Melting and freezing of small argon clusters

David J. Wales and R. Stephen Berry
Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637

(Received 16 October 1989; accepted 11 December 1989)

An investigation of melting, freezing, and coexistence phenomena is presented for small clusters $\text{Ar}_n$, $\text{Ar}_6$, $\text{Ar}_{13}$, and $\text{Ar}_{14}$ as specific representative examples. Combining the results of molecular dynamics simulations, especially short-time kinetic energy averages and quenching, with accurate calculations of the local minima and transition states illuminates the relationship between the potential energy surface and dynamical processes. The results are consistent with a recent general defect theory of melting.

I. INTRODUCTION

Clusters of atoms or molecules may exhibit solid-like and liquid-like forms which are quite similar to bulk matter in many respects. While various complicated kinds of equilibrium among isomeric forms of clusters may be found, a particularly interesting phenomenon is the occurrence of unequal freezing and melting temperatures, and a finite range of temperature and pressure within which solid and liquid clusters of a specific size may coexist. Experimental\textsuperscript{1} and theoretical\textsuperscript{2-6} studies show that clusters containing a specific number of atoms may exhibit sharp lower limit of temperature $T_f$ for the thermodynamic stability of the liquid form and a higher, sharp upper limit $T_m$ for the thermodynamic stability of the solid form. Hence a collection of such clusters in thermal equilibrium behaves like a statistical ensemble which, at temperatures and pressures within the coexistence region, is a mixture of two kinds of cluster: solid-like and liquid-like. In thermal equilibrium these forms occur in a ratio $K = [\text{solid}] / [\text{liquid}] = \exp(-\Delta F/kT)$ which is fixed by the difference in free energy $\Delta F$ between the solid and liquid forms. This is a dynamic equilibrium, with individual clusters passing between the chemical isomers.

If the two forms are to be observable in equilibrium then the mean frequency of passage between them must be low enough for the clusters to establish equilibrium values of their characteristic properties. This condition seems to be met in at least some cases, and in previous studies some qualitative conclusions have been made regarding the relation of the detailed form of the potential energy surface to the observed dynamical processes.\textsuperscript{4,7} Furthermore, a new statistical theory shows how the coexistence phenomena may be described for clusters in the size regime where the higher lying minima may be classified in terms of defect structures and Stirling’s approximation is reasonable.\textsuperscript{1}

Our object in the present work is twofold. First we wish to find a detailed, quantitative relation between the stationary points on the potential energy surface of a small cluster and coexistence phenomena. Second we must discover whether this new understanding is consistent with the general theory presented for somewhat larger systems.

We begin by analyzing the short-term averaged kinetic energy for $\text{Ar}_n$, $\text{Ar}_6$, $\text{Ar}_{13}$, and $\text{Ar}_{14}$ using a new graphical analysis to verify the results of the previous study.\textsuperscript{4} Then detailed quench results are given at regular intervals along each trajectory to show which regions of phase space the cluster is exploring at any given energy. We find that the quench results and internal energy variation may be rationalized from a knowledge of the local minima and transition states on the potential energy surface. Accurate calculation of the transition states, in particular, enables us to draw enlightening conclusions about the relation between the dynamical processes and the stationary points on the surface. In this way we are able to verify that the qualitative understanding developed in the previous work is broadly correct\textsuperscript{4} and expand upon it.

II. SIMULATION TECHNIQUES

The molecular dynamics and quenching techniques used have been detailed elsewhere,\textsuperscript{4,5} so we will only give a brief resume here. Verlet’s finite step integration algorithm\textsuperscript{8} was used to solve the classical equations of motion for argon atoms interacting via a pairwise Lennard-Jones 6-12 potential:

$$V = \sum_{i<j} 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right],$$

where $\sigma = 3.4$ Å and $\epsilon = 1.671 \times 10^{-14}$ erg (1 erg is $10^{-7}$ J). The time step used was $10^{-14}$ s and trajectories of $10^6$ time steps were run in each case. $10^4$ steps were run and discarded before every $10^5$ step trajectory to allow the system to equilibrate. This is a reasonable precaution since trajectories of a particular total energy are often set up by scaling the velocities from the final configurations of a previous trajectory by an appropriate factor. In these species a vibrational breathing mode corresponds to roughly 150 time steps and short-term kinetic energy averaging was performed over 500 time steps which is sufficient to include several vibrations.
Quenching was performed using the steepest descent method introduced by Stillinger and Weber in which the differential equation

$$\frac{dr}{dt} = -\nabla V$$

is solved beginning from chosen points in the molecular dynamics simulation. In this study coordinates at specific, regular points of the trajectory were taken as the starting geometries for quenches which followed the path of steepest descent until a local minimum was reached. In the runs described below quenches were performed either every 1000 or every 2000 time steps giving 1000 or 500 data points, respectively. Such a quench run, performed at a high kinetic energy, is a very effective way of finding (presumably) all the significant local minima on the potential energy surface. These results can then be checked, refined and used as starting points for the transition state searches described below. The choice of interval between quenches is governed by a balance between practicality (quenches are relatively expensive) and a desire to accumulate a reasonably large body of data points that is representative of the local minima samples over an entire trajectory.

