Thermodynamic properties of small aggregates of rare-gas atoms*

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The thermodynamic properties of small clusters of rare-gas atoms are determined from a biased random-walk Monte Carlo procedure. The cluster sizes studied range fro.n $N = 3$ to $N = 13$ atoms. The internal energy is calculated as a function of temperature. Each cluster exhibits an abrupt liquid-gas phase transition at a temperature much less than for the bulk material. An abrupt solid-liquid transition is also observed for $N = 11$ and 13. The entropy of fusion is $S \simeq 1.76$ e.u. For smaller clusters, the solid-liquid transition is more gradual. The bond-length distributions are calculated for each cluster at various temperatures. The fluctuations of bond lengths from their average values increase gradually with temperature until the melting temperature is reached, at which point there is a large, abrupt increase. The indications are that a harmonic normal-mode analysis is applicable only at temperatures substantially below the melting point and even there, the frequency spectrum is temperature dependent. For $N = 3$, the equilibrium structure is an equilateral triangle. An $N = 5$ cluster forms a trigonal bipyramid and for $N = 7$ the form is a pentagonal bipyramid. The nine-particle structure has symmetry C_{1h} and is a pentagonal bipyramid with two additional atoms, and the $N = 13$ cluster forms an icosahedron.

I. INTRODUCTION

Small aggregates of atoms or molecules have not been investigated to the same extent as very large systems because of a very fundamental difference in the boundary conditions. For large systems it is common practice to ignore the effect of the boundary (surface) in calculating most physical properties. The supporting argument is that the number of particles within range of the distorted local field, produced by the surface discontinuity, is negligibly small when compared with the total. For small clusters of atoms the situation is just the opposite. Surface effects dominate the system's behavior. As an example, consider a 1055-particle system organized on an fcc lattice. Over 800 of those particles are within two nearest-neighbor lengths of the surface and 500 are within one nearest-neighbor distance.

There are a number of phenomena in which small clusters of atoms are believed to play a central role. In the gas-liquid phase transition, the formation of small clusters in the gas is a precursor to the transition.[1] Hence, a description of the thermodynamic properties of these clusters is an essential element in analyzing the phase change. Some other areas where the properties of small aggregates manifest themselves are in the description of high-speed fluid jets,[2] Mössbauer recoil from small systems,[3] dense fluids, fine powders, normal and superconducting metallic crystal-

lites,[4] and possibly in providing insight into the regime of validity for cluster-expansion methods used in the analysis of many-body systems.

Of the limited number of previous works dealing with the thermodynamic properties of small aggregates, microscopic calculations have almost exclusively been limited to one of two different approaches. The normal-mode approach, for example, has been used by Burton in a series of calculations[5] designed to determine the thermodynamic properties of argon clusters as small as 13 atoms. In these works the atoms are initially located on an fcc lattice and their positions are varied until the total potential energy is minimized. With the location of the atoms thereby established, a normal-mode analysis is used to obtain the frequency spectrum and hence the thermodynamic properties. One interesting result of this work is that the entropy and free energy are not monotonic functions of the cluster size. For example, at temperatures $T \gtrsim 100$ K, the free energy shows a local minimum for cluster sizes of about $N = 43$ atoms, as does the entropy. One aspect of this work that is particularly difficult to understand is the part dealing with temperatures in excess of the bulk liquid-gas phase transition temperature $[T_B(\infty) \simeq 87$ K$]$. If, as one would expect, clusters do not form a bound state above $T_B(\infty)$, the normal-mode analysis is meaningless for $T \gtrsim T_B(\infty)$. In fact, the liquid-gas transition temperature for an N-atom cluster,

$T_B(N)$, should be substantially lower than its bulk-value for small clusters because the number of bonds per atom are not saturated. It will be shown that this is indeed the case. We suspect that the anomalous behavior of the entropy and free energy results from this deficiency in the theory. This view is fortified by recognizing that the anomalous entropy was calculated at $T = 93$ K, and the local minimum in the free energy was also observed only for temperatures $T \gtrsim T_B(\infty)$.

An inherent feature in the normal-mode analysis is the limitation that the equilibrium positions of the atoms are calculable only at $T = 0\ K$. Hence, in order for the resulting frequency spectrum to be justifiably used at nonzero temperatures, it must be assumed that the relative equilibrium positions of the atoms are temperature independent. It will be shown that this assumption is, in fact, not correct. Only for temperatures well below $T_B(N)$ are the equilibrium atomic positions insensitive to temperature changes. It is clear that the inability of this method to calculate the temperature dependence of the frequency spectrum seriously limits its reliability at higher temperatures and negates the possibility of observing any phase transition.

