach at temperatures in the solid-liquid coexistence region changed with the strength of the cluster-substrate interaction. Typically for intermediate substrates, $\epsilon_s^*=0.5$, a two-layer structure started to show. This structure is characteristic of adsorbed clusters. It was never observed in the free-cluster case and only suggested in the weakly adsorbed clusters. This is shown in Fig. 2, where the instantaneous configurations at various increasing temperatures were drawn at the end of 70 τ runs during the heating experiments. In the figure the connecting lines represent nearest-neighbor atoms at distances $<1.3r_0$.

Figure 3 displays the mean coordination number n_c as a function of temperature for different cluster-substrate interaction strengths. This quantity n_c behaves as expected for bulk LJ systems; it is constant over a wide range of temperatures and abruptly decreases at the melting temperature. Again, the meltinglike transition is clearly shown. However, it strong enough substrates [Fig. 3(d) and 3(f)] it appears as if two plateaux were present. The second plateau at $n_c \sim 5.5$ corresponds to the coordination number of the newly formed two-layer structures shown in Figs. 2(b) and 2(c). Most of the time these structures had nine atoms in the first layer and four in the second.

The presence of the two-layer structures, or *rafts*, suggested that two phenomena were taking place simultaneously as a function of temperature, melting, and surface wetting. Both phenomena can be summarized by drawing the phase diagram of the system in terms of the parameter ϵ_s^*, as given in Fig. 4. From the definition of T_m given in Eq. (5), this is a typical temperature where solid and liquid phases coexist. In Fig. 4, the solid line represents the loci of T_m values in a plot of temperature versus substrate strength. The bars on each point correspond to the width of the solid-liquid coexistence region. Above this solid line the clusters are liquidlike; below the line the clusters are solidlike. The existence of a wetting transition is suggested by drawing a dotted line through the solid dots obtained by slowly cooling a well-equilibrated hot and adsorbed cluster. The values of these points correspond to the following observations:

(1) When the substrate is weak, $\epsilon_s^*=0.2$, and while cooling the cluster, there was a transfer of kinetic energy from the atoms in the cluster to the center-of-mass motion. Thus, not only the cluster internal temperature was lowered further, but also the cluster evaporated as a whole from the surface. This evaporation took place at $T^*=0.2$ (solid dot in Fig. 4). The cluster dried the surface and froze while desorbing as a solid icosahedron.[16] We can say that in the process of cooling the system dynamically selected the region in configuration space corresponding to the solid cluster, but because of the ini-

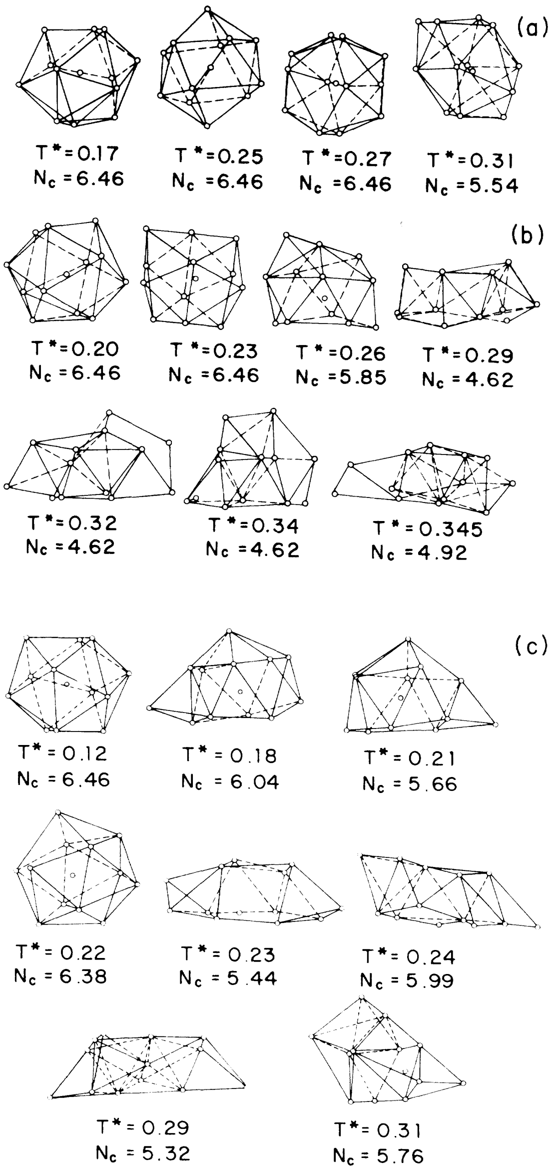

FIG. 2. Instantaneous cluster configurations of the adsorbed cluster onto the surface at different temperatures during a heating simulation experiment. (a) $\epsilon_s^*=0.2$; (b) $\epsilon_s^*=0.8$; (c) $\epsilon_s^*=1.1$. N_c is the coordination number calculated from the atomic coordinates of the configurations.

tial high temperature the system redistributed the available kinetic energy by accelerating the cluster center of mass away from the surface.