III. SHORT-TERM KINETIC ENERGY AVERAGES

In previous studies, the short-term kinetic energy averages (averaged over 500 time steps) were treated by "binning." The binned quantity was actually obtained by converting the thermal energy into an internal temperature assuming that the equipartition theorem may be applied to all the vibrational modes:

$$T_{\text{internal}} = \frac{2NE_{\text{kin}}}{(3N - 6)k}$$

where $N$ is the number of atoms, $E_{\text{kin}}$ is the kinetic energy, and $k$ is Boltzmann's constant. Binning means that an arbitrary set of intervals of internal energy are chosen and the observed short-term averaged internal energies are sorted according to the range in which they lie. This gives a distribution of internal energies to which one may fit a curve. Although this provides a readily interpretable result there is a loss of resolution and an element of arbitrariness involved in choosing the bin intervals and the best fit curve. In fact, with the trajectories of $10^6$ points used in the present study, this arbitrariness may be easily eliminated by plotting the cumulative probability function as described below. This increases the resolution of the results and reveals cases in which two peaks in the frequency distribution lie close together. The results of the unbinned cumulative distribution enable us to say with some confidence whether or not the true frequency curve is multimodal. Of course, the cumulative distribution function does not contain any extra information; furthermore fluctuations which are not resolved by binning may lead to small spurious kinks in the cumulative distribution function.

To calculate the cumulative distribution function a large number of quenches are first performed along some given molecular dynamics trajectory. The short-term averaged internal temperatures are then sorted into ascending order and plotted against a running integer. With 500 or more points this effective gives a continuous curve of the cumulative probability $F(T)$ because (when normalized appropriately)

$$F(T) = \int_0^T f(T')dT'$$

where $f(T)dt$ is the probability of the internal temperature lying between $T$ and $T + dT$ so that $f(T)$ is the probability function. Naturally, the steepest parts of the $F(T)$ curve correspond to peaks in $f(T)$ and relatively flat regions of

FIG. 1. Plots of the cumulative probability function of the short-time-averaged internal temperature for Ar$_2$, at a range of total energies spanning solid-like to liquid-like behavior. Multimodal behavior is indicated by flat parts of the curve away from the end points. Both bi- and trimodal behavior can be resolved in some of these plots.

(A) $E = -0.210 \times 10^{-12}$ erg, $N = 2.1 \times 10^6$ points
(B) $E = -0.217 \times 10^{-12}$ erg, $N = 2.1 \times 10^6$ points
(C) $E = -0.224 \times 10^{-12}$ erg, $N = 2.1 \times 10^6$ points
(D) $E = -0.231 \times 10^{-12}$ erg, $N = 2.1 \times 10^6$ points
(E) $E = -0.238 \times 10^{-12}$ erg, $N = 2.1 \times 10^6$ points
(F) $E = -0.245 \times 10^{-12}$ erg, $N = 2.1 \times 10^6$ points.
$F(T)$ correspond to zeroes of $f(T)$. Hence bimodality is indicated by a single flat region of $F(T)$ in between the upper and lower points; multimodality is indicated by more than one such plateau. The resulting curves are therefore just as easy to interpret and involve no loss of resolution.

A set of such curves is shown in Fig. 1 for Ar$_7$ at a series of increasing energies. As the total energy increases we can see that the system changes from unimodal behavior to bi- and trimodal distributions before it becomes unimodal again at high energies. This agrees with results of the previous studies. In contrast the plots for Ar$_8$ (Fig. 2) are all generally S shaped with no flat features, indicating that the system exhibits unimodal behavior. A suitable range of total energies at which to perform these simulations is easily found by monitoring the relative root-mean-square interatomic separation $\delta$, defined as

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

where the angle brackets indicate that an average is taken using the results at every time step. Lindemann's criterion states that systems with $\delta > 0.1$ are liquids. This is entirely consistent with previous simulations. In the solid-like regime $\delta$ is roughly the vibrational amplitude squared while in the liquid regime $\delta$ usually reaches a limiting value of about 0.25 before an atom evaporates within the million steps of these trajectories. Results for $\delta$ are plotted in the next section.