In another recent calculation on argon clusters by McGinty, a molecular dynamics technique was employed which numerically solves the classical equations of motion.[6] Artificial boundary conditions were used to define the cluster size. To what extent the artificial boundary condition affects the low-temperature results is not certain. We suspect, however, that many of the high-temperature data correspond to an artificially contained gaseous phase rather than to a free cluster bounded only by the mutual interaction of its constituents. A test of the sensitivity of the results to the dimensions of the boundary would help resolve this question. McGinty has recognized the probable existence of a solid-liquid phase transition but was unable to observe it. However, solidlike particle motions were observed at low temperatures and liquidlike motions were observed at high temperatures.

Burton has also performed a molecular dynamics calculation on a 55-atom argon cluster.[7] An abrupt change in the internal energy is observed at $T = 42$ K and the diffusion coefficients indicate that the change corresponds to a solid-liquid phase transition. There is no discussion of the boundary conditions. Assuming they are similar to those used by McGinty, the questions raised in relation to that work also hold here. Nevertheless, the solid-liquid phase transition is probably being observed in these calculations.

This article reports on the equilibrium thermo-dynamic properties of small clusters of xenon, krypton, and argon atoms, determined from a biased random-walk Monte Carlo procedure. The cluster sizes studied range from 3 to 13 atoms. A central conclusion of this work is that proper representation of boundary conditions is very important for evaluating small bounded aggregates. **Unless it is done with care the system modeled is other than what was intended.** This calculation takes full cognizance of that fact.

II. METHOD

The biased random-walk Monte Carlo method, used here to determine system properties, has been fully described by Wood.[8] A very brief description of that method follows.

The thermodynamic expectation value of a function $f(\vec{r})$, $\vec{r} = (\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$, for an N-particle system at temperature T in the Gibbs canonical ensemble is

$$\langle f \rangle = \frac{\int f(\vec{r}) P(\vec{r}) \, d\vec{r}}{\int P(\vec{r}) \, d\vec{r}} \ , \tag{1}$$

where $P(\vec{r})$ is the Maxwell-Boltzmann probability distribution,

$$P(\vec{r}) = \exp[-\beta U(\vec{r}_1, \ldots, \vec{r}_N)] \ . \tag{2}$$

The potential energy of the system is given by $U(\vec{r})$, $\beta = (kT)^{-1}$, and k is the Boltzmann constant. In practice, the averages are obtained by forming the sum

$$\langle f \rangle = n^{-1} \sum_{i=1}^{n} f(\vec{r}_{1i}, \vec{r}_{2i}, \ldots, \vec{r}_{Ni}) \tag{3}$$

for a sequence of n configurations, each specified by a $3N$-dimensional point $\{\vec{r}_{1i}, \ldots, \vec{r}_{Ni}\}$, $i = 1, \ldots, n$, obtained as a result of a particular random-walk procedure called a Markov chain. The first index on the vectors $\{\vec{r}_{1i}, \ldots, \vec{r}_{Ni}\}$ identifies the particle and the second index specifies a particular $3N$-dimensional point. A physically meaningful expectation value is obtained by generating a Markov chain in which each $3N$-dimensional point recurs, in the asymptotic limit of large n, with a frequency proportional to the Maxwell-Boltzmann probability distribution $e^{-\beta U}$. The prescription for achieving this is as follows: Initially the N particles are arbitrarily positioned spatially and those positions are specified by N vectors. Hence, a configuration is defined. The energy $U(\vec{r})$ and the probability $e^{-\beta U}$ of that configuration are calculated. A randomly chosen particle is then allowed to randomly move to a new location. This specifies a new configuration for which the energy and probability are calculated. According to a set of criteria relating to the relative probability of the new

configuration in relation to the previous one, the new configuration is either accepted or rejected. If accepted, that value of $f(\vec{r})$ is incorporated into the sum [Eq. (3)] and the entire procedure is repeated using the new configuration as a starting point. If rejected, the $f(\vec{r})$ of the previous configuration is added to the sum and the entire procedure is repeated, starting again with the old configuration. These criteria ensure that phase space is sampled ergodically and that the average value of any observable quantity so determined is of physical significance.

In previous works using this Monte Carlo scheme,[9] a finite number of particles are located inside a box of volume commensurate with the density of the system. The behavior of the bulk system is then simulated by replicating this box and its contents in all directions. This procedure establishes periodic boundary conditions. It must be understood that this or some equivalent procedure is absolutely necessary to properly simulate the infinite system. In the analysis of small clusters, the situation is entirely different. The boundary is free. Atoms must be allowed to search out the equilibrium configuration at each temperature considered, encumbered only by their mutual interaction as manifested in the probability distribution $e^{-\beta U}$. It is a general feature of the method that displaced atoms will gravitate toward locations of highest probability. This, of course, is a consequence of the bias introduced into the random walk by the Boltzmann probability distribution. The atoms do not, however, move monotonically toward regions of maximum probability, and occasionally an atom will be found a large distance away from a location of high probability. If the cluster intrinsically forms a bound state (liquid or solid) at the temperature at which the calculation is being performed, the atoms will eventually settle down into a spatially well-defined region with a well-defined binding energy. For aggregates investigated in this work, on the order of 2×10^5 configurations are necessary to obtain fully reliable data.

