Solid–liquid phase changes in simulated isoenergetic Ar$_{13}$

Julius Jellinek, Thomas L. Beck, and R. Stephen Berry

Department of Chemistry and the James Franck Institute, The University of Chicago, Chicago, Illinois 60637

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Simulations by molecular dynamics of 13-particle clusters of argon display distinct nonrigid, liquid-like and near-rigid, solid-like "phases." The simulations, conducted at constant total energy, display a low-energy region in which only the solid-like form appears, a high-energy region in which only the liquid-like form appears, and an intermediate band of energy—a "coexistence region"—in which clusters exhibit both forms. The intervals of time spent in each phase in the two-form coexistence region are long compared with the intervals required to establish equilibrium-like properties distinctive of each form, such as mean square displacement and power spectrum, so that well-defined phases can be said to exist. The fraction of time spent in each phase is a function of the energy. When a long simulation is separated into regions of solid-like and liquid-like behavior, the curve of the derived caloric equation of state is double valued in the two-phase range of energy, forming two well-defined, smooth branches. When, instead, the caloric curve is constructed from averages over all of a long run, its form is smooth and monotonic showing no trace of the "loop" that had been reported for earlier treatments with much shorter molecular dynamics runs, and which we could also reproduce with short runs.

I. INTRODUCTION

The melting transition remains one of the less understood among commonplace phenomena. One of the promising avenues to help elucidate this process is the study of solid-like and liquid-like clusters of atoms or molecules. Ordered and disordered clusters have been observed in the laboratory, so there is now a possibility that clusters will offer a new approach to experimental study of the transformations between such forms. On the theoretical side, simulations have given considerable insight into how we might expect solid-like and liquid-like clusters to behave, and analytical studies of models have begun to show how some aspects of melting and freezing of clusters arise as consequences of particular physical properties.

Simulations have been carried out both with molecular dynamics (MD) and Monte Carlo (MC) calculations. (For reviews, see Refs. 6 and 7.) The main finding of the simulation studies can be formulated as follows: small clusters (as small as seven atoms, or probably even less) exhibit two distinctly different forms, to which we shall refer in what follows as the rigid and nonrigid forms or phases. The two forms are named—and considered—like phases of bulk matter on the basis of several of their attributes, such as the radial distribution function, heat capacity $C_v$, relative root-mean-square (rms) bond length fluctuation, power spectrum, x-ray interference function, and caloric curve of state, all considered as functions of an external parameter, either total energy in MD studies or temperature in the MC method. A detailed discussion of the observed transition phenomenon and its implications can be found in Refs. 8–14.

In a recent study Natanson, Amar, and Berry addressed the issue of the microscopic mechanism underlying the abovementioned cluster behavior. Specifically, they concentrated on the question of how little physics must be put in, in order that a model exhibit the existence of liquid-like and solid-like forms of small clusters in terms of microscopic interactions. The partition functions for an N-atom cluster were calculated for extremely simple near-rigid and highly nonrigid models for the two structures. The transition temperature (which was then referred to as a "melting" temperature) was defined as the temperature at which the two partition functions (or the Helmholtz free energies) attained equal values. In a later study Berry, Jellinek, and Natanson addressed the question of necessary and sufficient conditions for the coexistence of two phases in small clusters, based on the analysis of the densities of states of the two forms. The primary conclusion from the model proposed by these authors is that for most substances, small clusters of $N$ particles should exhibit a temperature $T_f(N)$ ("freezing temperature") below which only the solid-like form is stable and a higher temperature $T_{m}(N)$ ("melting temperature") above which only the liquid-like structure is stable. For any temperature $T$ between $T_f(N)$ and $T_{m}(N)$ the two forms coexist in stable equilibrium, with an equilibrium constant $K(N,T)$ defined by the difference of the respective free energies.

The primary goal of the present study is to provide a computational probe of the coexistence phenomenon described in Refs. 16 and 17. It is not yet a test because the prediction of Ref. 16 is based on a canonical distribution, which we shall discuss in later communications; the present discussion is limited to a microcanonical ensemble. It is interesting to note that in their earlier, constant temperature MC study, Etters and Kaaber remarked on an "occasional tendency for the clusters to change from solid to liquid and, somewhat less often, from liquid to solid during the course of a single run." This observation was referred to by them as a "peculiar feature."

We report here results of extensive MD simulations of a 13-particle argon cluster. Theicosahedral geometry is the equilibrium structure of the ground state and thus, quite naturally, of the rigid, solid-like form. This geometry is an extremely stable structure. It offers no low-energy pathways
for isomerization taking the cluster from one solid-like structure to another permutational equivalent, or to other, higher potential minima with differing geometries. Passage from well to well requires promotion of one of the 12 atoms of the icosahedron, like the creation of a particle-hole pair, in order to establish any mobility. Hence this system offers a particularly clear case for the study of the rigid to nonrigid transition. (Clusters of other sizes have also been studied and will be described in a separate publication.) The experimental work of Farges et al.\textsuperscript{2} has shown clearly that the icosahedral geometry is a dominant structure in small clusters of fewer than 100 argon atoms.