Corresponding plots of $F(T)$ for Ar$_{13}$ and Ar$_{14}$ are given in Fig. 3. In the case of Ar$_{13}$ these results are limited in energy by the tendency of an atom to evaporate at higher energies. This never happened for any of the other species in the energy ranges of interest, probably because the barriers to rearrangement are significantly lower in these less symmetrical clusters. For Ar$_{14}$ only a few representative plots are shown because there is very little observable change from the solid-like regions. The Ar$_{13}$ plots clearly display a step for a wide range of total energies until the energy becomes sufficiently high for an atom to be lost in the course of a million-step trajectory. In contrast Ar$_{14}$ behaves more like Ar$_8$ in that the curves exhibit few features to disturb the smooth S bend which corresponds.
to a single peak in the probability density function of the internal temperature.

Hence the cumulative probability density functions of $Ar_{13}$ and $Ar_{14}$ appear to behave similarly to $Ar_7$ and $A_{89}$, respectively. The reasons for this are best appreciated in relation to the minima and transition states of the respective potential energy surfaces as we shall see.

**IV. QUENCH RESULTS AND THE POTENTIAL ENERGY SURFACES**

Quenches were performed for each cluster using the steepest descents method either every 1000 or 2000 steps for the same total energies as in the simulations described in the previous section. The object of this exercise is to obtain some idea of the regions of phase space sampled at the different energies for comparison with the internal energy variation and the potential energy surface. Here we assume that the distribution of minima found in the quenches reflects the probability of the system being associated with a particular local minimum at a given local energy, and thus measures the relative phase volumes of each catchment basin. By analyzing the change in this distribution with total energy we can obtain informative plots of the percentage of quenches ending in particular minima. Hence, we obtain a relatively direct picture of the probability that the phase point of the system is associated with a particular kind of minimum. This treatment of the data may be compared with the more detailed analyses of Amar and Berry\textsuperscript{10} in which residence times were estimated in order to obtain approximate rate constants for the various isomerizations.

First consider $Ar_7$. The four minima found in this case (as for the larger clusters) were first identified by Hoare and Pal\textsuperscript{11} (Fig. 4):

![Diagram of Ar7 minima](image)

**FIG. 4.** Minima for $Ar_7$: (a) the pentagonal bipyramid, $E = -0.2758 \times 10^{-12}$ erg; (b) the capped octahedron, $E = -0.2663 \times 10^{-12}$ erg; (c) the tricapped tetrahedron, $E = -0.2606 \times 10^{-12}$ erg; (d) the bicapped trigonal bipyramid, $E = -0.2596 \times 10^{-12}$ erg.

Energy/erg per atom

<table>
<thead>
<tr>
<th>Description</th>
<th>Energy/erg per atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentagonal bipyramid</td>
<td>$-0.3940 \times 10^{-13}$</td>
</tr>
<tr>
<td>Capped octahedron</td>
<td>$-0.3803 \times 10^{-13}$</td>
</tr>
<tr>
<td>Tricapped tetrahedron</td>
<td>$-0.3721 \times 10^{-13}$</td>
</tr>
<tr>
<td>Bicapped trigonal bipyramid</td>
<td>$-0.3707 \times 10^{-13}$</td>
</tr>
</tbody>
</table>

Transition states were calculated using the Cerjan–Miller method\textsuperscript{12} as explained elsewhere.\textsuperscript{13} For $Ar_7$, most of these transition states (Fig. 5) were first found by Berry, Davis

![Diagram of Ar7 transition states](image)

**FIG. 5.** Transition states for $Ar_7$: (a) single DSD process, bicapped trigonal bipyramid->capped octahedron, $E = -0.2554 \times 10^{-12}$ erg; (b) single DSD process, bicapped trigonal bipyramid->pentagonal bipyramid, $E = -0.2511 \times 10^{-12}$ erg; (c) single DSD process, capped octahedron->pentagonal bipyramid, $E = -0.2581 \times 10^{-12}$; (d) single DSD process, capped octahedron->bicapped trigonal bipyramid, $E = -0.2560 \times 10^{-12}$ erg; (e) edge-bridging process, bicapped trigonal bipyramid->pentagonal bipyramid, $E = -0.2439 \times 10^{-12}$ erg; (f) edge-bridging process, bicapped trigonal bipyramid->bicapped trigonal bipyramid, $E = -0.2431 \times 10^{-12}$ erg; (g) pentagonal bipyramid->tricapped tetrahedron, $E = -0.2512 \times 10^{-12}$ erg; (h) capped octahedron->capped octahedron, $E = -0.2523 \times 10^{-12}$ erg.
and Beck using the “slowest slides” method. A schematic diagram of the relevant features of the potential energy surface is given in Fig. 6.