(2) For intermediate substrates, $\epsilon_s^*=0.5$, the cooling process depends on the initial hot configuration. Various high-temperatures clusters corresponding to final configurations of the heating experiments reported in Fig. 1(c) were used as initial conditions. It was observed that the cluster could evaporate as a whole, or could freeze and end the cooling experiment at low temperatures as an adsorbed icosahedron. If the temperature of the initial configuration was just below T_m, the cluster always ended in its icosahedral structure adsorbed onto the surface. The solid dot in Fig. 4 corresponds to the temperature where a two-layer structure was detected in those experiments, ending at low temperature with the adsorbed icosahedron.

(3) For $\epsilon_s^*=0.8$ and during the cooling experiment, it was observed that the cluster switched back and forth between raft structures and the icosahedron in a fairly wide temperature domain. A typical temperature in this domain corresponds to the solid dot in Fig. 4. These experiments always ended with the cluster adsorbed in its icosahedral structure.

(4) For stronger substrates, $\epsilon_s^*=1.1$, again the cooling process was dependent on the initial configuration. If the temperature of the initial configuration was in the liquid region (above the solid line), the experiment ended at low temperatures with adsorbed 12-atom rafts and one atom detached from the original cluster but adsorbed on the surface as well. If the temperature of the initial configuration was lower than T_m but still in the solid-liquid coexistence region, the experiment ended at low temperatures with the cluster adsorbed in its icosahedral structure. Similar to case (3), rafts and icosahedra were detected over a temperature interval of about 0.03. Below the temperature corresponding to the solid dot in Fig. 4, the cluster remained adsorbed in the icosahedral structure.

The phase diagram obtained in Fig. 4 identifies three regions in the half-plane corresponding to solid clusters, below the solid line. For strong enough substrates, $\epsilon_s^*>\epsilon_w^*$, there is an orderly buildup of atoms on the surface giving rise to two-layer structures (rafts) with variable number of atoms on the second layer. A monolayer was not obtained for substrates as strong as $\epsilon_s^*=5.0$ because of atoms departing from the cluster but still adsorbed on the surface. Therefore, we can say that the

TABLE II. Surface behavior at the changeover temperature $T^*(\epsilon_i^*)$ when cooling an initial hot cluster.

Region I	Region II	Region III
Dry surface	Drying/wetting	Wet surface
Free cluster in its icosahedral structure runs away from surface	Cluster adsorbs in its solidlike structure (icosahedron)	Cluster adsorbs in a raft structure

cluster wets the surface and becomes a raft (region III). For weak enough substrates ($\epsilon_s^* < \epsilon_w^*$) the cluster remains in the icosahedral structure, and partially wets the surface (region II). In region I the substrate is weak, and the cluster desorbs, yielding a dry surface. The value ϵ_i^* is the point where the atom-atom and atom-substrate attractions become comparable. If the temperature is higher than T_m, below ϵ_i^* the cluster desorbs *as a whole;* above ϵ_i^* the cluster desorbs *atom by atom.* In Table II we summarized the aspects of the cluster at the changeover temperature $T^*(\epsilon_i^*)$.

C. Mean-square displacements

The mobility of the atoms in the cluster can be measured by following their mean-square displacement as a function of time:

$$\langle r^2(t)\rangle = \frac{1}{N}\sum_{i=1}^{N} \langle \,|\mathbf{r}_i(t)-\mathbf{r}_i(t_0)|^2\rangle \;. \qquad (6)$$

The initial time t_0 was taken equal to the last step in the 70τ runs generating the data of Figs. 1–3. From this value in time the cluster was led to evolve for another