The details of the computational procedure are discussed in Sec. II. The body of results is presented in Sec. III followed by evaluations and a discussion (Sec. IV). A brief summary is given in conclusion.

II. COMPUTATIONAL PROCEDURE

The potential in the total Hamiltonian

\[ H = \sum_{\ell, j} \frac{p_{\ell j}^2}{2m} + V(\{r_{\ell j}\}) \]  

(1)

of the 13-particle cluster was chosen as a sum of pairwise 6–12 Lennard-Jones (LJ) interactions:

\[ V(\{r_{\ell j}\}) = \sum_{\ell < j} V_q(r_{\ell j}), \]  

(2)

where

\[ V_q(r_{\ell j}) = 4\epsilon \left( \left( \frac{\sigma_{\ell j}}{r_{\ell j}} \right)^{12} - \left( \frac{\sigma_{\ell j}}{r_{\ell j}} \right)^{6} \right), \]  

(3)

and

\[ r_{\ell j} = |r_{\ell} - r_{j}|. \]  

(4)

The parameters of the LJ potential were chosen so as to correspond approximately to the real argon atom–atom interaction and precisely to the potential used in many previous models ($\sigma = 3.4 \times 10^{-8}$ cm, $\epsilon = 1.67 \times 10^{-14}$ erg).\textsuperscript{18}

The initial relative positions of the 13 atoms in the cluster corresponded to a structure obtained by slightly deforming the equilibrium icosahedral geometry. The initial momenta of the atoms were set to zero. The forces generated by the initial deformation caused the atoms to begin moving. The trajectory was propagated 2000 steps with a step size of $10^{-14}$ s to allow for proper equilibration of the cluster. Then, based on further propagation, different characteristics, such as mean kinetic energy per particle, velocity autocorrelation function, mean square displacement, etc., were calculated. These are discussed in Secs. III and IV. The calculations were repeated successively on a grid of increasing (or decreasing) energies. The final configuration of the previous run defined the initial positions of the atoms for the next run at a different energy. The initial values of the velocities for every new run were obtained by scaling the final velocities of the preceding run to give the desired value of the new total energy.

The Newtonian equations of motion were solved using the Verlet method.\textsuperscript{19} The time step of $10^{-14}$ s provided conservation of the total energy within 0.01%. The total momentum of the system was conserved with the same accuracy. The total angular momentum of the cluster (also initially zero because of the zero value of all the initial velocities) was not calculated, but over very long runs ($10^9$ steps) in the rigid limit no overall rotation was detectable in "snapshots" of the cluster. Although all the trajectories, including the very long ones, remained confined to the energy shell, only for short intervals were they time reversible. The initial configuration of the atoms could be recovered extremely accurately (to within a very small fraction of 1% of the coordinate values) after 2500 steps on a double precision machine; the errors in returning to the original values beyond this point accumulated rapidly (consistent with exponential divergence) with increasing length of the run. A 5000 step run, for example, returned to within 2% of the initial coordinates. A quadruple precision test run however, was again time reversible with accuracy significantly higher than even the 2500 step double precision propagation, to within one part in $10^{15}$ for 4000 steps. The implication of the results of these short test runs is that the main factor limiting the time reversibility is the round-off error.

The accuracy of the Verlet algorithm was compared with that obtained with Hamming's modified predictor–corrector method, which is a stable fourth-order integration procedure. The two algorithms led to practically identical trajectories in the phase space when the propagation was done with a step size of $10^{-14}$ s for 1000 steps.

As mentioned above, the change to each new energy was carried out by scaling the final velocities of the prior constant energy calculation. This scaling, which effectively is equivalent to "heating" or "cooling" the cluster, was done in very small increments to ensure equilibration within 2000 steps.

III. RESULTS

Consider first the curve of the caloric equation of state which expresses the functional relation between the mean kinetic energy per particle $E_{\text{kin}}$ and the mean total energy per particle $E_{\text{tot}}$ (or between $E_{\text{tot}}$ and the bath temperature $T$). This curve was generated in earlier studies by both the MDC\textsuperscript{12,13} and MCD\textsuperscript{11,14} methods. The qualitative features of the curves obtained by different authors were not uniform. Briant and Burton\textsuperscript{8} observed a loop-shaped part connecting two distinct branches of the curve, a solid-like branch extending to the lowest energies, and a liquid-like branch extending to high energies. No such loop was obtained in the other studies. A conjecture was put forward by Briant and Burton that the loop is a reflection of a first-order-like transition.