As the total energy is increased the quenches begin to find the higher lying minima above the pentagonal bipyramid (Fig. 7) in agreement with Amar and Berry’s results. The plots in this figure display the potential energies of the minima, scaled between 0 and 1, found from the sequence of quenches for particular trajectories. The global minimum energy, in this case corresponding to the pentagonal bipyramid, corresponds to the horizontal axis. These plots show us the number of different energy minima that are quenched to and their distributions along the trajectory. Hence, for trajectories (A)–(D) there are clearly four significant minima, while the (E), at lower total energy, only two minima are important (remember that when the curve lies on the horizontal axis the quenches are to the global potential energy minimum). The percentage of quenches ending at the four different minima is shown in Fig. 8, along with the variation of $\delta$. Note that the curves are essentially continuous throughout the melting region. Let us now compare them with the new results for Ar$_8$.

For Ar$_8$ there are two low-lying minima, the $D_{2d}$ dodecahedron, first called a dodecahedral by Bernal, and the capped pentagonal bipyramid, and a number of higher lying minima such as $C_{2v}$ and $D_{3d}$-bicapped octahedra and the stellated tetrahedron (Fig. 9):

![Diagram](image-url)

**FIG. 6.** Schematic view of the local minima and transition states for the Ar$_7$ potential energy surface. The saddles (open circles) are labeled to correspond with Fig. 4. Vertical lines indicate degenerate rearrangements.

**FIG. 7.** The variation of the final quench energy for the same molecular dynamics trajectories of Ar$_7$ as used in Fig. 1. (A) $E = -0.210 \times 10^{-12}$ erg, (B) $E = -0.217 \times 10^{-12}$ erg, (C) $E = -0.224 \times 10^{-12}$ erg, (D) $E = -0.231 \times 10^{-12}$ erg, (E) $E = -0.238 \times 10^{-12}$ erg. For trajectories of lower total energy all the quenches were to the pentagonal bipyramid. The energies are scaled from 0 to 1 in each plot, so that the pentagonal bipyramid is always on the horizontal axis. Four different quench energies are visible in (A)–(D), but only two are seen in (E) (the capped octahedron and the pentagonal bipyramid).
Six transition states were located for \( \text{Ar}_{8} \) as illustrated in Fig. 9, and a schematic diagram of the potential energy surface is given in Fig. 10. Two of the saddles were found with the aid of geometrically constrained optimizations, namely the edge-bridged pentagonal bipyramid, Fig. 8(F), and the structure shown in Fig. 8(C). These two saddles are particularly interesting because they have been suggested as possible transition states for the rearrangement of ligated clusters such as borohydrides and transition metal clusters. The latter in particular is analogous to the transition state for the single diamond-square-diamond (DSD) process for \( \text{B}_{3}H_{6}^{2-} \). In the DSD mechanism one edge breaks while another is formed perpendicular to it, as shown in Fig. 11. The low-lying edge-bridging transition state [Fig. 8(F)] has also been proposed previously, and seems to be much more important for argon clusters than it is for ligated clusters such as borohydrides. The patterns which emerge for transition states in different types of...

\begin{align*}
\text{Description} & \quad \text{Energy/\text{erg per atom}} \\
\text{Capped pentagonal bipyramid} & \quad -0.4140 \times 10^{-13} \\
\text{Dodecahedra} & \quad -0.4128 \times 10^{-13} \\
\text{C}_{2} - \text{bicapped octahedron} & \quad -0.4008 \times 10^{-13} \\
\text{D}_{3d} - \text{bicapped octahedron} & \quad -0.4004 \times 10^{-13} \\
\text{Stellated tetrahedron} & \quad -0.3964 \times 10^{-13} \\
\text{Polytetrahedral structure} & \quad -0.3933 \times 10^{-13} \\
\text{Polytetrahedral structure} & \quad -0.3922 \times 10^{-13} \\
\end{align*}
clusters are described in more detail elsewhere. Their significance for this study is discussed below.

