Rare gas clusters: Solids, liquids, slush, and magic numbers

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Simulations by constant energy molecular dynamics have been performed for numerous clusters in the size range \( N = 7 \)–\( 33 \). Detailed investigations have been conducted on the portions of the caloric curves in which the transition between rigid and nonrigid behavior occurs, to study the \( N \) dependence of the solid–liquid phase change. Clusters of several sizes display a coexistence of forms, each with a characteristic mean temperature, over a well-defined energy range in the transition region, as had been observed for the \( \text{Ar}_{13} \) cluster. Within the coexistence region, the high temperature form is solid-like and the low temperature form behaves in a liquid-like fashion. The caloric curves of state for these clusters take on two-valued forms when averages are calculated for each of the two “phases” separately; the two branches are smooth extensions of the curves from the single phase regions. Clusters of other sizes do not display this clear coexistence of phases, but appear to pass through a “slush-like” state during the melting transition. The coexistence behavior is not a smooth function of \( N \). The clusters \( \text{Ar}_{13} \) and \( \text{Ar}_{19} \), and to a certain extent \( \text{Ar}_{7} \), display high stability properties indicative of magic number behavior.

I. INTRODUCTION

The discovery of a rather sharp melting transition in small clusters of \( N \) atoms (\( N = 3 \) to \( N = 429 \)) via computer simulations in the 1970’s has stimulated increasing theoretical and experimental interest. The early simulations were carried out with both the molecular dynamics (MD) and Monte Carlo (MC) methods.1–7 The properties of clusters were studied as a function of total energy (MD) or temperature (MC), and the common finding of both methods was that the clusters studied passed from a rigid, solid-like structure to a nonrigid, liquid-like structure as the energy or temperature of the clusters was increased. Briant and Burton1 observed loop-shaped caloric curves for several of the clusters in constant energy MD simulations, which have since been found to be caused by computer runs that were too short to be interpreted in terms of equilibrium properties. Several studies reported a peculiar jumping from the heating to the cooling portions of the caloric curves in the melting region.4,6,8 Nauchitel and Persin, on the other hand, observed a simultaneous coexistence of a solid-like core with a liquid-like surface in the \( \text{Ar}_{55} \) cluster in MC simulations of the cluster within a constraining wall.9

In other theoretical work, a quantum statistical model was proposed which first rationalized the melting phenomenon observed in the simulations.10 Then, from a natural extension of the model,11 Bercy et al. argued that sharp but unequal melting and freezing temperatures exist for finite clusters. Below a temperature \( T_s \), only the solid-like form is stable; above a higher temperature \( T_m \), only the liquid-like form is stable. In the intermediate temperature range, the model predicts coexistence of the solid-like and liquid-like forms with the equilibrium between the coexisting forms given at each temperature simply by the exponential of the difference in free energies of the two forms at that temperature, analogous to a chemical equilibrium. This phenomenon would be a kind of phase change different from any ordinary phase transition of bulk matter, of any order.12

On the experimental side, electron diffraction experiments have been performed on molecular beam expansions of various materials. Solid-like, liquid-like, and amorphous structures in several materials have been inferred from the diffraction patterns at various nozzle source pressures.13–16 A detailed analysis of cluster structure is difficult with this technique, however, due to the broad distribution of cluster sizes in a beam. In the work of Farges et al., diffraction patterns are observed which are consistent with a predominance of five-fold symmetry axes in the clusters at low temperatures (approximately 20 K).17 To complement the diffraction experiments, Farges et al. carried out molecular dynamics simulations in which clusters were cooled rapidly to simulate the conditions in the jet. The calculated diffraction patterns from the simulations were very much like those observed in the experiments. The cooled structures were found to contain icosahedral subunits, either attached to each other or interlinked in some way. Other simulations have been performed which implicate the icosahedron and related structures in supercooled bulk monatomic liquids.18

Recently, experimentalists have observed large intensities for particular cluster sizes relative to clusters of similar sizes in the mass spectra of rare gas clusters produced in nozzle expansions. The investigators in Refs. 19–21 observed particularly high abundances for specific sizes of singly charged clusters of rare gas atoms; Stace reported similar increased intensities for charged iodine atoms and iodine molecules imbedded in argon clusters.22 These especially abundant clusters are often called by the convenient and colorful name of “magic number” clusters. Sizes of small

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Footnotes:

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clusters that are notably abundant, i.e., correspond to magic numbers, are the $N = 13$ and $N = 19$ cases. The unusual abundances, if they are a property of a system in equilibrium, can be related to the explorations of potential minima of Hoare and Pal, who found the lowest potential energy structures for $N = 13$ to be the icosahedron and for $N = 19$, the double icosahedron. Both of these possess pentagonal symmetry and are "closed shell" structures in the pentagonal growth sequence; moreover, no other structures for $N = 13, 19$ have energies near these most stable structures.