The use of free-surface boundary conditions introduces a conceptual situation that is not present when the system is enclosed in a well-defined volume. Equation (1) vanishes for $f(\vec{r}) = U(\vec{r})$, when integrated over all space, corresponding to an infinitely long random walk. That is, any finite system will ultimately decompose and the binding energy will approach zero as $|\vec{r}_i - \vec{r}_j| \to \infty$, for all i, j. Physically, this is not unexpected. If there exists no external containing force, such as walls, or if the system's own vapor pressure is not sufficiently great, there will be a net escape (evaporation) of atoms from the surface. The rate of evaporation depends on the relative strength of the binding energy compared to kT. As the temperature of the sample is increased, the probability that an atom will have energy enough to escape from the surface region increases until, at $T_B(N)$, this probability is so high that rapid dissociation takes place. The point is that all finite bound-state samples with free surfaces have only a "metastable" existence. Nevertheless, equilibrium properties of such systems can be determined provided the evaporation rate is slow compared to the relaxation time of physical properties. For example, an open beaker of alcohol at room temperature evaporates slowly enough so that its equilibrium properties are measurable, although it does not remain a bound-state liquid indefinitely. Ultimately, it evaporates into an essentially infinitely rarified gas. The situation is obviously more critical for small N, where the evaporation of one or two atoms is an appreciable fraction of the total. Under such circumstances the small system is substantially altered by the evaporation where, for a large system with $N \simeq 10^{23}$, it is not.

The key question with regard to a Monte Carlo simulation is not that $\langle U(\vec{r}) \rangle$ vanishes for an infinitely long random walk, as it surely must, but rather whether or not a meaningful average of system properties can be obtained for the sample in its so-called "metastable" bound state. In this regard, we have established a list of stringent criteria which must be satisfied before the results of any run are accepted as physically significant.

Before these are listed it is instructive first to describe a typical run. The initial configuration of N particles is generally taken to be on an fcc lattice with a bulk nearest-neighbor separation. Other starting configurations are discussed later. For approximately the first 10^4 configurations, predicted system properties change drastically. We call this the "initial transient," which is not included in the averaging process. If $T < T_B$, the system settles down after the transient and remains that way until the run is terminated. This is the region of the "metastability" which is interpreted as giving evidence of a well-defined bound state. Up to 5×10^5 configurations are computed per run. If $T > T_B$, there is never a region of metastability. The initial transient develops very quickly into a situation where all atoms are separated by large distances and $\langle U \rangle$ goes rapidly toward zero. That is, the configuration of highest probability is $\langle r_{ij} \rangle = \infty$, for all i, j, which is appropriate for an unbounded gas. The system is thus characterized by a well-defined bound state at the lowest temperatures but, at some point as the temperature increases, the characteristics of an unbounded gas begin to man-

ifest themselves. For cluster sizes investigated, this transition is fairly abrupt and it occurs at temperatures well below the liquid-gas transition temperature for the bulk system, $T_B(\infty)$.

The criteria for acceptance of a run are as follows.

(a) Over the entire run, except for the initial transient, the average bin energy never fluctuates by more than 5%. A bin contains about 300 configurations. Moreover, the over-all statistical error associated with any expectation value must be less than 1%.

(b) *The results are independent of step size.* The maximum allowed displacement of an atom from one configuration to the next (step size) is normally varied during the run so that a trial configuration is accepted about 50% of the time. This condition seems to speed up convergence of the predicted physical quantities. Step sizes are generally on the order of 0.3 Å. In test cases we varied the step length from 0.01 to 30 Å. The results are always the same; only the rate of convergence is affected. The observed transition temperature $T_B(N)$ is independent of the step length used. With regard to choosing step lengths that are extremely small, the initial transient will not be exhausted in 10^5 steps. If the step size is too large, that part of phase space corresponding to a bound state of the cluster may not be sampled in an acceptably small number of configurations. In the extreme then some care must be taken, a problem common to all Monte Carlo calculations. In fact, the biased random-walk scheme is useful only if the physically important part of phase space is sampled in a manageably small number of configurations. This is why it is important to choose a step length which optimizes this sampling.