Figure 12 shows the variation of the quench energies along trajectories at a range of total energies, and Fig. 13 shows a plot of the percentage of quenches ending at particular minima against the total energy, along with the superposed variation of δ. In this case only the two-lying minima (the capped pentagonal bipyramid and the dodecahedral) are important. Figure 12 shows that a third minimum is only located by quenches in the highest energy trajectory A, and that as the energy is lowered the system spends more time associated with the global minimum, crossing between wells less frequently. Comparing Fig. 13 with Fig. 7 for Ar7 shows there is little qualitative difference. In both cases there is a relatively smooth change in the distribution of quench energies with increasing total energy. This can also be seen in the detailed plots of the quench energies against time. What, then, explains the different behavior of the internal energy distribution functions? A qualitative theory has previously been developed in which the key characteristic is whether or not the sur-

FIG. 12. The variation of the final quench energy for the same molecular dynamics trajectories of Ar4 as used in Fig. 2. (A) \( E = -0.288 \times 10^{-12} \) erg, (B) \( E = -0.2562 \times 10^{-12} \) erg, (C) \( E = -0.296 \times 10^{-12} \) erg, (D) \( E = -0.304 \times 10^{-12} \) erg. For trajectories of lower total energy all the quenches were to the capped pentagonal bipyramid. The energies are scaled from 0 to 1 in each plot, so that the capped pentagonal bipyramid is always on the horizontal axis. In (B)-(D) only the dodecahedral and the capped pentagonal bipyramid are seen, whereas in (A) a few quenches lead to some of the higher lying minima.

FIG. 13. Plot of the percentage of quenches ending at particular Ar4 minima against energy (solid curves) and the corresponding variation of δ (broken curve), the relative root-mean-square interatom distance. For the solid curves the circles represent the results of simulation and the triangles the statistical results calculated by the method of Amar and Berry (Ref. 10).

FIG. 11. The diamond-square-diamond (DSD) process. As the notional edge linking atoms b and d breaks a new edge form perpendicular to it joining atoms a and c. The transition state involves a square face for the atoms in question, the rest of the cluster remaining relatively unaffected.
face has one minimum (i.e., one geometric isomer) whose energy is low enough that it is well separated from all the higher lying minima. The potential surface of Ar₇ has such a minimum in the pentagonal bipyramid, but for Ar₈ there are two low-lying minima with very similar energies and then various higher lying minima. For both Ar₇ and Ar₈ it appears that the kinetic energy the cluster must have in order to pass between minima in an observable time interval is roughly a factor of two greater than the barrier height. That is, the effective activation energy seems to be about twice the barrier height. By quenching along trajectories between -0.238 and -0.245 x 10⁻¹² erg for Ar₇ we find that the system first escapes from the lowest minimum in a trajectory of 10⁶ time steps when the available kinetic energy is more than about 1.9 times the barrier height. This must reflect the relative accessibility of the saddle region, i.e., the “entropy of activation” as a function of energy, as we shall discuss elsewhere. For Ar₈ the ratio of the available kinetic energy to the barrier height when the system first escapes from the deepest well to the dodecadeltahedron in a 10⁶ time-step trajectory is about 2.2.

To explain the kinetic energy distribution functions for Ar₇ and Ar₈ we turn the previous interpretation on its head. In earlier work the bimodal curves are interpreted as being due to the cluster spending significant intervals of time in two different regions of configuration space, one associated with a relatively deep, solid-like minimum and the other a multiwell region of higher potential energy. On the other hand, we could restate the results by saying the bimodality occurs because an intermediate range of kinetic energies is sampled significantly less frequency than certain other ranges. To discover which parts of the trajectories can be identified with the different features of the cumulative distribution function direct visualization was employed. The 500 points corresponding to average kinetic energies in distinctive parts of the distribution function were saved for the Ar₇ trajectory in Fig. 1(D). Using our Stellar GS1000 graphics supercomputer we then examined the sequences of points as animated movies.

The results were striking and unambiguous: the parts of the trajectory which contribute to flat regions of the cumulative distribution function correspond to averages which sample a saddle region, usually when the system changes from one minimum to another, whereas steep regions do not. Two features are therefore required for multimodality to be observed: First, the saddle crossings must be relatively infrequent events at the total energy in question. Second, the average kinetic energy for the 500 step sequences in which a crossing occurs must be intermediate between the average kinetic energies of 500 step sequences for which the system remains associated with two different wells. Not all of the 500 step sequences taken from flat regions involved actual saddle crossings: sometimes the system was observed to reach the transition state geometry and then “bounce” back to the original well. In detail the regions of the cumulative distribution function in Fig. 1(D) were identified as follows:

1) For average kinetic energies corresponding to internal temperatures around 19.5 K the 500 step sequences are associated with the pentagonal bipyramidal structure.
2) For internal temperatures around 17 K the 500 step sequences involve the lowest saddle linking the capped octahedron and the pentagonal bipyramid.
3) For internal temperatures around 13.25 K the 500 step sequences are associated with the capped octahedral structure.
4) For internal temperatures around 18 K the 500 step sequences involve the saddle between the capped octahedron and the bicapped trigonal bipyramid (or the tricapped tetrahedron).
5) For internal temperatures around 12.5 K the 500 step sequences are associated with the bicapped trigonal bipyramid or the tricapped tetrahedral geometries.