We repeated the calculation of $E_{\text{kin}}$ vs $E_{\text{tot}}$ for a 13-particle argon cluster in order to clarify the structure of the transition region. The procedure of slow heating (increase of $E_{\text{tot}}$) and slow cooling (decrease of $E_{\text{tot}}$) generated practically identical results. These results are presented in Fig. 1. The value of $E_{\text{kin}}$ was obtained as a time average calculated in two ways: by short-time averaging over consecutive sets of 500 time steps which corresponds to averaging over vibrations, such as the "breathing" motion of the cluster (the typical time scale for this motion is about 150 time steps for a breathing cycle), and by long-time averaging computed over the entire run ($5 \times 10^9$ to $10^9$ time steps). The curve in Fig. 1
A. The single-phase cases: The solid-like region

Consider first the situation in which the total energy per particle $E_{tot}$ in the cluster is less than $E_f$. In Fig. 3 the time dependence of $E_{kin}$, averaged over 500 propagation steps, is shown for three different fixed values of $E_{tot} < E_f$. The feature to be noticed is that the fluctuations in the short-time average of $E_{kin}$ are quite small, especially at lower values of $E_{tot}$, as in Fig. 2(a). Occasional “jumps” down at energies $E_{tot}$ close to $E_f$ correspond to permutational rearrangements of atoms that carry the structure from one icosahedron to a permuted equivalent. Computer snapshots of the cluster shown in Fig. 3 clearly demonstrate this. The period of transition between icosahedral structures is characterized by a decrease in $E_{kin}$ because it corresponds to passing over a local barrier on the potential energy surface while $E_{tot}$ is kept constant.

The degree of mobility of atoms, which is one fairly direct index of rigidity of the cluster, can be characterized by such quantities as the root-mean-square (rms) bond length fluctuation $\delta$, the mean square displacement, and the velocity autocorrelation function. Figure 4 shows the relative rms bond length fluctuation $\delta$, where

$$
\delta = \frac{2}{N(N-1)} \frac{\sum_{ij} \langle (r_{ij} - \langle r_{ij} \rangle)^2 \rangle}{\langle r_{ij} \rangle},
$$

and $\langle \cdot \rangle$ is the time average calculated along the entire trajectory ($5 \times 10^4$ time steps); $r_{ij}$ is defined by Eq. (4); $N$ is the number of atoms in the cluster. The mean fluctuation $\delta$ is plotted as a function of the number of atoms in the cluster expressed in terms of the “internal temperature” $T_i$ defined as

$$
T_i = \frac{2N}{3N - 6} \frac{E_{kin}}{k},
$$

where $E_{kin}$ is the long-time average of the kinetic energy, $k$ is the Boltzmann constant, and the factor $3N - 6$ results from the conservation of the total linear and angular momenta in the MD simulations. As can be seen from Fig. 1, the long-time average $E_{kin}$ shows only a slight increase when $E_{tot}$ changes from $E_{tot} = E_f$ to $E_{tot} = E_m$. In terms of temperature these values of $E_{kin}$ are about $T_i \approx 34$ K. As is seen in Fig. 4, $\delta(T_i)$ has a small positive slope in the region $T_i < 34$ K, reflecting the thermal expansion of the solid-like cluster.

The mean square displacement $\langle r^2(t) \rangle$ of the particles in the cluster, as a function of time,

$$
\langle r^2(t) \rangle = \frac{1}{Nn_i} \sum_{i=1}^{n_i} \left[ \sum_{t=1}^{N} \left[ r_i(t_0 + t) - r_i(t_0) \right] \right]^2,
$$

is plotted in Fig. 5; $n_i$ is the number of different time origins.

The curve corresponding to $E_{tot} < E_f$ shows a very clear leveling off after a small initial rise. The slopes of the long-time part of these curves are the corresponding diffusion coefficients $D(E_{tot})$:

$$
D = \frac{1}{6} \frac{d \langle r^2(t) \rangle}{dt}.
$$

The flattening of the low-energy curve of Fig. 5 corresponds to $D = 0$ and reflects the solid-like nature of the cluster at these low energies. Note that the times used to define $D$ may
FIG. 2. The distribution of short-time averages of the kinetic energy ($E_{\text{kin}}$) at five total energies: (a) $E_{\text{tot}} = -4.72 \times 10^{-14}$ erg/atom, (b) $E_{\text{tot}} = -4.28 \times 10^{-14}$ erg/atom, (c) $E_{\text{tot}} = -4.04 \times 10^{-14}$ erg/atom, (d) $E_{\text{tot}} = -3.88 \times 10^{-14}$ erg/atom, (e) $E_{\text{tot}} = -3.61 \times 10^{-14}$ erg/atom. The smooth curves are the result of a least squares fit to the sum of two Gaussians. The vertical scale is in absolute counts.
extend only to the time required for a particle to migrate roughly across the diameter of its cluster.

