

Coexistence of Multiple Phases in Finite Systems

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(Received 13 August 1993)

Dynamic coexistence of several phaselike forms, a solid, microcrystalline phase, a homogeneously melted phase, and phases exhibiting a solid core and a melted surface, is found in isothermal molecular dynamics simulations of magic-number rare gas clusters. We present a mean-field model showing that the observed behavior is possible if (a) the core and surface both undergo finite-system analogs of first-order transitions with overlapping coexistence regions and (b) the mode-softening defects of the core exhibit an attractive interaction with the vacancy-floater pairs on the surface.

PACS numbers: 64.60.My, 05.70.Fh, 36.40.+d, 64.70.Dv

The melting-freezing phase transition of small systems, notably clusters and nanophase materials, has attracted increasing interest both experimentally [1] and theoretically [2-4], primarily to connect dynamics at the molecular level to the familiar macroscopic phase transition. A theoretical framework was developed [3-5] indicating that clusters may exhibit sharp but unequal limiting temperatures for freezing and melting. Clusters showing this behavior have a finite range of temperature and pressure within which solid and liquid clusters of a specific size may coexist. Within this band of temperatures the equilibrium ratio of solidlike and liquidlike forms changes smoothly. The theory of this phenomenon, as presented until now, is restricted to changes among homogeneous phases and does not treat behavior with heterogeneous phases such as surface-melted [6] or nonwetted [7] structures. Similarly, the concept of surface melting has grown into an area of mounting attention on both the experimental [8] and theoretical [9,10] sides.

The occurrence of coexistence phenomena [11,12] and surface melting [6] in different accounts of the same argon clusters raises the question of what role surface melting has in phase changes of clusters. To resolve this issue we used Nosé's equations of motion and a (12,6) Lennard-Jones potential and conducted isothermal molecular dynamics (MD) simulations of Ar_{55} and Ar_{147} clusters in a temperature range in which surface and homogeneous melting is possible.

What we call "phase" in the context of small clusters must be understood to be a form that exhibits the equilibrium properties we associate with bulk phases, at least for time intervals long enough to permit spectroscopic probing. The coexistence of two phases of a cluster thus normally means that the cluster passes between the different phases, spending relatively long intervals in each but visiting them all, for average times whose ratios are the exponentials of the free energy differences in units of kT .

To recognize dynamic phase coexistence in isothermal MD, one computes short-time averages (STA's) of the cluster's potential energy ϕ or total energy E_{tot} over a few of its breathing periods. At temperatures below the onset of phase coexistence the distribution of STA energies is unimodal, reflecting only vibrational motion around the

icosahedral ground state. At higher temperatures the STA potential energy distribution is bimodal or multimodal, exhibiting a series of distinct bands [see Fig. 1(a)]. Ar_{55} exhibits first one and then two additional, narrow bands corresponding to structures in which one and two atoms ("floaters"), respectively, have popped out of the surface and occupy the otherwise empty outer shell, leaving behind vacancies in the surface. At higher tempera-

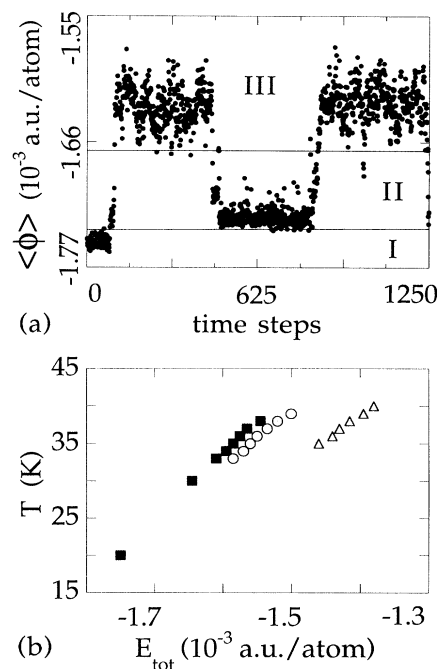


FIG. 1. The short-time averaged potential energy $\langle\phi\rangle$ for Ar_{55} at 35 K (a) and the caloric curves of the different potential energy regions (b). In (a) each point represents an average over 1800 time steps of 3×10^{-15} s each. We find dynamic coexistence between the solid ground state (region I), two surface-melted phases with one and two floaters, respectively, (region II), and a homogeneously melted phase, in which the core and the surface of the cluster show liquidlike behavior (region III). In (b) the solid phase is represented by squares, surface-melted by circles, and homogeneously melted by triangles.