Points on the curve around 11.5 K correspond to such processes as passage over the lowest saddle connecting the pentagonal bipyramid and the bicapped trigonal bipyramid. Note that these features contrast with a previous interpretation of the bimodal kinetic energy distribution function for Ar₇ where the two peaks are associated with the equilateral triangle (minimum) and linear (transition state) geometries. This reflects the much simpler topology of the Ar₇ potential energy surface, which results in more frequent saddle crossing events.

Why, then, do we not resolve the two minima for Ar₈ or the fourth minimum for Ar₇? For Ar₇ the two low-lying minima are very similar in energy. Hence no region of intermediate kinetic energy that is sampled infrequently is seen because the short-term averaged internal energies are practically the same in the two wells, so that the second condition above is not satisfied. Hence the relatively rare saddle-crossing events are simply subsumed in the tail of the distribution at the low kinetic energy side of the curve.

It is already understood why multimodal behavior disappears at high total energies even for Ar₇. This is simply because at high energies an averaging occurs over large regions of phase space because the cluster moves rapidly among the different minima. At lower energies the cluster is associated with particular minima for long enough for certain regions of kinetic energy to be sampled relatively infrequently, but this is not the case at high energies where saddle-crossing events become relatively common on the time scale over which averages are calculated. The ramifications of this result for our interpretation of cluster phase coexistence are discussed in the next section. Note that all the above arguments are consistent with the general scheme proposed in the earlier work.

The most important low-lying minima for Ar₁₃ and Ar₁₄ are shown in Fig. 14, and some of the calculated transition states connecting these minima in Fig. 15. The transition states for Ar₁₃ confirm the earlier descriptions of cap plus vacancy formation. The lower lying transition states do indeed involve the concerted motion of several atoms so that the new cap is not the same atom that moves out of the vacancy site. However, there is one higher energy process in which the capping atom is the one that migrates and leaves a defect behind [Fig. 15(C)]. Sketches of the more important features of the potential energy sur-
faces for both clusters are shown in Fig. 16. Quench results are shown in Fig. 17 and the changing distributions of the quench energies with the total energy are shown in Fig. 18. The quenches give a good indication of how the trajectories for Ar₁₃ sample many different minima at high total energies, while for Ar₁₄ the global minimum is predominant in all the trajectories. For Ar₁₃ the range of accessible energies in such long simulations is limited by the evaporation of atoms at high total energies, but this is not a significant constraint.

Ar₁₃ behaves quite like Ar₇, in that there is one principal low-lying minimum and a number of higher energy

FIG. 14. Some of the local minima for Ar₁₃ and Ar₁₄: (A) Ar₁₃ centered icosahedron \( E = -0.7407 \times 10^{-12} \text{ e.r.g.} \); (B), (C), and (D) different capped icosahedra with energies \(-0.6925 \times 10^{-12} \text{ e.r.g.}, -0.6917 \times 10^{-12} \text{ e.r.g.} \) and \(-0.6930 \times 10^{-12} \text{ e.r.g.} \) respectively; (E) Ar₁₃ \( E = -0.6608 \times 10^{-12} \text{ e.r.g.} \); (F) Ar₁₃ \( E = -0.6615 \times 10^{-12} \text{ e.r.g.} \); (G) Ar₁₃ \( E = -0.6267 \times 10^{-12} \text{ e.r.g.} \); Minima for Ar₁₄: (H) capped centered icosahedron, \( E = -0.7995 \times 10^{-12} \text{ e.r.g.} \); (I) Ar₁₄ \( E = -0.7246 \times 10^{-12} \text{ e.r.g.} \); (J) Ar₁₄ \( E = -0.6632 \times 10^{-12} \text{ e.r.g.} \).