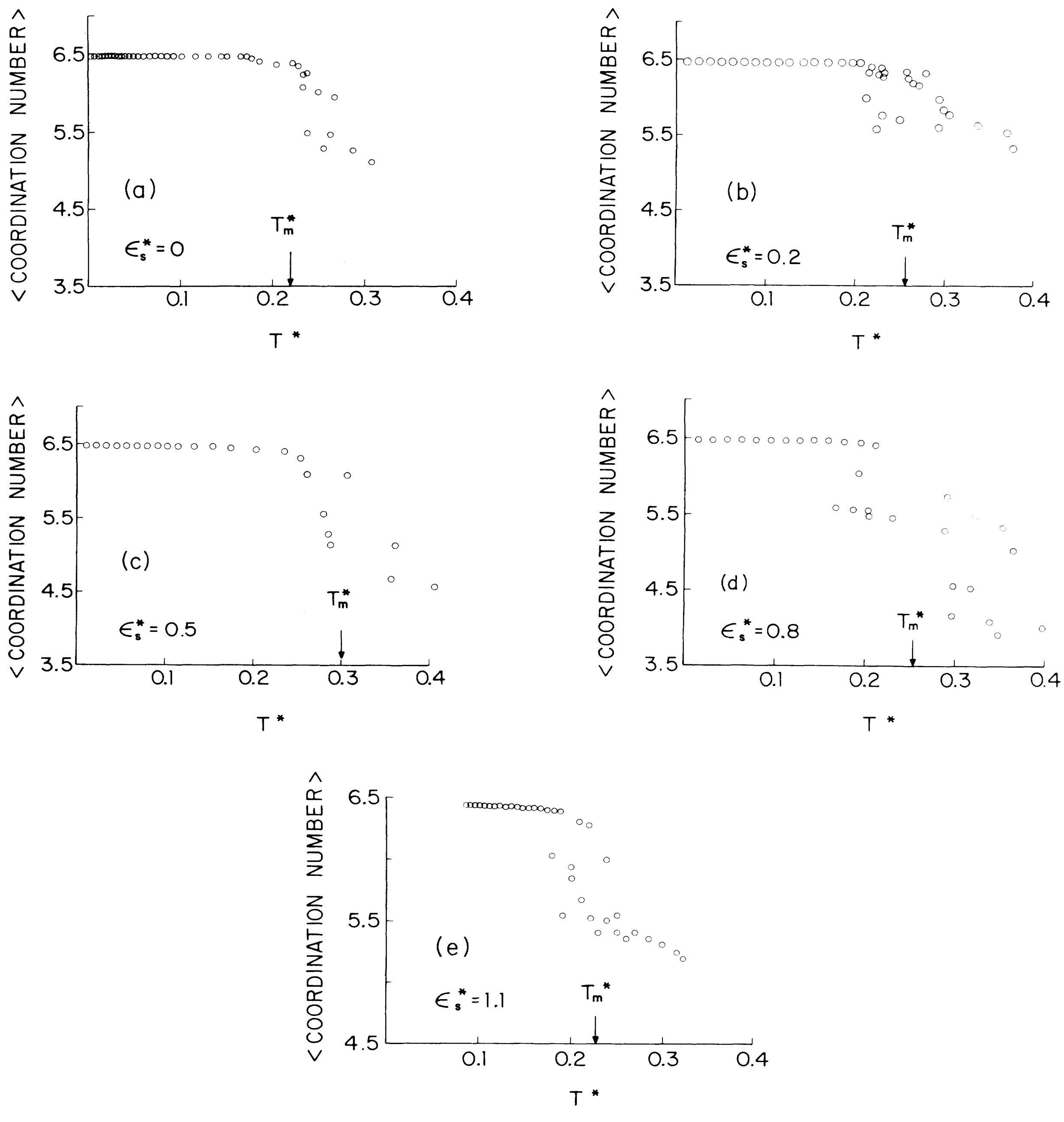

FIG. 3. Mean coordination number as a function of reduced temperature for the (a) free cluster and (b)–(d) supported clusters.

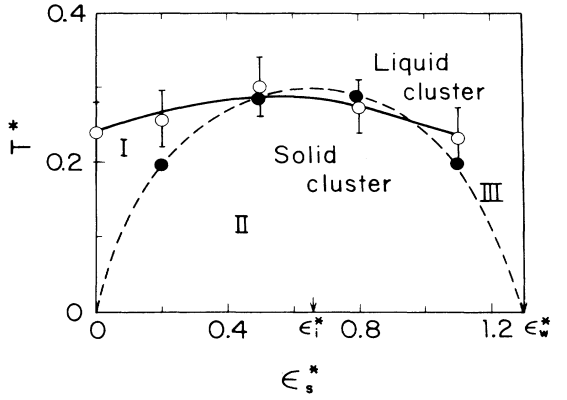

FIG. 4. Phase diagram in the temperature–substrate-strength plane, showing loci of the melting temperature (solid line). Above this line the cluster is in the liquidlike phase and below in the solidlike phase. The dotted line separates three regions. Region I is a dry surface, region II corresponds to clusters adsorbed on the surface in the icosahedron structure, and region III is a wet surface with clusters adsorbed as rafts.