Two experiments have been performed which have been interpreted as evidence of two phases in small clusters of argon containing a foreign probe molecule. Stace measured unimolecular decomposition rates of singly charged argon clusters containing a molecule of dimethyl ether, and found the reaction depended strongly on backing pressure. The results were interpreted as due to a liquid–solid phase change in the argon portion of the clusters. Gough, Knight, and Scoles determined the peak frequency and linewidth of the $v_3$, transition of SF$_6$ imbedded in clusters of argon atoms produced in a nozzle expansion, as a function of backing pressure. Both the frequency shift and peak width are strongly dependent on nozzle conditions. The authors attributed the observed spectral behavior to a distribution of cluster sizes. Eichenauer and LeRoy have now reinterpreted these results by carrying out MC simulations on single clusters of an SF$_6$ molecule imbedded in argon atoms. They are able to reproduce the peak widths and spectral shifts observed by Gough et al. in the simulation of a single cluster, and they claim that the spectral behavior is due to a phase coexistence in the clusters consistent with the kind predicted in Ref. 11 and not to a distribution of cluster sizes.

We recently reported a detailed study of the solid–liquid phase change in Ar$_{13}$. Extensive constant energy MD simulations were performed for the interval of energies over which the melting transition occurs, and a coexistence of two forms was observed in this energy range. Below an energy $E_r$, only the solid-like icosahedral structure is observed, the distribution of coarse-grained kinetic energies is a single Gaussian, and the power spectrum resembles that of a molecule undergoing oscillations of well-defined frequencies. Near $E_r$, the cluster does begin to "soften" as the forces become increasingly nonlinear and the density of low frequency modes increases, although no diffusion is evident below $E_r$. Above a different, higher energy $E_m$, the cluster displays the properties of a liquid. The power spectrum there exhibits large scale diffusive motion and frequent snapshots reveal continual transitions among disordered structures. The distribution of the coarse-grained kinetic energies is again a single Gaussian, but with a peak width much broader than for the solid. The cluster does not lose atoms to evaporation until it reaches energies well above that where liquid-like behavior begins.

In the interval $E_r < E < E_m$, however, the cluster displays a coexistence phenomenon that can be thought of as a new kind of phase change. In that range of energy, the distributions of short-time averaged kinetic energies exhibit a bimodal form. When these short-time averages are themselves plotted as a function of time, one sees that a given form persists for long periods of time relative to a characteristic vibra-
tional period. When averages are calculated for the dynamical properties over each of the two forms separately, the high temperature form (low potential energy, since the total energy is conserved in the isolated cluster) displays the properties of a near-rigid solid while the low temperature form (high potential energy) behaves in a liquid-like fashion. The fraction of time spent in the low temperature form increases with increasing $E$, as does the frequency of transition between the two forms. The caloric curve generated by averaging the temperature over each entire constant energy run is a monotonic function of $E$, with no region of negative or zero slope.

In related work, Amar and Berry have recently performed MD simulations of the melting transition in $\text{Ar}_r$. Along with the calculation of the equilibrium properties of the cluster through the melting transition, periodic steep-descent quenches were carried out to determine the potential minima about which the system oscillates. From this analysis the authors determined the rates of passage between the various geometrical isomers accessed by the cluster as it begins to melt. Long trajectories were calculated and no loop was observed in the resulting caloric curve, as was found with shorter runs.\(^1\)

The current paper is second in a series of three studies investigating the physical mechanisms for the solid–liquid phase changes in small rare gas clusters. We have now conducted detailed investigations of the solid–liquid phase change of many clusters in the size range $N=7$ to $N=33$. The current study extends the calculations performed on $\text{Ar}_{13}$ in order to study the $N$ dependence of the melting behavior. We find a coexistence phenomenon similar to that of $\text{Ar}_{13}$ for several of the cluster sizes in this range, and certain of the clusters exhibit the high stability properties expected for magic numbers. A brief review of the computational method is given in Sec. II. The procedure used for the isolation of the transition region on the caloric curves is discussed in Sec. III. The results of the simulations are presented in Sec. IV followed by discussion and conclusions in Secs. V and VI, respectively.

II. COMPUTATIONAL METHOD

In the constant energy MD method, Lagrange’s or Hamilton’s equations are solved for the system of interest, given a potential function between the atoms and the initial coordinates and momenta of the particles. In our simulations we chose the pairwise Lennard-Jones potential with the parameters used by most workers in this area, which, although not the most accurate, correspond rather well to the experimentally obtained values for argon:

$$\sigma (r_\sigma) = 4\varepsilon \left\{ \left( \frac{\sigma}{r_\sigma} \right)^{12} - \left( \frac{\sigma}{r_\sigma} \right)^6 \right\},$$

with $\varepsilon = 1.67 \cdot 10^{-14}$ erg and $\sigma = 3.4 \cdot 10^{-8}$ cm. A thorough discussion of accurate pair and three-body potentials appears in the review article of Barker and Henderson.\(^3\) The Verlet “leap frog” algorithm\(^4\) was used to solve Lagrange’s equations and a step size of $10^{-14}$ s resulted in time reversibility of the equations of motion to well beyond the relaxa-

tion time of any dynamical quantity calculated. The total energy, $E$, of the clusters was conserved to within $0.01\%$. Further computational details can be found in Ref. 27 and the references therein.