Consider next the velocity autocorrelation function defined as

$$C(t) = \frac{\langle \mathbf{v}(t_0 + t) \cdot \mathbf{v}(t_0) \rangle}{\langle \mathbf{v}(t_0) \rangle} = \frac{\sum_{i=1}^{N} \sum_{j=1}^{N} \mathbf{v}_i(t_0 + t) \cdot \mathbf{v}_j(t_0)}{\sum_{j=1}^{N} \sum_{i=1}^{N} \mathbf{v}_j(t_0)}$$

A typical curve for $E_{\text{tot}} < E_f$ is displayed in Fig. 6(a). Note the relatively strong first "reflection" of the particles indicated by the deep well in the curve corresponding to a large prompt reversal of $v$ for rather short times and the persistence of the correlation for quite a long time. These features are indicative of a rigid structure, with particles bouncing back to their equilibrium positions and beyond. A further corroboration of the solid-type behavior of the cluster for $E_{\text{tot}} < E_f$ is furnished by the power spectrum $I(\omega)$, the Fourier transform of the velocity autocorrelation function,

$$I(\omega) = 2 \int_{0}^{\infty} C(t) \cos \omega t \, dt$$

The frequency distribution obtained from the curve (a) of Fig. 6 is shown in Fig. 7(a) for a relatively cold solid. The distinct peaks and lack of translational motion $[I(\omega = 0) = 0]$ are well-accepted attributes of solid-like behavior. Figures 6(b) and 7(b) correspond to an energy just below $E_f$ and display the smoothing that is characteristic of a softening solid, but no diffusion. (See Sec. IV, following.)

1. The liquid-like region

We turn now to analysis of the results for $E_{\text{tot}} > E_m$ to show that in this energy range the cluster is again a single-
FIG. 6. The normalized velocity autocorrelation functions at three total energies: (a) $E_{\text{tot}} = -4.92 \times 10^{-14}$ erg/atom, (b) $E_{\text{tot}} = -4.36 \times 10^{-14}$ erg/atom, (c) $E_{\text{tot}} = -3.61 \times 10^{-14}$ erg/atom. The converged curves are averages over 600, 300, and 300 independent time origins, respectively.

FIG. 7. The power spectra obtained from the velocity autocorrelation functions of Fig. 6. The units of $I(\omega)$ are $10^{14}$ s$^{-1}$.  

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phase but nonrigid aggregation of atoms, corresponding to a liquid-like form. In Fig. 8 the time dependence of $E_{\text{kin}}$ is shown for $E_{\text{tot}} > E_m$. The fluctuations in the value of $E_{\text{kin}}$, each of which is again calculated as average over 500 time steps, are markedly larger than those for $E_{\text{tot}} < E_f$ (cf. Fig. 2). The increased "freedom" in the particle motion reflects the floppy structure of the cluster. Examination of the snapshots of the cluster at different instants reveals a fluctuating structure, clearly not icosahedral, with high atomic mobility resulting in frequent rearrangements. This high mobility of atoms for $E_{\text{tot}} > E_m$ (or $T_f > 34$ K) is clearly displayed in Fig. 4. The value of the rms fluctuation $\delta$ increases by a factor of 4 for $T_f > 34$ K as compared to $T_i < 34$ K (or $E_{\text{tot}} < E_f$).

The time-dependent quantities also reflect the liquid-like behavior of the cluster for $E_{\text{tot}} > E_m$. The mean square displacement for $E_{\text{tot}} = -3.61 \times 10^{-14}$ erg/atom (Fig. 5) shows a linear increase with time implying a finite diffusion coefficient. The slope of the curve begins to drop off for times larger than 900 steps (not shown), corresponding to diffusion across to the opposite boundary of the finite cluster. The velocity autocorrelation function shown in Fig. 6(c) has a much shallower reflection minimum than that of the rigid form and the longer-time correlations are lost entirely.

The power spectrum calculated from the curve (c) of Fig. 6 displays especially well some characteristic features of a fluid-like phase. The absence of sharp peaks in the spectrum is one indication of the absence of well-defined vibrational modes, and the nonzero intensity for $\omega = 0$ implies the presence of classic fluid-like soft modes, corresponding to diffusive motion, in the cluster.

In long runs for energies corresponding to the liquid region, an atom was observed to evaporate from the cluster. The three open circles in the liquid region of Fig. 1 just to the right of the two-phase region, at energies of $-3.72$, $-3.64$, and $-3.61 \times 10^{-14}$ erg/atom, correspond to runs that resulted in evaporation, respectively, after 126 000, 136 000, and 460 000 steps. That these intervals get longer, rather than shorter, as the energy increases we take to mean only that the rate of evaporation in MD simulations at these energies is significantly more sensitive to the (randomly chosen) initial configuration than to the energy. The problem of evaporation rate and its temperature dependence will be investigated more systematically in the course of isothermal simulations now in progress.