(c) *The results are independent of the initial configuration.* We have used various initial configurations, such as an fcc lattice, where the nearest-neighbor distance has been varied by an order of magnitude. We have chosen random initial conditions with the restriction that $|\vec{r}_{ij}| \leq R$, all i,j. The range $0.5 \leq R \leq 10\sigma$ has been used. Results for the physical quantities always remain unchanged. The number of configurations required to overcome the initial transient is affected, however. In fact, if the initial positions of the particles are chosen absurdly, for example, such as that the initial particle separations are very large, it is clear that an unacceptably large number of configurations may be required to bring the particles close enough to establish a bound state. Some modest care must be taken in this regard.

(d) *Results are not accepted if evaporation of one or more particles takes place during the run.* When $T_B - T \leq 1.0$ K, evaporation of one or two

particles may take place during the course of a run. What this means is that bound state is on the verge of instability and reliable thermodynamic averages are hard to obtain.

To summarize, any finite physical system subject to free-surface boundary conditions is at best metastable. Surface atoms will ultimately escape (evaporate) from the material. The rate of evaporation depends on the strength of the binding forces in relation to the temperature. As the temperature is increased the probability that an atom will have energy enough to escape from the surface region increases. At high enough temperatures this probability is very high and the substance dissociates very rapidly. The Monte Carlo method is apparently simulating this physical fact accurately.

A more conventional approach to this investigation is to enclose the cluster in a box of finite dimensions. Only configurations in which all particles remain inside the box are accepted in the averaging process [Eq. (3)]. Thus, the cluster volume is defined and any particle found outside of this volume is no longer considered part of the cluster. Upon rejecting a configuration, another random move is initiated from the previous configuration. Using this approach there is no question about the convergence of the integrals in Eq. (1) because the volume integrations are constrained to the region enclosed by the box.

The influence of the box boundary condition on calculated system properties is predictable. For $T < T_B$, results should be independent of the box size providing its dimensions are greater than the largest bond length (interparticle separation) encountered in the averaging process. Since particles never reach the boundary under such circumstances, they cannot be influenced by it. For boxes smaller than this minimum size ($\frac{1}{2} L \leq \sigma$ for $N = 13$), the system properties must be affected by the walls because they act to compress the cluster and hence they correspond to an external pressure. For $T > T_B$, the calculated system properties are expected to depend strongly on the dimensions of the box boundary condition. For *any* box size, the particles ultimately distribute themselves uniformly inside the box. Hence, the larger the box, the less dense the system, and the smaller the internal energy. This condition, of course, corresponds to an artificially constrained gas.

The results of our calculations, using box boundary conditions, totally corroborate the expectations cited in the previous paragraph. Moreover, the results are entirely consistent with data obtained using free-surface boundary conditions. Detailed results are presented in Sec. III.

The potential energy of the aggregates investigated here is represented by a Lennard-Jones 6-12 pair interaction

$$U(\vec{r}_1, \ldots, \vec{r}_N) = 4\epsilon \cdot \sum_{i<j} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right].$$

The parameters (σ, ϵ) are approximately Ar (3.40 Å, 119.8 K), Kr (3.6 Å, 171 K), and Xe (4.06 Å, 229 K).[10] The internal kinetic energy for the N-particle system is $\langle K \rangle = (3N-6)kT/2$, or it can be obtained from the virial theorem. The six degrees of freedom associated with the translation and rotation of the cluster as a whole are not considered.

III. RESULTS

Results were obtained by omitting the first 3 $\times 10^4$ configurations and then taking statistical thermodynamic averages over additional configurations until the standard error in the internal energy was approximately 0.5% or less. To achieve this accuracy approximately 1.2×10^5 configurations were necessary for the smaller clusters at low temperatures, but for larger clusters at high temperatures 4×10^5 configurations were sometimes required.

Figure 1 shows the temperature dependence of the total internal energy for different-sized clusters. The data terminate at the liquid-gas transition temperature. Thirteen-particle clusters show an abrupt change in the internal energy at $T = 34$, 49, and 66 K for Ar, Kr, and Xe, respectively. Below these transition temperatures the clusters are characterized by small atomic displacements from spatially well defined positions. Operationally this information is obtained by observing the change in the vectors which locate each particle spatially, as the number of configurations are increased. Typically, in the first few thousand configurations of the Markov chain the particles move from their initial positions into locations of high probability, and thereafter oscillate about these positions with an amplitude small compared with the distance between neighboring atoms. In summary, these clusters exhibit solidlike behavior. Above the transition temperature, the atoms exhibit no preferential location in space but move about in a well-defined volume of the same dimensions as the cluster. This information, coupled with the fact that the clusters have negative internal energy, is interpreted as evidence of a liquid state. Hence, these abrupt energy changes apparently represent the liquid-solid phase transition. This viewpoint is fortified by comparing the ratios of the melting temperatures for bulk Ar, Kr, and Xe to those calculated for the 13-particle clusters. They