The initial structures for the various clusters were chosen to correspond almost to the potential minima determined by Hoare and Pal.\(^23\) In the size range $N=7$ to $N=22$, the minimum potential energy structures are all based on a growth sequence of pentagonal symmetry. The sequence of structures is generated by the addition of atoms to adjacent faces of the pentagonal bipyramid ($N=7$), the icosahedron ($N=13$), and the double icosahedron ($N=19$). These three structures correspond to the three closed shell structures of perfect pentagonal symmetry in the growth sequence. For $N=26$ and $N=33$, the initial structures were chosen to be the 13-atom icosahedron with either 13 or 20 atoms decorating the 20 faces. These structures are not the global potential minima, but correspond to locally stable structures close in potential energy to other slightly more stable structures. We mention here that even though a simulation is started with a structure of this kind, the system is able to “find” other geometrical structures, even at energies well below the onset of diffusive motions in the clusters. For example, in the $N=22$ cluster two initial structures were chosen: the 13-atom icosahedron with nine atoms on the surface of the cluster, and the more stable 19-atom double icosahedron with three atoms decorating the “waist” of the structure. The $(13 + 9)$ structure underwent a spontaneous transition to the $(19 + 3)$ cluster before any diffusion was observed, with an accompanying rise in the mean kinetic energy of the cluster. Thus, the simulation itself may act as an effective probe of available structures.

The lowest potential energy structures were slightly distorted in a random fashion, and the propagation was initiated, with all the velocities equal to zero. This way the total linear and angular momentum begin (and stay) at zero. The forces due to the distortions induced internal motions corresponding to a temperature of approximately 5 K. The energies of the clusters were then carefully increased through the phase change in the manner described in Ref. 27. The trajectories were calculated for lengths of time necessary to ensure that the various quantities calculated had converged to stable values, although some of the calculated quantities, e.g., mean temperature ($T$) and rms bond length fluctuation ($\delta$), were brought only to convergence within $3\% - 4\%$ instead of 1\% (as in the $\text{Ar}_{13}$ case) due to computer time constraints. The general shapes of the resulting curves are, however, clear. For example, no loop is observed in any of the caloric curves, but small fluctuations are evident about the mean values. Several static and dynamical quantities were calculated along each trajectory; these quantities and the method of calculation are briefly summarized below.

A. Static quantities

(1) The mean kinetic energy, which is essentially the temperature of the system provided there is equipartition of the kinetic energy amongst the $(3N - 6)$ degrees of freedom,
where \( N \) = number of atoms, \( k = 1.381 \times 10^{-16} \text{erg/K} \) is the Boltzmann constant, and \( \bar{E}_{\text{kin}} \) is the average kinetic energy. Two kinds of averages were calculated: the kinetic energy was averaged over the whole trajectory (the corresponding temperature will be denoted \( T \)) and also over 500 step intervals along the trajectory to give short-term temperatures \( (T_{\text{cs}} \text{, for coarse grained}) \), so that we could follow the time evolution of the coarse-grained kinetic energy, and thus potential energy, since the total energy is conserved. The short time averages are over approximately three vibrational periods in the cluster, so the averaging process washes out the large fluctuations in the kinetic energy due to the "breathing" motion of the cluster while one is still able to follow the time evolution of the system.

(2) The distribution of \( T_{\text{cs}} \)'s. The values of short-time averaged kinetic energies are binned in order to obtain the equilibrium distribution at a given energy.

(3) The relative rms bond length fluctuations:

\[
\delta = \frac{2}{N(N-1)} \sum_{i<j} \left( \langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2 \right)^{1/2} \langle r_{ij} \rangle.
\]

The \( \langle \rangle \) average implies averaging over an entire run.

### B. Dynamical quantities

(1) The mean-square displacement,

\[
\langle r^2(t) \rangle = \frac{1}{N} \sum_{i=1}^{N} [r_i(t) - r_i(0)]^2,
\]

where the \( \langle \rangle \) average is over many independent time origins. The slope of this curve gives the diffusion constant

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

The diffusion constant is necessarily zero in the long time limit due to the finite extension of the clusters, but it is meaningful to calculate it over time intervals less than the time it takes one atom to migrate across the cluster. Long runs are necessary to obtain converged results (often \( 2 \times 10^3 \) steps or more).

(2) The normalized velocity autocorrelation function (VAF),

\[
C(t) = \frac{\langle v(t) \cdot v(0) \rangle}{\langle v^2(0) \rangle}.
\]

The \( \langle \rangle \) averaging is again over a large number of independent time origins, as well as over all particles.

(3) The power spectrum,

\[
I(\omega) = 2 \int_0^\infty C(t) \cos \omega t \, dt.
\]

The power spectrum is merely the Fourier transform of the VAF via the Wiener–Khintchine theorem. The integration was carried out as a discrete sum over the period of time in which the VAF decays to a zero value. This quantity characterizes the number of oscillators at a given frequency, and is a very informative indicator of the transition from rigid, quasi-periodic-type motion to nonrigid, chaotic-type motion. Note that \( I(\omega = 0) \) is proportional to the diffusion constant.