tures, a wider band appears at much higher energies. The latter represents clusters with an amorphous structure which we denote "homogeneously melted" (HM) as opposed to the structures in the two lower energy bands with floater-vacancy pairs and a solid core, which we call "surface melted" (SM). At still higher temperatures the SM bands disappear and only the band corresponding to energies of the HM phase remains. For Ar₁₄₇ we also find several bands in the phase transition region, the maximum number of floater-vacancy pairs being five. The minimum dwell time in each phase can be estimated to be of the order of 600 breathing periods.

Figure 1(b) shows the caloric curve of Ar₅₅ obtained by averaging separately over the energy regions I, II, and III of Fig. 1(a). With increasing temperature we find a twofold coexistence of the solid and SM phases, a threefold coexistence with the additional HM phase, and a twofold coexistence of SM and HM. We can distinguish four characteristic temperatures for the freezing-melting transition. They are, in ascending order, T_{sf} and T_{cf} , denoting the lower limits of the existence range of a liquid surface, then a liquid core, respectively, and therefore defined as the respective freezing-limit temperatures, and T_{sm} and T_{cm} representing the corresponding upper limits, the melting limits.

The probability distributions that a particle be the distance d from the center of mass show the pronounced shell-like structure of the Mackay icosahedra in region I, with no intershell motion between the shells. In region II the shell-like structure persists, although the peaks flatten slightly. There is, however, an additional nonzero contribution for values of d greater than that of the outermost shell due to floaters. In region III particle exchange between all shells occurs; the cluster becomes amorphous.

From the slopes of the shell-by-shell mean square displacements the diffusion coefficients D_j^i for each shell i , ranging from 1 (center particle) to 4 (outer shell) for Ar₅₅, and energy region j can be computed. From the solid to the HM phase the diffusion constant of each shell in Ar₅₅ at 35 K increases by 1 to 3 orders of magnitude. The stiff, localized motion of the particles in the solid transforms into delocalized, diffusive motion characteristic of a liquid. Whereas D_4^{III} hardly differs from D_1^{III} , D_4^{II} has 4.5 times the value of D_1^{II} . The absolute value of D_4^{II} , however, still lies an order of magnitude below the values of the HM case. We conclude that the floater-vacancy

pairs exhibit diffusive motion, but that their motion is more restricted than any particle motion in the HM phase.

We have also computed the vibrational entropy $\sigma_{vib}^{(h)}$ in a harmonic approximation for a sample of quenched states of Ar₅₅ along the trajectory and identified their structure by computer visualization. We see an almost linear rise in the entropy for states with a solid core and zero to two floaters and a saturation at the three-floater state. The entropy estimate $\sigma_{vib}^{(h)}$ only gives a lower bound for the vibrational entropy, since in the SM phases the floaters explore the anharmonic parts of the potential and even go high enough to cross saddles fairly easily. An upper bound, $\sigma_{vib}^{(f)}$, obtained from a free-volume approximation without floater-floater interactions, shows saturation close to the half-empty shell levels. The simulations indicate an intermediate situation, so that the actual saturation is likely to occur at slightly larger values than indicated by $\sigma_{vib}^{(h)}$ but significantly lower than by $\sigma_{vib}^{(f)}$. The saturation of the vibrational entropy for floater numbers that are small compared to the number of particles on the cluster surface, together with the strong rise in entropy of amorphous structures with increasing ϕ , explains how homogeneous melting overcomes surface melting.