Summarizing the analysis presented above we conclude that the 13-particle argon cluster exhibits two distinctly different structures and types of behavior at low and high values of the total energy per particle $E_{\text{tot}}$. For $E_{\text{tot}} < E_f$ the cluster has the structure and properties of a solid-like aggregation; it behaves like a nonrigid floppy molecule or a liquid in the range $E_{\text{tot}} > E_m$.

**B. The two-phase case**

Our next step is to examine the behavior of the cluster in the region $E_f < E_{\text{tot}} < E_m$ and to show that for each energy in this region both the solid-like and the liquid-like forms can be observed. Figure 1 shows that the two branches of $E_{\text{kin}}$, representing the short-time (500 step) averages in the range $E_f < E_{\text{tot}} < E_m$, are, respectively, continuations of the low energy ($E_{\text{tot}} < E_f$) "rigid" and the high energy ($E_{\text{tot}} > E_m$) "nonrigid" branches of the caloric curve of state. Even without closer examination of time histories, this observation

![Graph](image)

**FIG. 9.** The time dependence of $E_{\text{kin}}$ (short-time averages) for three energies in the two-phase region: (a) $E_{\text{tot}} = -4.20 \times 10^{-14}$ erg/atom, (b) $E_m = -4.16 \times 10^{-14}$ erg/atom, (c) $E_m = -3.99 \times 10^{-14}$ erg/atom. The snapshots in (b) show the transition from a low-kinetic energy form with one atom removed from the original icosahedral structure back to the icosahedral rigid form. The open and darkened arrows indicate the values of $E_{\text{kin}}$ and $E_f$, respectively.
leads naturally to the supposition, that for every energy in this intermediate range the cluster can exhibit both its rigid and nonrigid forms. This supposition is consistent with earlier simulations, of course, Etters and Kaelberer very nearly pursued the issue to test its validity, one surmises from their comments. The analysis presented below substantiates this by comparing the results of simulations for $E_{\text{tot}}$ in $(E_r, E_m)$ with those for $E_{\text{tot}} < E_r$ (solid-like phase) and $E_{\text{tot}} > E_m$ (liquid-like phase).

The time dependence of $E_{\text{kin}}$ (short-time averages) for three different energies in the range $(E_r, E_m)$ is shown in Fig. 9. The common feature of the three curves is the bimodal distribution of “temperatures”: the values of $E_{\text{kin}}$ appear for each $E_{\text{tot}}$ to fluctuate around two different temperatures, a lower one $E_{\text{kin}}^i$, and a higher one $E_{\text{kin}}^h$. The manifold of all of the $E_{\text{kin}}^i$ and $E_{\text{kin}}^h$ for all $E_{\text{tot}}$ in $(E_r, E_m)$ forms the two overlapping branches in Fig. 1. Note that in Fig. 9, the time intervals spent by the cluster in each of the two phases defined by $E_{\text{kin}}^i$ and $E_{\text{kin}}^h$, respectively, are orders of magnitude longer than the period of the characteristic vibrational motions in either the rigid or nonrigid form. The fraction of the total time spent in each of the two forms, however, is a function of $E_{\text{tot}}$; we shall return to a detailed discussion of this point. The cluster spontaneously makes transitions between the two phases; the durations of the transition periods themselves are quite brief. Snapshots of the cluster in the two phases reveal two distinctly different forms. The form with high-kinetic energy is manifestly a vibrating icosahedron; the form with low-kinetic energy is similar to the floppy shapes of the nonrigid phase shown in Fig. 8. The latter can frequently be recognized as an icosahedron with one particle plucked out and put onto the surface. The time evolution of the structure (see Fig. 9) in the low-kinetic energy form indicates loose atom–atom binding and high atomic mobility. The high-kinetic energy phase, by contrast, exhibits a stable icosahedral structure even when its energy is high enough to cause vibrations of large amplitude. All this suggests that we identify the high-kinetic energy (high internal temperature $T_i$) form as a rigid, solid-like phase and the low-kinetic energy (low $T_i$) form as a nonrigid, liquid-like phase of the cluster. The reason $T_i$ is higher in the rigid form than in the nonrigid form is that both forms correspond to the same $E_{\text{tot}}$, and the potential energy is higher for the liquid-like phase than for the solid-like phase.

In order to further facilitate the comparison of the cluster’s behavior in the two-phase region with that in the solid-like and liquid-like single-phase regions, we selected portions of each trajectory for a given $E_{\text{tot}}$ in $(E_r, E_m)$ and labeled them according to two phases, i.e., according to whether the corresponding values of $E_{\text{kin}}$ fell onto the $E_{\text{kin}}^i$ branch or the $E_{\text{kin}}^h$ branch. All the portions of the same phase were grouped together, giving us two different classes of trajectory segments with time spans long relative to the short-averaging time. The quantities of interest were then calculated separately for each of the two phases.