### III. PROCEDURE FOR ISOLATING THE TRANSITION REGION ON THE CALORIC CURVE

The following general procedure was employed in searching for the portion of the caloric curve in which the transition from rigid to nonrigid structures occurs. The original configuration was generated by the procedure discussed above, resulting after equilibration in a mean temperature of approximately 5–10 K. These initial conditions generally resulted in rigid structures undergoing small oscillations about the equilibrium structure. No diffusion is observed at these low energies, and the rms bond length fluctuations are below 5%. Snapshots reveal the slightly distorted equilibrium structure, and the distribution of \( T_{\text{cs}} \) values is a single narrow Gaussian. At the other extreme of high \( E \), large scale diffusive motion occurs as exhibited by the power spectrum, and the \( \delta \) (relative rms bond length fluctuation) values are 25%–30%. Even though the system undergoes highly nonrigid, diffusive motion at high energies, the cluster generally holds together for thousands of vibrational periods. All clusters studied undergo a transition from the rigid, solid-like form to the nonrigid, liquid-like form with increasing \( E \). Previous authors have reported as much for a large range of cluster sizes.

The next step was to focus carefully on the range of energies within which the phase change occurs. Two quantities calculated as averages over a whole run vividly exhibit different aspects of the transition from rigid to nonrigid structures. The relative rms bond length fluctuation, \( \delta \), undergoes a gradual, nearly linear increase with energy at low \( E \) before any rearrangements take place. Then, as the system attains enough energy to cross the potential barriers to rearrangement, the fluctuations begin to rise. For the \( \text{Ar}_{11} \) case, this rise is very abrupt, while for other clusters, the onset of relative motions is in many cases not so drastic (see Fig. 1). At any rate, the fluctuations undergo at least a three-fold increase as the system passes from the rigid to nonrigid limit, which is a clear indicator of the onset of rearrangements in the clusters. This finding is entirely consistent with the general Lindemann criterion for bulk melting.

The other quantity which reflects the onset of large amplitude motions is the diffusion coefficient obtained from the power spectrum. When \( I(\omega = 0) \) assumes a substantial (say 15%–20% of the maximum intensity) nonzero value, the system is sampling at least some relatively flat portions of the potential surface on a regular basis. When the system is raised to a higher \( E \), the cluster is free to sample larger portions of the potential surface and spends a large fraction of time undergoing transitions between local minima.

The onset of large scale bond length fluctuations and the onset of diffusion do not occur at the same energy, however, and give different information concerning the motions in the clusters. Generally, \( \delta \) starts to increase at energies lower than those at which substantial diffusion occurs. This can be explained as follows: \( \delta \) is a very sensitive function of the onset of transitions between forms in the clusters. If the cluster undergoes one transition from one stable form to another which results in the changing of one or several of the interparticle bond lengths, \( \delta \) must increase sharply. Since both \( \langle r_{ij}^2 \rangle \) and \( \langle r_{ij} \rangle^2 \) are averaged over an entire run, \( \delta \) does not
tures are relatively low, the cluster can jump from one structure to another quite frequently, but as long as it spends many vibrational periods in each potential well, no diffusion will be observed in the power spectrum, since the passage time is on the order of one or at most a few vibrational periods. The locations on the caloric curves of the onset of large fluctuations in bond lengths and regular diffusive motions give information, then, concerning the potential surface in the vicinity of the lowest potential energy structure.

Once the approximate energy range of the phase change between rigid and nonrigid forms had been isolated for each size of cluster, based on the two criteria described above, we focused our calculations on this energy range to look for behavior similar to that observed for Ar$_{13}$. The coexistence behavior in Ar$_{13}$ begins slightly after the onset of large scale fluctuations in the bond lengths and disappears at energies where the (full-run average) power spectrum, $I(\omega)$, has a value at $\omega = 0$ of approximately 20% of the maximum intensity. We will refer to this region of the caloric curves as the "transition region." Long trajectories (usually $1 \times 10^6$ steps) were calculated to obtain equilibrium distributions of the $T_{eq}$ values, and in analogy with the calculations performed on Ar$_{13}$, we first looked for bimodal distributions of $T_{eq}$'s to determine whether the same coexistence phenomenon might occur for other cluster sizes.

IV. RESULTS

Simulations were performed on the following cluster sizes: $N = 7, 8, 9, 11, 13, 14, 15, 17, 19, 20, 22, 26, 30$. All of the clusters studied undergo a transition from a near-rigid structure to a nonrigid form which remains bound for thousands of vibrational periods. The caloric curves for the phase changes are presented in Fig. 2. Each caloric curve increases monotonically with energy; no loop is observed for any of the clusters of the sort that had been seen in shorter runs. We also observed loops in the caloric curves when the energy of the cluster was increased rapidly. Notice that the 13-atom caloric curve shows a smaller slope in the region of the phase change than do the other clusters. The 19-atom case also displays a relatively large drop in slope as the liquid phase appears, but not as great as for Ar$_{13}$. The caloric curves of several other clusters exhibit unambiguous but smaller changes in slope where the cluster melts. The decline in slope of $T(E)$ indicates an increase in the heat capacity in the transition region. Certainly the behavior of the heat capacity of the 13-atom cluster is most like that expected at a first-order-like phase transition, but still even this example shows nothing like a discontinuity in the curve which would indicate a true singularity.