100τ. In the case of the free cluster, the total angular momentum was eliminated and the temperature redefined as $T^* = 2\langle E_{\rm kin}^* \rangle/(3N-6)$. In Fig. 5 is shown the instantaneous and averaged behavior of $r^2(t)$ as a function of elapsed time for four typical temperatures corresponding to the liquidlike phase [Figs. 5(a) and 5(b)], coexistence of solid and liquid phases [Figs. 5(c) and 5(d)], and solidlike phase [Figs. 5(e) and 5(f)]. As can be seen, the low-temperature behavior is periodic, as should be in a solid, and averages out to a constant low value at long times. The $\langle r^2(t) \rangle$ curve at high temperatures rises linearly, as is characteristic of bulk liquids [Fig. 5(b)], but it tends at long times to a maximum constant value consistent with the finite volume of the cluster. In other words, the atoms cannot move further away from the available volume, or evaporation takes place. Finally, in the intermediate-temperature regime, the mean-square displacement tends to a constant value in a steplike manner. For adsorbed clusters, due to the overall motion of the center of mass with respect to the surface, it was not possible to eliminate the z component of the angular momentum. The clusters were thus rotating on the surface, a situation that masked the time behavior of $\langle r^2(t) \rangle$ at high enough temperatures.

D. Metastable states

Upon very fast cooling processes it was possible to trap the cluster in metastable states at low temperatures. Two situations were studied thoroughly. In the first, the free cluster was quenched into a structure corresponding to a local minimum of the potential-energy surface. This structure corresponded to a potential-energy value of 0.2 above the icosahedron value. From this structure an extremely low heating process was carried out, i.e., the velocities were scaled by 3% at each step. The total-energy–versus–temperature curve is shown in Fig. 6(a). The cluster remained in the local minimum as temperature was increased until evaporation took place without acquiring other liquid configurations. The slope of the solidlike branch is lower than in Fig. 1(a) and the melting transition was not detected. In the second situation, a monolayer raft with triangular symmetry[12] was trapped at low temperatures on a strong substrate ($\epsilon_s^* = 2.0$). Slow heating from this initial configuration yielded the results plotted in Fig. 6(b). The monolayer raft heated up until reaching a temperature where a second layer started to build up. At this point a discontinuous transition took place generating two branches at high temperatures. The lower-energy branch corresponds to 3D liquidlike structures; the upper branch corresponds to a two-layer raft where one atom is evaporating. The abrupt jump in temperature is due to the fact that the system abruptly changes to two different regions of phase space where the potential energy is lower; thus the kinetic energy (or temperature) adjusts to keep the total energy constant.

For very strong substrates, $\epsilon_s^* = 2.0$, 3.0, and 3.5, several heating experiments were started from an initial low-temperature icosahedral structure trapped on the surface. Upon heating the cluster changed into raft structures before losing one of its atoms. The departing atom remained adsorbed on the substrate (side evaporation). For even stronger substrates, $\epsilon_s^* = 2.0$ and 5.0, experiments starting from the icosahedral next to the surface showed that this configuration was not longer stable but changed into a raft after a 70τ run. The $\epsilon_s^* = 4.0$ substrate originated rafts with 11 atoms in the first layer and further heating produced side evaporation of one atom. The $\epsilon_s^* = 5.0$ substrate originated a monolayer of 13 atoms for a short period of time. If this configuration was led to evolve 200τ more, side evaporation of one atom was observed.

IV. SUMMARY

The conclusions of this study can be summarized as follows.

The 13-atom cluster supported on the surface in the free-cluster configuration of minimum energy (icosahedron) undergoes an equilibrium structural transition on the surface as the temperature is increased. It changes from the icosahedron, solidlike structure at low temperatures to a set of liquidlike structures at high temperatures, analogous to the melting transition of bulk materials. The transition is broad because the solidlike and liquidlike structures coexist over a finite range of temperatures. The slope of the solidlike curve is consistent with the classical specific-heat value of a set of $3N$-6 harmonic oscillators.