Without being recognized as such, the multiple phase coexistence reported in this study for isothermal MD simulations with free boundary conditions has also been observed in Monte Carlo simulations of Ar₅₅ clusters placed within a hard constraining sphere [11].

Building upon the results from these computer experiments we devise a simple melting theory for the equilibrium and dynamics of phases of small systems, expanding the validity range of a model that describes the coexistence of homogeneous phases [4] by including heterogeneous phases. The model presented here uses a formal separation of the cluster's statistical mechanical properties into the cluster core, the surface layer, and the floaters, respectively. We suppose each cluster has N atoms, which we write as $N = N_M(n) + a$ in the proximity of the Mackay numbers $N_M(n)$ with index n , where a can be either positive or negative. In the ground state the surface contains $N_s \equiv N_n - a\Theta(-a)$ particles, where $N_n \equiv N_M(n) - N_M(n-1)$ and Θ is the Heaviside function. In this case there are also $a\Theta(a)$ floaters. We express the partition function Z_N in terms of the number of core or internal defects m_c , of surface defects m_s , and of floaters m_f :

$$Z_n = V Z_{vib}^{(0)} \exp(-\beta E^{(0)}) \underbrace{\sum_{m_c=0}^{N_c} \sum_{m_s=-a\Theta(-a)}^{N_n/2} \sum_{m_f=a\Theta(a)}^{N_{n+1/2}}}_{m_s - m_f + a = 0} \tilde{Z}_c(m_c) \\ \times \left\{ \prod_{i=s,f} \tilde{Z}_{vib}^{(i)}(m_i) \frac{N_i!}{m_i!(N_i - m_i)!} \right\} \exp\{-\beta N_s [\Delta e^{(st)}(m_s, m_f) + e_{int}(m_c, m_s, m_f)]\}.$$

In the absence of entropic and energetic interlayer interactions, which we assume to be contained in e_{int} , the normalized part of Z_N factors into contributions from each subsystem. m_f and m_s cannot vary independently, since we allow no

particles to evaporate from the outermost layer. Restricting ourselves to the magic number case, $m_s = m_f$ holds. $\beta \equiv 1/kT$, V is the cluster volume; $E^{(0)}$ and $Z_{\text{vib}}^{(0)}$ denote the potential energy and the vibrational partition function of the ground state, respectively.

For the core we follow Wales and Berry [4]: Using a quasiparticle formulation and working in the limit of a low density of defects, a simple consideration of the allowed permutations and a mean-field assumption for the energy leads to

$$\tilde{Z}_c = \frac{N_c}{m_c!(N_c - m_c)!} \frac{1}{\Lambda^{3m_c}} \left(\frac{V_c}{N_c} \right)^{m_c} e^{-\beta N_c e^{(c)}},$$

where N_c is the number of possible defect sites in the core, $\Lambda \equiv (h^2/2\pi M k T)^{3/2}$, M being the quasiparticle mass, $e^{(c)} \equiv (E^{(c)} - E^{(0)})/N_c$ is the energy deviation of the core from the ground state, and V_c is the core volume. $\tilde{Z}_{\text{vib}}^{(i)}$, $i = s, f$ are the normalized vibrational partition functions and $\Delta e^{(sf)} \equiv (E^{(s)} - E^{(f)})/N_s$ is the energy difference between the surface and floater systems. The permutational partition function of the floater system can be approximated by a binomial coefficient since the motion of the floaters around one site is long compared to

the typical breathing frequencies and the number of excluded sites is small for typical floater numbers in the phase transition region.

Whereas an energy expansion in terms of the number density of particles is not expected to be useful for a condensed system, an expansion of $e^{(c)}$, $\Delta e^{(sf)}$, and

$$e_{\text{int}} = \sum_{l,l'=1}^{\infty} \sum_{i \neq j = c,s,f} [a_{l,l'}^{(ij)} + b_{l,l'}^{(ij)}(\beta)] \rho_i^l \rho_j^{l'}$$

in terms of the number densities of defects $\rho_c \equiv m_c/N_c$ and $\rho_i \equiv m_i/N_s$, $i = s, f$ is appropriate if the systems of quasiparticles are reasonably dilute.