Several of the clusters studied display a bimodal distribution of $T_{eq}$ values over an interval of energies, as Ar$_{13}$ does: $N = 7, 9, 11, 13, 15, 19$. Representative distributions are shown in Fig. 3. Notice that the spacing between peaks in the bimodal curves decreases in going from $N = 7$ to $N = 9$ to $N = 11$, but then increases again at $N = 13$ followed by a decrease for $N = 15$. No bimodal distribution is detected for the $N = 17$ case, but $N = 19$ again displays a clear bimodal distribution. The bimodal distributions for these clusters exhibit the same behavior as that observed in Ar$_{13}$: the low

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Caloric curves. (a) The Ar$_{13}$ caloric curve. The \( \bullet \) correspond to long time averaged kinetic energies. The \( \Delta \) correspond to the locations of the two maxima in the bimodal distributions of short-time averaged kinetic energies (see Fig. 3). The limits of the bimodal behavior define $E_m$ and $E_f$, as well as $T_m$ and $T_f$. Other clusters studied that display similar bimodal behavior are the $N = 7, 9, 11, 15$, and 19 clusters. (b) Caloric curves for the $N = 13, 11, 9, 8, \ 8, \ \text{and} \ 7 \text{clusters (left to right), (c) } N = 19, 17, 15, \ \text{and} \ 14, \ (d) \ N = 33, 26, 22, \ \text{and} \ 20. \ \text{None of the clusters display a loop-shaped portion in the caloric curves.}}$
\end{figure}
temperature peak appears at a well-defined energy, grows in magnitude relative to the high temperature peak as the energy is increased, and finally the distribution goes back over to a single, broad Gaussian form. No cluster above \( N = 19 \) displays such distributions of the \( T_{eq} \)'s, and somewhat surprisingly, \( N = 8 \) and \( N = 14 \) do not show bimodal distributions for any energy studied.

The time evolutions of the \( T_{eq} \)'s in the clusters which do display bimodal distributions over a range of energies are quite similar to that observed for \( N = 13 \). In each such case, the system spends long intervals of time in one form or the other relative to the characteristic vibrational period, and the transitions between forms occur rapidly relative to this time scale. Periodic snapshots of the cluster geometries in the coexistence region show the high temperature form generally to be vibrationally distorted forms of the structures of lowest potential energy found by Hoare and Pal. The distortions are due, of course, to the large kinetic energy of the system. The low temperature form, on the other hand, appears to correspond to a variety of other more irregular structures. For example, with \( N = 7 \), one sees the pentagonal bipyramidal structure for the high temperature form and often the other polytetrahedral structures found by Hoare and Pal among the low temperature structures (see Ref. 28). Several snapshots are presented along with the plots of \( T_{eq} \) for various cluster sizes to display the structures found in the different forms (Fig. 4).

The clear separation of time scales for the survival of a given form vs the passage time between forms allows one to calculate meaningful averages over each of the two forms separately. That is, the residence time in one form or the other is long enough to establish well-defined properties for that form prior to the rapid passage to the other form. The dynamical quantities were thus calculated for each form as in the \( \text{Ar}_{13} \) case, by averaging separately over each peak in the bimodal distribution of \( T_{eq} \)'s. Converged curves were obtained for the VAF's and resulting power spectra by performing simulations of at least 10 ns duration. For all clusters that display bimodal behavior in the equilibrium distribution of their \( T_{eq} \) values, more diffusion is observed in the low temperature form than in the high temperature form, and the power spectrum of the low temperature form also

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**FIG. 3.** The distributions of short-time averaged kinetic energies \( \langle T_{eq} \rangle \) in the transition region. The 500 step-averaged kinetic energies are binned over a long trajectory to obtain the equilibrium distributions. Notice that the \( N = 8 \) and \( N = 14 \) clusters do not exhibit a bimodal form in the transition region. (a) \( N = 7 \) at a low energy in the coexistence region, (b) \( N = 7 \) at a slightly higher energy, (c) \( N = 8 \), (d) \( N = 9 \), (e) \( N = 11 \), (f) \( N = 13 \), (g) \( N = 14 \), (h) \( N = 15 \), and (i) \( N = 19 \). The approximate energies at which the distributions were calculated can be obtained from the caloric curves of Fig. 2.
FIG. 4. The short-time averaged kinetic energy \( (T_{\text{av}}) \) vs time. Notice that for the clusters that display the sudden jumps in kinetic energy, a given form persists for periods of time long relative to the characteristic vibrational period \( (\tau_{\text{vib}} = 150 \text{ steps}) \). (a) \( N = 7 \) at \( E = -3.07 \times 10^{-14} \) erg/atom, (b) \( N = 9 \) at \( E = -3.56 \times 10^{-14} \) erg/atom, (c) \( N = 19 \) at \( E = -5.06 \times 10^{-14} \) erg/atom. Snapshots are presented at several points to display the structures corresponding to a given form. Notice the double icosahedral structure of the second two structures presented for \( N = 19 \). The first structure has a single atom (number 4) removed from the terminal position of the double icosahedron and placed on the surface.