In Fig. 10 the mean square displacement $\langle \mathbf{r}^2 \rangle$ of the atoms in the cluster is shown as a function of time for $E_{\text{tot}} = -4.13 \times 10^{-14}$ erg/atom, which is in the range $(E_r, E_m)$. The two branches (s) and (l) correspond to the two classes mentioned above. The (s) branch calculated for the high-kinetic energy form shows a trend almost identical to that exhibited by the solid-like structure at $E_{\text{tot}} < E_r$, while the (l) branch corresponding to the low kinetic energy form increases linearly with the time like the corresponding curve for the liquid-like cluster for $E_{\text{tot}} > E_m$ (cf. Fig. 5). A small diffusion coefficient in the solid-like phase [the nonzero slope of the (s) branch in Fig. 10] can be understood if one recognizes that for $E_{\text{tot}}$ in the range $(E_r, E_m)$ the rigid form of the cluster is “hot.” By contrast, the liquid-like phase in this range is “cold.” This also rationalizes the lower value of the diffusion coefficient for the nonrigid form in the range $(E_r, E_m)$ [the slope of the branch (l) in Fig. 10] than in the range $E_{\text{tot}} > E_m$ (cf. Fig. 5).

The velocity autocorrelation functions calculated separately for the high kinetic energy form and the low kinetic energy form of the cluster for $E_{\text{tot}}$ in the two-phase range are shown in Fig. 11. For any energy in this range the hot solid-like and cold liquid-like forms have smaller differences in their first reflection minima and the long-time correlations than the differences between those same quantities taken at two different energies from the two one-phase regions (cf. Fig. 6). The power spectra $I(\omega)$ calculated for the two forms at the same value of $E_{\text{tot}}$ in $(E_r, E_m)$ are displayed in Fig. 12. At the high internal temperature $T_i$ of the solid-like form the local peak structure in the curve for that phase disappears. The differences, however, in the power spectra for the solid-like and the liquid-like forms are still quite clear. The distribution for the solid-like phase has a peak more pronounced than that for the liquid-like phase. The intensity at $\omega = 0$ for the solid-like form is much smaller than the corresponding intensity for the liquid-like form, despite the fact that the solid-like phase is the hotter of the two. The small nonzero value of $I(\omega = 0)$ for the solid-like phase gives rise to the

![Figure 10](https://example.com/figure10.png)

**Fig. 10.** The mean square displacement vs time of the solid-like (s) and liquid-like (l) forms in the two-phase region at $E_{\text{tot}} = -4.13 \times 10^{-14}$ erg/atom. The converged curves are averages over 1504 and 482 independent time origins, respectively.

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small positive slope of the curve (s) in Fig. 10, i.e., to a small diffusion coefficient, as mentioned above.

The main inference to be deduced from the results presented in this subsection is that at any energy in the range \( (E_T, E_m) \), a 13-particle argon cluster may exist in two forms which can be identified unambiguously as solid-like and liquid-like phases. After spending time in one of the two phases the cluster spontaneously "switches" to the other and eventually back again. The relative time spent in each of the phases is a function of \( E_{\text{tot}} \). The time intervals spent in each form are very long relative to times required to establish the properties diagnostic for a well-defined phase, so that there is the clear time-scale separation necessary for considering the system in terms of two phases.

IV. DISCUSSION

We start by comparing the caloric curve of state shown in Fig. 1 with that reported by Briant and Burton\(^8\) (BB). The BB results were obtained as time averages over their entire runs. Each internal temperature \( T_i \) (or \( E_{\text{kin}} \)) for a 13-particle cluster was computed by BB as an average over 10,000 steps, a step being \( 10^{-14} \) s. A notable feature of the BB curve of \( T_i \) vs \( E_{\text{tot}} \) is the loop-shaped portion connecting the low-energy and high-energy portions of the graph. By calculating their averages over entire runs, rather than by examining the long-time behavior of short-time, coarse-graining averages, Briant and Burton missed the phenomenon of the coexistence of two phases in the range \( (E_T, E_m) \). This phenomenon clearly exhibits itself in our Fig. 1 as two overlapping branches, that is, the two-valued character of the caloric function, with the two branches representing the liquid-like and the solid-like phases of the cluster. The two values of \( E_{\text{kin}}, E_{\text{kin}}' \) and \( E_{\text{kin}}'' \), for each \( E_{\text{tot}} \) \( (E_T, E_m) \) were produced, as described above, from averages over 500 steps with the step size of \( 10^{-14} \) s. Coarse graining with an interval of 500 steps is long enough to average out the effects of the vibrational motions of the cluster, but short enough to assure that the rigid and nonrigid forms persist for many averaging intervals, and thereby remain distinguishable. In order to generate a single-valued, long-time average value of \( E_{\text{kin}} \) (or \( T_i \)) for the energies in the range \( (E_T, E_m) \) a proper averaging over the two phases must be performed. Such a long-time average of \( E_{\text{kin}} \) can be represented as