Explicitly neglecting fluctuations, we can replace the sums in Z_N by their dominant terms in a maximum term approximation. These can be found for fixed, sufficiently large N by taking the natural logarithm, applying Stirling's approximation and differentiating with regard to m_c and m_s . We restrict ourselves to terms of order smaller than cubic-defect-floater densities, incorporating terms linear or quadratic with respect to ρ_c and ρ_s into $e^{(c)}$ and $\Delta e^{(sf)}$ by renormalizing the coefficients of the energy expansion. We obtain two equations for β , where we use $\rho_c \equiv \bar{m}_c/N_c$ and $\rho_c \equiv \bar{m}_s/N_s$ instead of the extremum values \bar{m}_c and \bar{m}_s [13]:

$$\beta = \beta_c(\rho_c, \rho_s) \equiv \frac{\ln(1/\rho_c - 1) + \ln(V_c/N_c \Lambda^3) - (\xi_2/N_c)\rho_s}{\partial e^{(c)}/\partial \rho_c + (\xi_1/N_c)\rho_s}, \quad (1)$$

$$\beta = \beta_s(\rho_c, \rho_s) \equiv \frac{N_s \partial \sigma_{\text{vib}}/\partial \rho_s + \ln(1/\rho_s - 1) + \ln(N_f/\rho_s N_s - 1) - (\xi_2/N_s)\rho_c}{\partial \Delta e^{(sf)}/\partial \rho_s + (\xi_1/N_s)\rho_c}. \quad (2)$$

Here $\xi_1 \equiv N_s [\tilde{a}_{1,1}^{(cs)} + \tilde{a}_{1,1}^{(cf)}]$, $\xi_2 \equiv N_s \beta [\tilde{b}_{1,1}^{(cs)}(\beta) + \tilde{b}_{1,1}^{(cf)}(\beta)]$ (with the renormalized expansion coefficients denoted by tildes), and $\sigma_{\text{vib}} \equiv \ln[\tilde{Z}_{\text{vib}}^{(s)} \tilde{Z}_{\text{vib}}^{(f)}]$ were introduced for simplicity. If we assume that the temperature-dependent contributions to the interlayer interaction energies, $\tilde{b}_{1,1}^{(cs)}$ and $\tilde{b}_{1,1}^{(cf)}$, e.g., describing the coupling of core and surface defects by phonons, are linear in the temperature $T = 1/k\beta$, ξ_2 is independent of β .

In the case of vanishing interlayer interaction, i.e., $\xi_1 = \xi_2 = 0$, Eqs. (1) and (2) relate β to ρ_c and ρ_s , respectively. For this case Eq. (1) has been analyzed in Ref. [4]: One only finds turning points for $\beta(\rho_c)$ if $\partial^2 e^{(c)}/\partial \rho_c^2$ can be negative, i.e., if there are net attractive forces between the quasiparticles of the core. $\beta(\rho_s)$ has a pair of turning points in the physically reasonable interval $0 \leq \rho_s < \frac{1}{2}$ only if σ_{vib} is sufficiently nonlinear in ρ_s there. A sufficient condition for this is σ_{vib} showing a saturation behavior for values of ρ_s much smaller than $\frac{1}{2}$ [13]. This seems to be what our simulation results show for Ar₅₅.