displays a higher density of low frequency oscillators, indicating "softer" motions (Fig. 5). When compared to the spectra of the limit rigid and nonrigid forms near the transition region, the high temperature form displays a spectrum that is closely related to the rigid form and the low temperature form exhibits properties more reminiscent of the nonrigid form. The spectrum of the high temperature form is that of a "hot solid" undergoing large amplitude vibrations about the equilibrium structure, while the spectrum of the low temperature form is that of a "cold liquid" where the oscillations are about a less stable structure (or structures). This is quite plausible in light of the foregoing discussion, but would perhaps seem counterintuitive if one encountered the phenomenon naively—i.e., that the colder form, not the warmer, has

FIG. 5. The power spectra of the velocity autocorrelation functions in the coexistence region. The spectra presented correspond to averages over each of the two forms separately for the clusters that have a bimodal form for the \( T_{\text{av}} \) values. Notice that the low temperature form has a larger intensity at \( \omega = 0 \) and a higher intensity of low frequency motions for each cluster size. (a) \( N = 9 \) high temperature form at \( E = -3.62 \times 10^{-14} \) erg/atom, (b) \( N = 9 \) low temperature form at the same energy, (c) \( N = 15 \) high temperature form at \( E = -4.85 \times 10^{-14} \) erg/atom, and (d) \( N = 15 \) low temperature form at the same energy. Typical spectra for the limit solid and liquid forms can be found in Ref. 27.
V. DISCUSSION

The $Ar_{13}$ and $Ar_{19}$ clusters exhibit several properties which reflect the high stability of their minimum energy structures: $\Delta T_e$ is substantially larger for these clusters than for those nearest in size, $T_e$ is at least $5$ K higher than that observed for the other clusters that show coexistence, and the temperature ($T$) at which fluctuations become large in the bond lengths is much higher for these two structures. The $N = 7$ cluster also shows a large $\Delta T_e$ relative to the $N = 9$ and $N = 11$ clusters, but the initial pentagonal bipyramid does not possess the great stability of the icosahedral structures and thus liquid $Ar_7$ appears at a lower temperature ($T$) than $Ar_{13}$ or $Ar_{19}$. The temperature where rearrangements begin to occur is noticeably higher for $Ar_7$ than for $Ar_8$, however.

These findings lead to the conclusion that there are two and perhaps three structures ($N = 13, 19$, and perhaps $7$) in the sequence of clusters in the size range $N = 7$ to $N = 33$ which display properties in their phase equilibrium which suggest unusual stability, particularly for their solid forms. One might therefore apply the name magic numbers to them, in this regard. This special stability is attributed to their filled shell structures, particularly associated with their relation to the icosahedral growth sequence. By far the dominant structure in the growth sequence is the $N = 13$ icosahedron with perfect icosahedral symmetry; this structure is clearly very stable relative to clusters of similar size.

The argon clusters studied with $N > 19$ do not display the coexistence behavior. The number of possible isomers for these clusters is quite large and the isomers have similar potential energies. None of them has a single, stable structure which has a much lower potential energy than the other isomers. Consequently, as any of these cluster’s samples several potential minima during the course of a simulation, it typically yields a unimodal distribution for the $T_e$ values. However, when snapshots are taken at arbitrary intervals along the trajectory, one can often see the $N = 13$ and $N = 19$ structures as part of the larger cluster. This immediately raises the question, “Can one observe surface melting in clusters with $N > 19$?” We thus calculated the mean-square displacement for the atoms that decorate the surface of the underlying $N = 13$ or $N = 19$ structures vs. the displacement for the interior atoms. The surface atoms did show a slightly larger initial rise in the mean-square displacement, but at energies well below the point where any diffusion was observed for the surface or interior atoms, rearrangements began to occur in which the atoms of the interior 13- or 19-atom structure exchanged with those in the outer shell. These rearrangements appear to be highly collective in nature, and thus the picture of a rigid core surrounded by a diffusive, liquid-like exterior is not accurate for isolated clusters of up to 33 atoms. For the case of $Ar_{13}$, however, there does appear to be a range of energies where the motion of the single surface atom over the faces of the underlying icosahedron is competitive with insertion. These topics will be discussed further in Ref. 30.

Extensive mechanistic studies have now been performed which indicate that nearly all of the motions occurring as the clusters begin to undergo rearrangements are highly collec—

FIG. 6. The $N$ dependent transition temperatures. The $\Delta$ are the $T$ values at which the rms bond length fluctuations ($\delta$) rise sharply. The dashed lines correspond to the coexistence temperature ranges $\Delta T_e = (T_m - T_f)$ for the clusters that have a bimodal form for the $T_e$ values.