The ratio of substrate-cluster to atom-atom interactions is found to be crucial in all of the results. The melting temperature T_m, the liquid-branch slope, and the desorption mechanism depend on the substrate strength. Besides, in the cooling experiments, a wetting-like transition is apparent by analyzing the cluster structures as a function of temperature. Typically, rafts are formed before the set of 3D liquidlike structures is

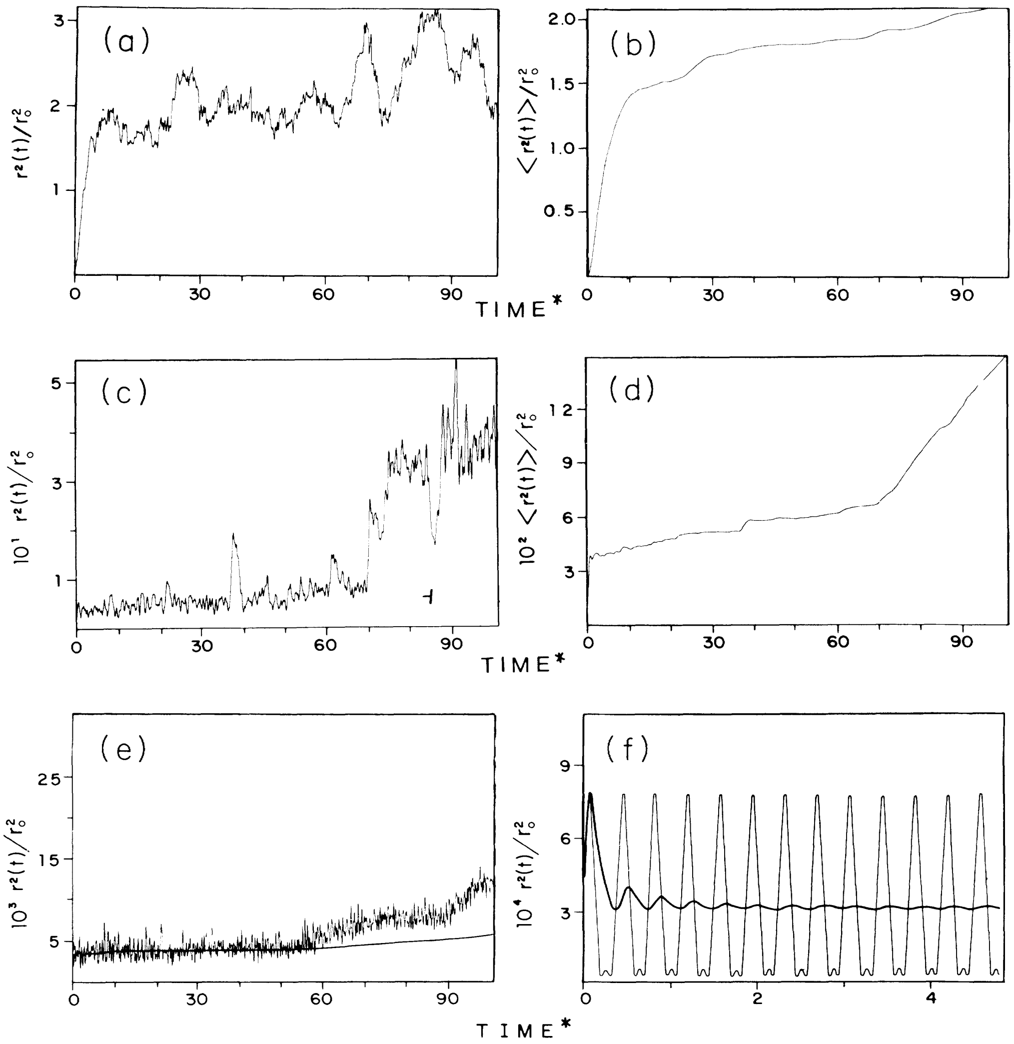

FIG. 5. Mean-square displacement of the atoms in a free cluster as a function of time. (a) and (b) show the liquid cluster at $T^*=0.30$; (c) and (d) show the solidlike coexistence region at $T^*=0.24$; (e) shows the solid cluster at $T^*=0.067$; and (f) the very cold cluster at $T^*=0.02$.