compare closely. The entropy of fusion is $S \simeq 1.76$ e.u. (1 e.u. = 1 cal/mole deg) compared with 3.35 e.u. for the bulk sample.[11] We have also observed an abrupt melting transition for $N = 11$, although the change in internal energy is less than for $N = 13$. For cluster sizes smaller than $N = 11$, no abrupt transition is observed. Instead, a gradual transition from solid to liquid occurred over a fairly broad range of temperatures. In order to verify that the observed melting transition is physical rather than a computational artifact, the configuration of the high-temperature liquid phase was used as an initial condition for the 13-particle cluster, at temperatures well below the apparent melting point. Then up to 4.8×10^5 configurations were generated, with the result that the atoms relaxed back to the previously determined lattice configuration. This experiment was repeated with the same result for several different cluster sizes. The converse of this experiment was also performed. In all cases, there is no indication that the initial configuration influences the ultimate outcome of the calculation.

Figure 2 contains a plot of the liquid-gas transition temperature $T_B(N)$ for N-particle rare-gas clusters. For example, $T_B(3) = 20$ K and $T_B(13) = 45$ K for Ar. For bulk argon $T_B(\infty) = 87$ K, which is displayed by the uppermost dashed line for comparison purposes.[12] As for the liquid-solid transition temperature, the different ratios of $T_B(\infty)$ bulk Ar, Kr, and Xe agree closely with the same ratios for the clusters. The liquid-gas transition occurs abruptly, apparently over a temperature range of less than 1 K. As discussed earlier, the transition manifests itself, at temperature $T \gtrsim T_B$, by a monotonic decrease in the binding energy toward zero, as the number of configurations generated is increased. This behavior is accompanied by an increasing separation of the particles from one another. The clusters simply fall apart.
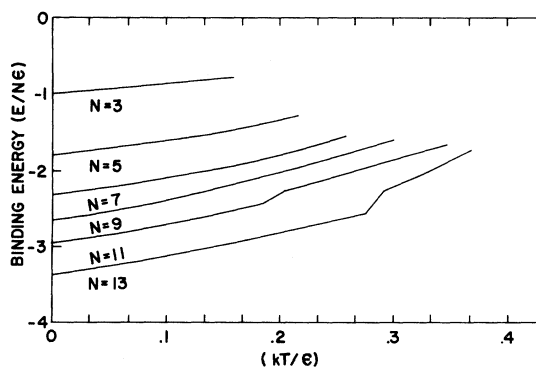

FIG. 1. Binding energy of different-sized clusters ($N = 3$ to $N = 13$), as a function of temperature.
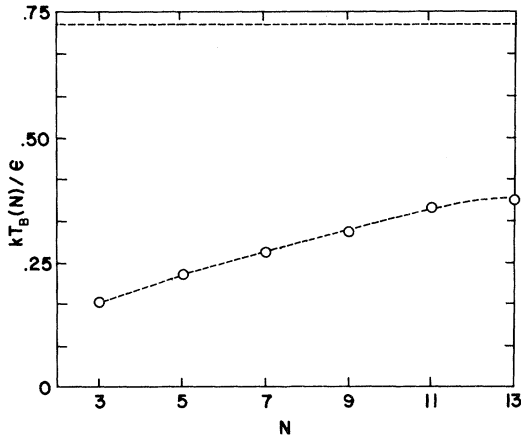
FIG. 2. Liquid-gas transition temperature as a function of cluster size. The circles represent the data and the dashed lines are an observational aid.

Figures 3–8 contain the thermodynamic expectation values for the number of bond lengths (interparticle separations) as a function of interparticle separation. This quantity is directly proportional to the pair distribution function. Figure 3 shows the bond length distribution for $N = 13$, in arbitrary units, at three different temperatures. For Ar, the temperatures are 1, 10, and 33 K, which span the solid regime. The first peaks occur for separations in the vicinity of $r_{ij} \simeq 1.12\sigma$. This is precisely the position of the minimum in the pair potential. At $T = 1.0$ K, there are two peaks in this region. However, as the temperature is increased from 1 to 10 K, they slowly move together into a single broad maximum.

Figure 4 shows the bond length distribution for $N = 11$. The curve at $kT/\epsilon = 0.3333$ in Fig. 4 is in the liquid regime of the cluster, whereas the plot at $kT/\epsilon = 0.2083$ represents the solid phase below

the melting temperature. The results for cluster sizes $N = 3$, 5, 7, and 9 are shown in Figs. 5–8.

A general feature of the clusters is that the peaks in the bond length distributions are all well resolved at the lowest temperatures, corresponding to a small half-width at half-maximum Δ_{ij}. This indicates a definite lattice structure. Increasing the temperature shifts the maxima to larger bond separations r_{ij}. However, only the outermost maxima (long bond lengths) are substantially affected. As mentioned earlier, the innermost peak stays close to $r_{ij} \simeq 1.12\sigma$ for all temperatures considered.