\[
E_{\text{kin}} = \frac{\alpha E_{\text{kin}}' + \beta E_{\text{kin}}''}{\alpha + \beta},
\]

where \( \alpha \) and \( \beta \) are the relative times spent in the low- and high-kinetic energy forms, respectively. Of course, if one were to neglect the passage time between the two forms, \( \alpha + \beta \) would be 1. To achieve proper averaging over two phases, the runs must be long enough to assure convergence of \( \alpha \) and \( \beta \). Our results show that runs \( 10^5 \) steps long define the values of \( \alpha \) and \( \beta \) with uncertainties (standard deviations) of about 8%. Runs of the order of \( 10^6 \) steps are needed to reduce the uncertainties to within 1%. With runs of that length, our long-time averages of \( E_{\text{kin}} \), for energies in the two-phase range (see Fig. 1) do not reproduce the loop of BB. The \( 10^4 \) propagation steps used by BB are not enough to produce reliable averages in the two-phase region; this be-

comes immediately evident by examining our Fig. 9 or Fig. 16 of BB.\(^8\)

As Fig. 1 shows, the long-time averaged value of \( E_{\text{kin}} \) varies only very slowly in the range \( (E_T, E_m) \). The representative internal temperature \( T_i \) corresponding to this range is approximately 34 K. The abrupt change in the value of the rms bond length fluctuation \( \delta(T_i) \) in the vicinity of \( T_i = 34 \) K (see Fig. 4) corresponds to the transition from the single-phase solid-like region, for which \( E_{\text{tot}} < E_T \), to the single-phase liquid-like region, defined by \( E_{\text{tot}} > E_m \). The intermediate points in the vertical portion of the graph represent the value of \( \delta(T_i) \) averaged over the two forms of the cluster at energies \( E_{\text{tot}} \) \( (E_T, E_m) \). The transition from the single-phase rigid form to the single-phase nonrigid form occurs when \( \delta \) approaches the value 0.1. This fits remarkably well with the Lindemann criterion\(^2\) which associates bulk melting with a relative fluctuation in the interparticle separation of about 10%. It is interesting and reassuring to note that the behavior shown in Fig. 4 is very similar to results for the temperature dependence of \( \delta \) obtained by Etters and Kaelberer\(^5\) in their MC studies of small clusters.

As mentioned above, the relative time spent by the cluster in its rigid and nonrigid forms, when both are accessible, is a function of \( E_{\text{tot}} \). We now introduce the quantity \( K(\text{E_{tot}}) \) defined as

\[
K(\text{E_{tot}}) = \frac{\alpha}{\beta}.
\]

In Fig. 13 we show the dependence of \( K^{-1}(\text{E_{tot}}) \), the ratio of times spent in the solid-like to liquid-like forms, on the total energy per particle. For values of \( E_{\text{tot}} \) for which \( K(\text{E_{tot}}) > 1 \) \( (K < 1) \) the coarse-grained history of the cluster shows a preponderance of the liquid-like (solid-like) phase. If \( K(\text{E_{tot}}) = 1 \) the cluster will spend, on average, equal time in each of the two forms. Invoking the ergodicity hypothesis one can relate the long-time behavior of a system with its ensemble behavior. In the present context we can translate the repeated spontaneous transitions between the rigid and nonrigid forms in the cluster's long-time evolution into the coexistence of liquid-like and solid-like clusters in a micro-canonical ensemble defined by a fixed value of \( E_{\text{tot}} \). This translation permits us to call the two-phase range of energies \( (E_T, E_m) \) a coexistence range, and the quantity \( K(\text{E_{tot}}) \) an (energy) equilibrium constant giving the ratio of the number of liquid-like clusters to solid-like clusters in an equilibrated ensemble of 13-particle clusters with a fixed total energy, analogous to the conventional equilibrium constant \( K(T) \) for a canonical distribution.