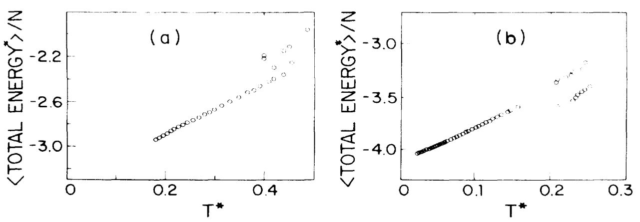

FIG. 6. Experiments on clusters in metastable states. (a) Total energy per atom as a function of reduced temperature for the free cluster initiated in a state with potential energy equal to -3.2ϵ; (b) total energy per atom as a function of reduced temperature for a raft adsorbed on an $\epsilon_s^*=2.0$ substrate.

reached by the system. The result is a phase diagram in the temperature–versus–substrate-strength plane where three regions are clearly separated for $T<T_m$: (1) For strong substrates the cluster wets the surface and ends the cooling process as an adsorbed cluster with layered structure; (2) for weak substrates the surface remains dry, since by lowering the temperature the cluster freezes while running away from the surface; (3) for intermediate substrate strengths the cluster freezes while adsorbed on the surface and ends the cooling process at low temperatures in the icosahedral structure, partially wetting the surface.

The mobility of the atoms in the free cluster was followed for runs long enough to observe the maximum constant value of the mean displacement compatible with the finite size of the system. For finite systems the long-time behavior of $\langle r^2(t) \rangle$ is a constant which changes with temperature. Eventually this constant reaches a maximum value before atoms start to evaporate. The overall behavior of the mean-square displacement as a function of time is therefore different than in bulk systems since the slope at long times vanishes for solid clusters and for liquid clusters as well. It is meaningless to speak of transport coefficients in these finite-size systems.

Finally, several heating and cooling experiments were performed on clusters trapped in metastable states by a fast-cooling process. Slow heating from these states led to odd behavior that should not be confused with equilibrium situations.

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[1] T. P. Martin, Phys. Rep. **95**, 167 (1983); Angew. Chem. **98**, 197 (1986).

[2] M. R. Hoare, Adv. Chem. Phys. **40**, 49 (1979).

[3] E. Blaisten-Barojas and D. Levesque, Phys. Rev. B **34**, 3910 (1986).

[4] J. Farges, M. F. de Feraudy, B. Raoult, and G. Torchet, Surf. Sci. **106**, 95 (1981); J. Chem. Phys. **78**, 5067 (1983); **84**, 3941 (1986); S. S. Kim and G. D. Stein, J. Colloid Interface Sci. **87**, 180 (1982); J. W. Lee and G. D. Stein, Surf. Sci. **156**, 112 (1985).

[5] R. D. Etters and J. Kaelberg, J. Chem. Phys. **63**, 2045 (1975); Phys. Rev. A **11**, 1068 (1975); J. B. Kaelberer and R. D. Etters, J. Chem. Phys. **66**, 3233 (1977).

[6] C. L. Briant and J. J. Burton, J. Chem. Phys. **63**, 2045 (1975); E. Blaisten-Barojas and H. C. Andersen, Surf. Sci. **156**, 548 (1985); J. Jellinek, T. L. Beck, and R. S. Berry, J. Chem. Phys. **84**, 2783 (1986).

[7] J. D. Honeycutt and H. C. Andersen, J. Chem. Phys. **91**, 4950 (1987).

[8] S. Iijima and T. Ichihashi, Phys. Rev. Lett. **56**, 616 (1986); M. José-Yacamán, Appl. Catal. **13**, 1 (1984); J. M. Dominguez, A. Vázquez, A. J. Renouprez, and M. José-Yacamán, J. Catal. **75**, 101 (1982).

[9] P. Gallezot, M. Avalos-Borja, and H. Poppa, Langmuire **1**, 342 (1985).

[10] F. F. Abraham, Phys. Rep. **80**, 339 (1981).

[11] M. Weissmann and N. V. Cohan, J. Chem. Phys. **72**, 4562 (1980).

[12] I. L. Garzón and E. Blaisten-Barojas, Chem. Phys. Lett. **124**, 84 (1986).

[13] C. Ebner and W. F. Saam, Phys. Rev. Lett. **38**, 1486 (1977).

[14] L. Verlet, Phys. Rev. **159**, 98 (1964).

[15] E. Blaisten-Barojas, Kinam **6**, 71 (1984).

[16] I. L. Garzón, M. Avalos, and E. Blaisten-Barojas, in *Physics and Chemistry of Small Clusters*, Vol. B158 of *NATO Advanced Science Institute Series*, edited by P. Jena, B. K. Rao, and S. N. Khanna (Plenum, New York, 1987), p. 193.