The half-widths, however, all increase steadily with temperature. Figure 9 illustrates the behavior of the peak at $r_{ij} \simeq 1.8\sigma$ for the 13 particle system. The half-width increases linearly until $kT/\epsilon = 0.2833$. At this temperature, the last peak ($r_{ij} \simeq 2.16\sigma$) is very badly resolved and at higher temperatures it cannot be seen at all. Consequently, the half-width of the peak at $\sim 1.8\sigma$ increases dramatically, changing from 0.061σ at $kT/\epsilon = 0.2833$ to 0.124σ at $kT/\epsilon = 0.2916$—an increase of more than 100% for a degree rise in temperature for argon. The half-width of the other peak ($\sim 1.12\sigma$) also increases abruptly at this temperature, as does the internal energy.

These are indications of a major structural change within the cluster—the resulting disorder corresponding to the entropy increase during melting. Similar results are obtained for smaller clusters, except that the abrupt change near the melting temperature becomes more diffuse.

Our observations are in agreement with Fisher,[13] who states that the half-width of the first peak in the pair distribution function increases abruptly during melting and that the position of the first peak is temperature independent.
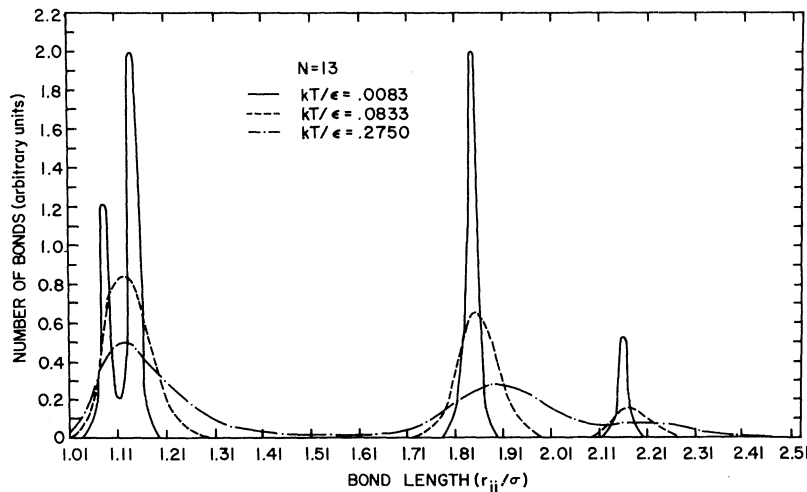

FIG. 3. Distribution of bond lengths for $N = 13$, as a function of bond length, at various temperatures.
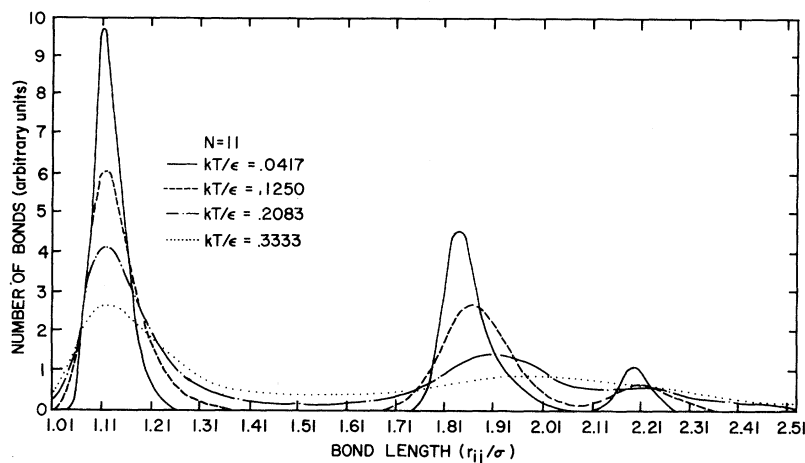
FIG. 4. Distribution of
bond lengths for $N = 11$, as
a function of bond length,
at various temperatures.

It is instructive to write the bond length as $\vec{r}_{ij}$ $=\vec{u}_i - \vec{u}_j + \vec{R}_{ji}$, where $\vec{u}_i = \vec{r}_i - \vec{R}_i$. In the solid regime, $\vec{u}_i$ is the displacement of the ith particle from its equilibrium lattice position $\vec{R}_i$. Clearly, the positions of the maxima in the bond length distributions (Figs. 3–8) specify the values of $\vec{R}_{ij}$ and the half-widths of the peaks measure $\langle |\vec{u}_i - \vec{u}_j| \rangle$ (brackets indicate a thermal average). Hence, the fluctuation of the bond lengths r_{ij} about their mean values R_{ij} is approximately $\langle |\vec{u}_i - \vec{u}_j| \rangle \simeq \Delta_{ij}$. Moreover, the mean departure of an individual atom from its lattice position is roughly half this value, i.e., $\langle |\vec{u}_i| \rangle \simeq \frac{1}{2}\Delta_{ij}$. Thus, the increase of the half-widths Δ with temperature is a measure of the atomic vibrational amplitudes. In the fluid state, $\langle |\vec{u}_i - \vec{u}_j| \rangle$ obviously cannot be interpreted in this fashion. It simply measures the fluctuation of bond lengths about their mean value R_{ij}.