The larger diffusion coefficient and the higher density of softer modes.

We define a quantity, $\Delta T_e$, which gives an indication of the extent of the coexistence range in terms of temperature (mean kinetic energy) for a given cluster. This quantity is just the difference between the highest temperature at which the solid-like form is observed ($T_m$) and the lowest temperature at which the liquid-like form is observed ($T_f$). These temperatures correspond, respectively, to the location of the high temperature maximum for $E = E_m$ and the low temperature maximum for $E = E_f$ in the bimodal distribution of $T_{x}$'s. $\Delta T_e$, as well as $T_f$ and $T_m$ are presented in Fig. 6. Clearly, $\Delta T_e$ is not a simple function of $N$, but depends on the detailed structure and dynamics of the cluster under consideration. However, several features are worth noting. The coexistence temperature range is large for the clusters with $N = 7, 13$, and $19$ relative to the clusters nearest in size. Also, notice that $T_f$ for both $Ar_{13}$ and $Ar_{19}$ is at least $5$ K higher than for the neighboring sizes, due to the relative stability of the icosahedral and double icosahedral structures. The mean temperature (long time average, $T$) at which large fluctuations in the bond lengths begin to occur is also indicative of the stability of the original structures (Fig. 6). We define this temperature to be the approximate temperature at which the third derivative of the $\delta(T)$ curve reaches its first maximum, i.e., the point at which the change of the curvature is greatest. Again, the $N = 13$ and $N = 19$ clusters exhibit their high stability by the elevated kinetic energy necessary to induce rearrangements relative to clusters of similar size. We also mention that, for several clusters, caloric curves were generated in which the high energy, liquid-like cluster was slowly cooled through the transition region. As long as the cooling process was carried out very slowly, the clusters returned to the original structure and the same caloric curve was generated. However, for the larger clusters, it becomes more and more unlikely that a cooling process will return the cluster precisely to its original structure due to the large number of possible geometrical isomers with similar potential energies.
tive motions carrying the clusters from one local potential minimum to another, corresponding to structural isomerization. That is, as the energy is increased beyond a certain critical value, the cluster can begin to pass over saddle points to access other isomeric structures, and these barrier crossings signal the onset of melting. As an example, the near-rigid Ar$_{13}$ icosahedron transforms into one other particular structural type as it begins to undergo rearrangements, namely the icosahedron with one atom removed from the outer shell of 12 atoms and placed on one of the remaining faces of the icosahedron. This particle-hole isomer has a greater binding energy per atom than any of the alternate structures found by Hoare and Pal. It would be tempting to predict that the passage between the icosahedron and this particle-hole structure occurs by a motion where the atom “pops out” of the original icosahedron to the surface, leaving a hole where it had been. In fact, something quite different occurs. One atom is squeezed out by a highly collective motion, leaving a hole on the opposite side of the cluster. These topics are treated in depth in Refs. 29 and 30.

Nauchitel and Persitin, using a confined cluster model, argue that the $N = 55$ argon cluster displays surface melting based on MC simulations of the cluster confined by a wall. Kristensen et al., however, with free clusters for their model, observed a jumping between the heating and cooling portions of the calorific curve in constant energy MD simulations of an isolated Ar$_{55}$ cluster, more reminiscent of the Ar$_{13}$ behavior. On the basis of this contradiction, we can now only say that the approximate minimum cluster size for which surface melting is unambiguous has not yet been determined. A possible upper limit of this minimum comes from the study by Weber and Stillinger of a 250-molecule water cluster. They found that this cluster melts from the surface inward as the energy is increased. We are currently searching for the minimum cluster size required for distinct liquid-like behavior on the surface of the free, isolated cluster.

The phase transition behavior of the clusters as a function of $N$ can thus be divided into two, and probably three descriptive categories. For the size range $N = 7$–19, several of the clusters display a coexistence of forms and thus a caloric curve that is two-valued over a well-defined energy range. From the viewpoint of dynamics, the coexistence corresponds to fast, infrequent “jumps” between solid and liquid forms, much as in the unimolecular isomerization reaction of an isolated molecule. In this size interval, the coexistence temperature range $\Delta T_c$ generally decreases with increasing $N$, but is clearly not a monotonous function of $N$. The second range of sizes begins with $N = 20$ and ends with cluster sizes that display a simultaneous coexistence of phases, i.e., a solid-like core and a well-defined liquid-like outer shell, if this is truly a general phenomenon. In this size range, no bimodal distribution in the $T_c$ values has been observed in the clusters studied, yet no clear surface melting occurs. The motions over the potential surface appear to be highly collective; atoms are frequently interchanged between the surface of the cluster and the core. In a sense, the transition region corresponds to the creation of a slush before the onset of large scale diffusive motion. The third category of melting behavior corresponds to the larger clusters where surface melting or other types of phase coexistence in a single cluster would be apparent. Some mention of this type of behavior is made in a paper by Luo et al., where the melting of small alkali halide clusters is studied.