Graphically evaluating (ρ_c, ρ_s) for descending values of β we obtain the possible combinations of phases that can coexist at each fixed inverse temperature β . The coexistence regions of the core and of the surface-floater system are specified by $[\beta_{\text{cm}}, \beta_{\text{cf}}]$ and $[\beta_{\text{sm}}, \beta_{\text{sf}}]$, respectively, where the interval limits are the β values of the turning

points of Eqs. (1) and (2), respectively. If these regions do not overlap, the system exhibits separate twofold coexistence of S ($\rho_c, \rho_s \approx 0$) and SM ($\rho_c \approx 0$ and $\rho_s \neq 0$), on the one hand, and SM and HM ($\rho_c \approx 1$ and $\rho_s \neq 0$), on the other hand. For overlapping intervals a fourfold coexistence of all four possible phases, i.e., of S, SM, HM, and a mechanically unlikely core-melted phase ("CM", $\rho_c \approx 1$ and $\rho_s \approx 0$), is embedded between twofold coexistence regions of (S,CM) and (SM,HM). From our model we infer that a threefold coexistence as found in the simulations can be explained only if interlayer interactions are taken into account.

Figure 2 shows $\beta(\rho_c, \rho_s)$ for a negative, i.e., energy-decreasing temperature-dependent interlayer interaction $\xi_2 < 0$ and the other parameter values suitable to describe Ar₅₅. A coexistence of S, SM, and HM takes place between β_{cf} and β_{sm} . For $\beta_{\text{cf}} < \beta < \beta_{\text{sf}}$ and $\beta_{\text{cm}} < \beta < \beta_{\text{sm}}$ we find a (S,SM) and (SM,HM) coexistence, respectively. Analyzing different values of ξ_1 and ξ_2 we conclude that the multiple phase coexistence of S, SM, and HM we find in MD simulations can only be explained within the framework of a mean-field model if the interactions between core defects and floater-vacancy pairs are sufficiently energy lowering, i.e., that these quasiparticles either attract each other or have a mode-softening effect on

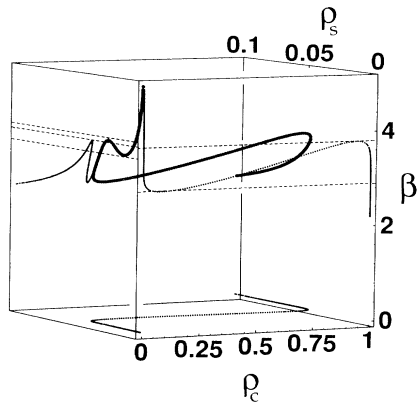


FIG. 2. The inverse temperature β (in units of $1/\epsilon$ with $\epsilon = 1.67 \times 10^{-7} J$) as a function of the density of core defects ρ_c and surface vacancies ρ_s for $\xi_1 = 0$ and $\xi_2 = -10$ and parameters adequate for Ar₅₅ (see Ref. [13]). β_{sm} , β_{cf} , and β_{sf} (with $\beta_{sm} < \beta_{cf} < \beta_{sf}$) are represented by dashed lines in the (β, ρ_s) basal plane, β_{cm} and β_{cf} ($\beta_{cm} < \beta_{cf}$) by dashed lines in the (β, ρ_c) basal plane.

the phonon spectrum, or both. Clusters whose interatomic forces lead to a net repulsion of these quasiparticles will not exhibit a melted surface, since this phase would imply the existence of the “dual” core-melted phase. Mechanical considerations, however, make the appearance of such a phase unlikely for clusters of atoms with simple, pairwise central forces. Parameter dependencies necessary for the existence of multiple phase behavior can be extracted from our model [13].

The phase coexistence behavior we find in Ar₅₅ and Ar₁₄₇ allows us to make some general remarks on the nature of the surface-melting transition. As opposed to earlier suggestions [6], it resembles more a finite system’s counterpart of a normal first-order transition, rounded by finite-size effects [14,15], than the small-system analog of a weak first-order transition. The solid surface clearly does not lose its local stability at the same temperature

the liquid surface gains it. This stems from the fact that the entropy of the surface seems to saturate for a very low density of surface vacancy-floater pairs and cannot be treated as linear in the number of floaters within the transition range.

The authors thank Dr. J. Rose and Dr. H.-P. Cheng for helpful discussions. R.E.K. gratefully acknowledges the financial support of the German National Scholarship Foundation.

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