The structure specified by the average positions of the atoms, in the solid phase, was determined from the average bond lengths with the aid of

three-dimensional models. For $N = 3$ the preferred structure, at the lowest temperatures, is an equilateral triangle. An $N = 5$ cluster forms a trigonal bipyramid and $N = 7$ a pentagonal bipyramid. The nine-particle cluster, having symmetry C_{1h}, is a pentagonal bipyramid with two additional atoms. It is found that larger clusters are formed by adding atoms to the basic pentagonal structure. The pentagonal growth mechanism has been discussed in detail by Hoare and Pal.[14] Their method of calculation is to determine the minimum-energy structure by moving each particle iteratively until the total potential energy is minimized. Only zero-temperature structures are calculable. Structures for *all* clusters considered in our Monte Carlo work correspond very closely to those obtained by Hoare and Pal.[14] For example, in the limit of 0 K, the 13-particle cluster forms an icosahedron with bond lengths 1.083σ and 1.139σ, as compared to Hoare and Pal, who obtain 1.083σ and 1.137σ. This is in disa-
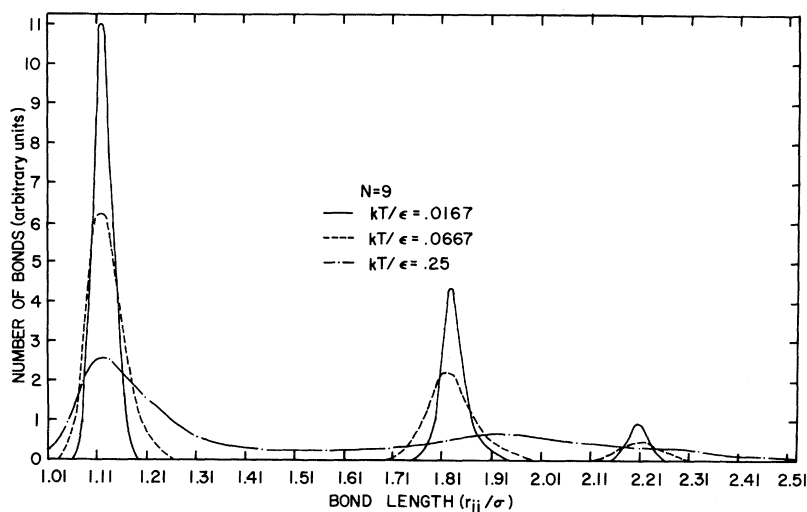

FIG. 5. Distribution of
bond lengths for $N = 9$, as
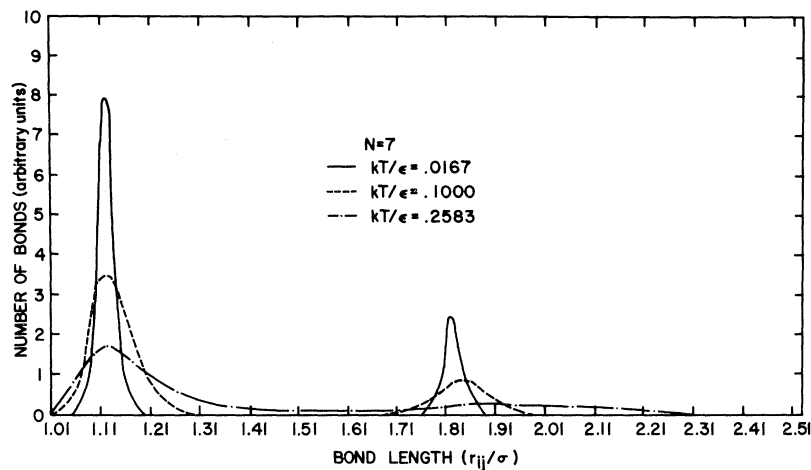a function of bond length,
at various temperatures.

FIG. 6. Distribution of bond lengths for $N = 7$, as a function of bond length, at various temperatures.

greement with Burton's[5] results of 1.117σ and 1.173σ. Similarly, our binding energy compares very closely to Hoare and Pal,[14] 44.35 and 44.327, respectively, in units of ϵ. The agreement is remarkable and extends to all other cluster sizes as well. For $N = 13$, we observe no lattice phase change from the icosahedron structure below the melting temperature, although disorder does increase with increasing temperature. Similar results are reported for the smaller clusters. Table I displays the equilibrium vector locations of all atoms for clusters with $N = 3$–13, in units of σ.