FIG. 15. Saddles found from the lowest energy minima of Ar₁₃: (A) icosahedron--capped icosahedron (6B), \( E = -0.6835 \times 10^{-12} \text{ e.r.g.} \); (B) icosahedron--capped icosahedron (6D), \( E = -0.6761 \times 10^{-12} \text{ e.r.g.} \); (C) edge-bridging process, icosahedron--capped icosahedron (6C), \( E = -0.6754 \times 10^{-12} \text{ e.r.g.} \); (D) icosahedron--capped icosahedron (6E), \( E = -0.6592 \times 10^{-12} \text{ e.r.g.} \); (E) icosahedron--capped icosahedron (6B) icosahedron--capped icosahedron (6C), \( E = -0.6789 \times 10^{-12} \text{ e.r.g.} \); (F) icosahedron--capped icosahedron (6F), \( E = -0.6578 \times 10^{-12} \text{ e.r.g.} \). Saddles found from the lowest minima of Ar₁₄: (G) capped icosahedron--capped icosahedron, \( E = -0.7678 \times 10^{-12} \text{ e.r.g.} \); (H) edge-bridging process, capped icosahedron--capped icosahedron, \( E = -0.7864 \times 10^{-12} \text{ e.r.g.} \); (I) capped icosahedron--capped icosahedron, \( E = -0.7660 \times 10^{-12} \text{ e.r.g.} \); (J) capped icosahedron--capped icosahedron, \( E = -0.7173 \times 10^{-12} \text{ e.r.g.} \).
minima which are visited with increasing frequency as the total energy rises. Specifically, there are three nearly degenerate minima corresponding to one atom promoted from the icosahedral shell to the surface (centered, capped nido-icosahedra), and then, at still higher energies, there are many other minima. $\text{Ar}_{14}$, on the other hand, is like $\text{Ar}_8$ in that its cumulative internal energy distribution function has no plateaus, implying that there are no intermediate ranges of internal energy that are sampled infrequently. However, unlike $\text{Ar}_8$, $\text{Ar}_{14}$ has a unique minimum energy geometry which is reasonably well separated from all the other higher minima. This example demonstrates that the existence of one unique low-lying structure is not sufficient to guarantee multimodal behavior in the internal energy distribution function. This condition is, however, probably necessary, as discussed in the following section.
FIG. 17. The variation of the final quench energy for the same molecular dynamics trajectories of $\text{Ar}_{13}$ (top row) and $\text{Ar}_{14}$ (bottom row) as used in Fig. 3. For $\text{Ar}_{13}$ (top row); (A) $E = -0.494 \times 10^{-12}$ erg, (B) $E = -0.520 \times 10^{-12}$ erg, (C) $E = -0.546 \times 10^{-12}$ erg. For $\text{Ar}_{14}$ (bottom row); (A) $E = -0.588 \times 10^{-12}$ erg, (B) $E = -0.616 \times 10^{-12}$ erg. For both clusters trajectories of lower total energy always gave the global minimum only. The energies are scaled from 0 to 1 in each plot, so that the centred icosahedron and the capped centred icosahedron are always on the horizontal axis for $\text{Ar}_{13}$ and $\text{Ar}_{14}$ respectively. The most common alternative quench minima in (A)–(C) are nido-capped icosahedra.

FIG. 18. Plots of the percentage of quenches ending at particular $\text{Ar}_{13}$ (left) and $\text{Ar}_{14}$ (right) minima against energy and the corresponding variation of $\delta$, the relative root-mean-square interatom distance.
V. DISCUSSION

Finally, we are in a position to resolve, at least in qualitative terms, the two outstanding issues which motivated this study: first, what are necessary and sufficient conditions for multimodal internal kinetic energy distribution functions to be observed, and second, what does this entail for the theory of coexistence phenomena in small clusters? For us to observe ranges of internal kinetic energy that are sampled infrequently in simulations, the potential energy surface must have some minima which are well separated in energy from the rest. Furthermore, if there is just one low energy structure, well separated from the higher minima, then it must have no low-energy degenerate rearrangements available, as discussed below. A degenerate rearrangement is one in which the same geometry is recovered but with identical atoms permuted in a way that is not equivalent to a rigid body rotation. If there is more than one low energy structure, well separated from the higher lying minima, then there must be no low energy degenerate or nondegenerate rearrangements possible amongst the low-lying minima for bimodality to be observable.