Comparison of the velocity autocorrelation function and the power spectra in the two-phase region (Figs. 11 and 12) with those in the single-phase regions \( E_{\text{tot}} < E_T \) and \( E_{\text{tot}} > E_m \) (Figs. 6 and 7) shows softening of the solid form and stiffening of the liquid form in the coexistence range as compared to the corresponding limit forms in the single-phase regions. It is not unreasonable to assume that softening (stiffening) begins in the single-phase region, as \( E_{\text{tot}} \) increases (decreases), and carries over to the coexistence range. An interesting question is whether the softening and stiffening remain continuous in points \( E_{\text{tot}} = E_T, E_m \) or they undergo any jump on the borders of the coexistence range. A
related question is how sharply one can define the values of $E_f$ and $E_m$. In principle, $E_m$ is the energy of the saddle which, when surpassed, allows virtually every trajectory to explore all the permutational equivalents of any well of the potential surface to which it has access, on essentially one common time scale not very different from the vibrational time scale; $E_f$ correspondingly might be thought to be the energy of the lowest saddle connecting any geometrically inequivalent solid-like isomers so that if $E_{\text{tot}} < E_f$ a cluster in one potential well cannot escape to any other geometrically inequivalent well on a time scale comparable to the vibrational period. This definition permits solid–solid isomerization among permutationally different but geometrically equivalent isomers, if they are separated by sufficiently low barriers. (It could also give rise to oscillations between a pair of equivalent wells if $E_{\text{tot}} > E_f$.) One could probe the lowest "transition trajectories" by initiating trajectories at or near the top of the lowest barrier. While such an approach would demonstrate the obvious feasibility of such trajectories for well-to-well passage, it may be very inefficient as a means to determine the measure of such trajectories, which is the issue in principle of whether one can identify $E_f$ with the energy of a mechanical barrier. The practical question is whether $E_f$ has been adequately bracketed by the highest energy at which only the rigid form is found and the lowest energy at which both forms occur. The runs should be long enough to make the energy range of this bracket independent of the duration of the run. In our simulations the duration of the runs was chosen to achieve convergence of the calculated properties. With these runs there were no indications of duration dependent changes in the energy bracketing of $E_f$.

The values of $E_f$ and $E_m$ were determined in our simulations from the appearance and disappearance, respectively, of transitions of the cluster between its two limiting forms in
a sequence of converged runs performed for a fine grid of energies $E_{\text{tot}}$. Observations (pictures) of the configurations of the cluster are not sufficient to identify a transition from one phase to another. A liquid-like 13-particle cluster, e.g., may pass briefly in its time evolution through a perfect icosahedral structure which does not mean, however, that a transition to a solid-like form occurred. Only if the trajectory remains in a part of configuration space associated with a particular phase for a time interval long enough to display the characteristic properties for that phase, may we identify the cluster as being in that particular form. Thus, residence for only one or two of the coarse-graining intervals is not enough to justify calling that interval evidence for a phase. One could refine this point by varying the coarse-graining interval to shorter and shorter times.

As a final remark we note that originally the phenomenon of a finite range of coexistence of solid-like and liquid-like phases for small clusters was obtained\textsuperscript{16,17} considering a canonical ensemble of clusters. In the present study we examined how this phenomenon exhibits itself in the time evolution of a cluster whose total energy is fixed, i.e., under the conditions corresponding to a microcanonical ensemble of clusters of a single composition (13 atoms). A study, simulating the conditions corresponding to a canonical ensemble, is currently under way whose results will be reported shortly.

V. SUMMARY

In this communication we presented detailed results pertaining to the behavior of an isolated 13-particle argon cluster at different values of its total energy. The main emphasis was on establishing the existence of two forms, a solid-like phase and a liquid-like phase, and showing that there is a finite range of total energies ($E_p, E_m$) within which the cluster spends long time intervals in each phase, undergoing spontaneous transitions from one form to the other in the course of its time evolution. $E_p$ is the energy below which the cluster retains its solid-like structure for the whole duration of long converged runs. $E_m$ is defined as an energy above which the cluster remains all the time in its liquid-like phase.

The two limiting forms and the differences between them were identified by calculating and comparing a number of physical quantities, ($E_{\text{kin}}$ vs $E_{\text{tot}}$, RMS bond length fluctuation, mean square displacement, diffusion coefficient, velocity autocorrelation function, and power spectrum), as well as by computer snapshots. The two different forms accessible to the cluster at each energy from the range ($E_p, E_m$) were identified as a solid-like phase and a liquid-like phase by comparing the corresponding physical characteristics to those of the limiting forms.

Invoking the ergodicity hypothesis, we interpreted the ($E_p, E_m$) range as a coexistence range. In an ensemble of clusters defined by any (fixed) energy $E_{\text{tot}}$ from this range one can expect to find both rigid and nonrigid clusters. The equilibrium constant $K(E_{\text{tot}})$, defining the relative number of clusters in each of the two forms, is a function of $E_{\text{tot}}$.

In performing the computations we paid particular attention to problems of equilibration and convergence. Our experience shows that runs as long as $10^5$ steps, of $10^{-14}$ s, are needed to produce reliable results for this system. This is particularly so if one is interested in averages over the two phases in the coexistence range. Our long-time averaged caloric curve of state (Fig. 1), does not show the distinctive loop-shaped region of the curve of Briant and Burton\textsuperscript{2}; we interpret this to mean that $10^5$ integration steps are not enough to obtain the correct average over the two phases, since we also obtained loops when we used runs of only $10^3$ steps or less.

At present, we are extending the study reported here to clusters of other sizes. Among the questions to be answered in a forthcoming publication are: (1) How does the extent of the coexistence range depend on the number of particles in the cluster? (2) What is the specificity of the rigid–nonrigid transitions in the clusters of magic vs nonmagic numbers?

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