A matter of terminology calls for discussion here. We have until now attempted to be consistent in using $T_f$ to mean “freezing temperature” in the sense of the lower bound of stability for the liquid and $T_m$ to mean “melting temperature” in the sense of the upper bound of stability for the solid. One might describe the first appearance of liquid in a process of increasing $E$ or $T$ as “melting”—or one could reserve that term for the disappearance of the last bit of solid. Similarly, in reducing $E$ or $T$, “freezing” could mean the first appearance of solid or the disappearance of liquid. The new kind of phase change—we hesitate to use “phase transition,” although we do consider it sort of a phase transition—forces us to invent or extend some definitions in order to be precise in our description of the phenomenon. We propose to use melt and freeze to denote the first appearance of liquid and solid phases in warming and cooling processes, respectively, and to use “liquefy” and “solidify” to indicate the disappearance of solid and liquid forms, respectively, again in warming and cooling processes. (We realize that this terminology suggests that $T_f$ and $T_m$ should be replaced with “$T_{il}$” and “$T_{li}$,” but, having adopted the former, continue to use them.)

We now address one final question concerning the sampling technique used in the constant energy simulations, namely, “How completely are we sampling the accessible phase space?” Several indicators lead us to believe that we are indeed covering the energy shell adequately with a single trajectory. We prepare the initial state of the low-energy structure by choosing the initial distortion so that it is extremely unlikely that the motion of the cluster is localized in one normal mode. As an interesting point, we mention here that the calculated power spectrum of the three-particle argon cluster at low energies exhibited two sharp peaks with a ratio of heights of 2:1. These peaks correspond to three normal modes of the three particle equilateral triangle with central, pairwise potentials with one peak doubly degenerate. Also, we were careful to obtain values for the average quantities which had converged to within a few percent. This long time averaging is very important in the transition region since the clusters can remain in one form for very long time intervals before jumping to another form, and one must average over many of these transitions. In addition, the heating process we employed was found to be reversible for several cluster sizes in that the caloric curves had the same form whether they were obtained by raising or lowering the energy; the temperature distributions and other properties did not depend on how the system had been prepared.

Finally, Davis, Jellinek, and Berry recently reported on the relation of sampling in the canonical ensemble to the constant energy simulations for the Ar$_{13}$ cluster. Both constant temperature MD and MC calculations were performed, and the agreement in the calculation of both static and dynamical quantities of the clusters in the two ensembles (microcanonical and canonical) is very good even though the system is small. The constant temperature methods in-
herently lead to a larger sampling in the phase space of the cluster due to the fluctuations induced by the implied coupling to an infinite heat bath,\textsuperscript{28} so the very close agreement implies that the constant energy simulations are sampling the important portions of the phase space effectively.

\section{VI. CONCLUSION}

Several clusters behave similarly to $\text{Ar}_{13}$ in that the same new kind of solid--liquid phase change occurs over a well-defined energy range indicated by the onset and disappearance of the bimodal form for the distributions of $T_{\text{cs}}$'s, the mean temperature obtained by averaging kinetic energies over short intervals. In this energy range, a coexistence is observed between two basic forms; the high temperature form corresponds to oscillators undergoing large-amplitude vibrations about the structure of lowest potential energy for that cluster size, and the low temperature form generally is a less stable, irregular structure displaying diffusive, low-frequency motion. The fraction of time spent in the high temperature form decreases with increasing energy, while the frequency of transitions between forms increases with energy. There is a clear separation of the time scales for the time spent in a given "phase" vs the (shorter) passage time between phases in the coexistence region. The caloric curve thus has a two-valued form in the transition region for these clusters. We emphasize that the coexistence observed corresponds to a dynamic equilibrium with the clusters "jumping" between the two forms. Only in an observation of an ensemble of clusters of one of these sizes would one see both solid and liquid forms coexisting.

The $\text{Ar}_{13}$ and $\text{Ar}_{19}$ (and to some extent the $\text{Ar}_{7}$) clusters display high stability properties in the melting transition and can thus be referred to as magic numbers for the phase change. Three clusters ($N = 8, 14, \text{and } 20,$ as well as others), however, do not display the bimodal distribution of the $T_{\text{cs}}$ values in the transition region. One thing notable about these clusters is that these sizes correspond to the addition of a single atom to the magic number clusters ($N = 7, 13,$ and $19$).

The magic numbers we observe have been identified as predominant species in the mass spectra of positively charged rare gas clusters.\textsuperscript{19-22} Perhaps the stability of the neutral magic number clusters in the melting transition lends weight to the argument that the magic number behavior in the mass spectrometry studies depends to some extent on the stability of the neutral clusters.

The microscopic mechanisms for the solid--liquid phase changes in the small argon clusters have been investigated, as mentioned above, and will be the topic of two forthcoming papers.\textsuperscript{29,30} The magic number and coexistence phenomena are explained in terms of the isomers accessed by the clusters and the reaction coordinates for the motions between the isomers.

\section{ACKNOWLEDGMENT}

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\footnotesize
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