For both Ar$_8$ and Ar$_{14}$ increasing the thermal energy does not lead to significant population of higher-lying minima before the cluster is apparently quite liquid like ($\tilde{\delta} > 0.1$). Instead the additional thermal energy is accommodated in degrees of freedom which involve interconversion of the capped icosahedron for Ar$_{14}$ or the capped pentagonal bipyramid and the dodacauldelahedron for Ar$_8$. For the latter cluster there are relatively low-lying degenerate and nondegenerate rearrangements available such as those corresponding to transition states (A), (C), and (F) in Fig. 10. In Ar$_7$ and Ar$_{13}$ additional thermal energy can only be accommodated in this way up to a point, because for these more symmetrical, more rigid systems no degenerate rearrangements are possible at low energies. This leads us to consider the topological and symmetry characteristics of the potential energy surface (or more precisely, the minima and transition states on that surface) which result in multimodality and to expand upon the ideas of Beck and Berry.$^4$

Both Ar$_7$ and Ar$_{13}$ have no low energy degenerate rearrangements available. The lowest energy rearrangement of Ar$_7$ is the single DSD process which converts the pentagonal bipyramid into the capped octahedron. For Ar$_{13}$ the lowest energy rearrangement lies at even higher energy—there are no low energy DSD or edge-bridging processes available. In Ar$_8$, however, there are low energy rearrangements (both degenerate and non-degenerate) linking the two low energy structures, while for Ar$_{14}$ there are several relatively low energy degenerate rearrangements available. For multimodal internal energy distributions to be observed the primary requirements is therefore that increasing the total energy results in the system spending progressively more time associated with minima of different energies, in agreement with Bixon and Jortner’s model calculations.$^7$ Bi- or multimodal behavior is not observed on melting in systems exhibiting low energy degenerate rearrangements (or nondegenerate for a set of low energy structures); the only flat region(s) in the cumulative distribution function of the kinetic energy appear at the ends of the range of this function, not in intermediate positions. At still higher energies, when the cluster is only liquid-like, there are no intermediate ranges of kinetic energy that are sampled infrequently simply because the system samples so much of the potential energy surface on the time scale of the averaging.

In a larger, more complicated system the complexity of the potential energy surface is such that infrequently sampled ranges of internal energies may not be resolved at all, except perhaps for magic number clusters such as Mackay icosahedra.$^{20}$ In small clusters such as Ar$_7$ and Ar$_{13}$, however, coexistence involves the accessibility of distinct sets of minima with rather different energies. The minima associated with solid-like behavior are more compact and lower in energy, while those associated with liquid-like behavior involve more open structures which lie higher in energy. Of course, liquid-like behavior necessarily involves passage among several wells of the latter type. Hence, in Ar$_7$ and Ar$_{13}$ the conditions which bring about multimodal distributions in the kinetic energy are the same as those which result in coexistence being observed. Our final conclusion for small clusters is therefore that multimodal behavior and coexistence are most likely for systems with no low energy degenerate or nondegenerate rearrangements available for the lowest energy minimum or set of minima.

The lowest energy rearrangements available normally involve single DSD processes or edge-bridging mechanisms in these small systems. Hence knowledge of the lowest lying minima coupled with topological considerations (such as those performed by King for borohydrides$^{21}$) enables us to make predictions about the dynamics and coexistence properties of a given cluster. For example, since the trigonal bipyramid, the dodacauldelahedron, the capped pentagonal bipyramid, and the tricapped trigonal prism all have topologically feasible, degenerate single DSD or edge-bridging processes we would not expect any of these systems to exhibit multimodality or coexistence. In fact, this simple geometrical rationalization appears to be consistent with all the known results of computer simulations of small argon clusters. This result may be contrasted with the problem of understanding the rearrangement rates of the close-boranes, B$_n$H$_{2n-3}$, or carbonanes, C$_n$B$_{2n-1}$H$_{2n}$. For the latter molecules a successful theory requires an analysis of orbital symmetry selection rules as well as topological considerations.$^{22}$

In a larger system, such as a higher order Mackay icosahedron with, say, one cap there will certainly be low energy degenerate rearrangements possible. However, this does not mean that coexistence will not be observed because in this case melting is associated with the motion of more than just a few atoms. Hence our conclusions are consistent with the defect theory of melting presented elsewhere.$^1$ In the latter theory we assume that sets of structures with equal numbers of defects (vacancies) have similar energies and form a ladder of excited structures.
Solid-like/liquid-like coexistence in these more complex systems is unlikely to be correlated with any distinct features in the kinetic energy distribution curves; the large number of minima and transition states mean that we will probably be unable to resolve any such features. However, for magic number clusters of intermediate size, such as Mackay icosahedral Ar$_{55}$, the unique low-lying minimum might produce a distinctive feature in the distribution curve around the coexistence region of total energy.

ACKNOWLEDGMENTS

This work was funded in part by a Grant from the National Science Foundation.