The Monte Carlo method provides further evidence that a structure having fivefold symmetry is preferred over an fcc arrangement, for small values of N. The existence of such structures in condensing metal vapors has been experimentally reported by several investigators.[15]

Figure 10 shows the binding energy per particle, in units of ϵ at $kT/\epsilon = 0.0083$, as a function of N. The dashed line is a least-squares fit through the data points, which are represented by the circles. For systems containing a small number of interacting particles, it is generally argued that the total system energy should be directly proportional to the total number of bonds, i.e., $E \sim N(N-1)$. In that case, a plot of E/N versus N is represented by a straight line, which should continue until the number of bonds per particle become saturated. Figure 10 does not conform to this simple argument; E/N is not linear in N.

In order to determine the quantitative effect of finite box boundary conditions on predicted phys-
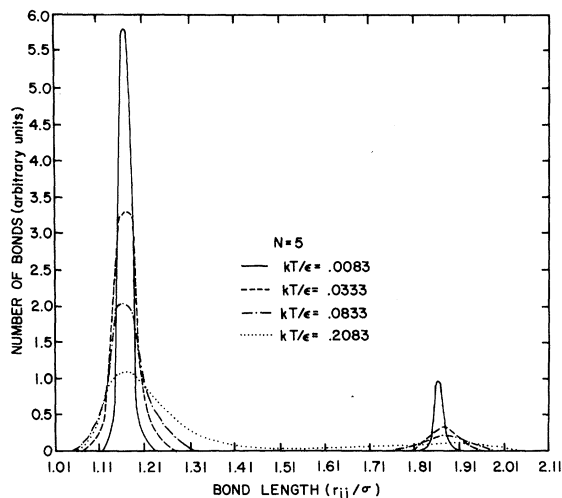

FIG. 7. Distribution of bond lengths for $N = 5$, as a function of bond length, at various temperatures.
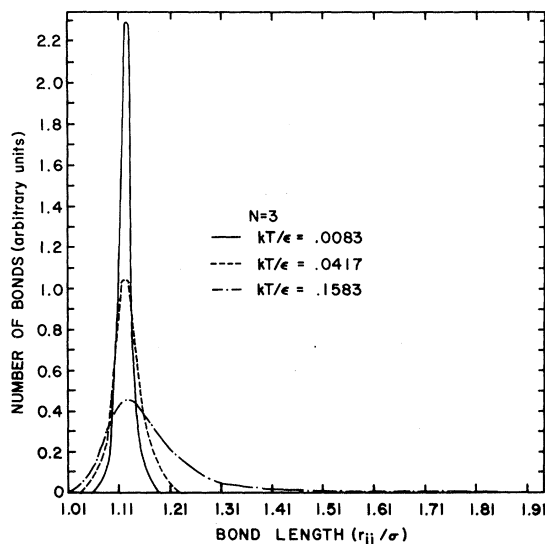

FIG. 8. Distribution of bond lengths for $N = 3$, as a function of bond length, at various temperatures.
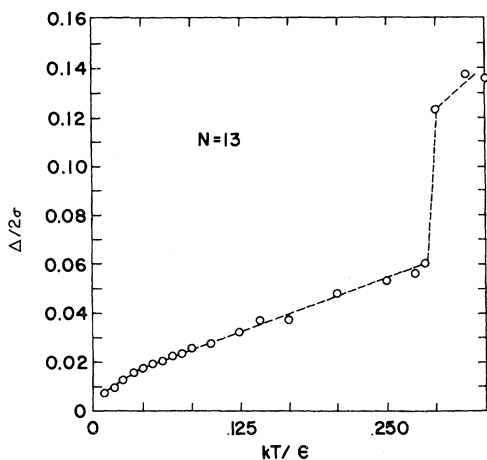
FIG. 9. Fluctuation of bond lengths from their equilibrium values for $N = 13$, as a function of temperature.

ical properties, the average potential energy was determined for clusters enclosed in boxes with different volumes, as discussed in Sec. II. The results are shown in Fig. 11 for $N = 3$, at various temperatures. At temperatures below the liquid-gas transition the energy is independent of box size, unless the enclosed volume is made too small. The critical box size, below which the energy is volume dependent, increases with increasing temperature. For $kT/\epsilon = 0.0413$ (5 K for argon) the critical box radius is $\sim 0.8\sigma$, whereas, for $kT/\epsilon = 0.0826$ (10 K for argon), it is $\sim 1.3\sigma$. This increase is undoubtedly due to thermal expansion of the cluster.

A potential-energy minimum occurs for box radii near 0.8σ, which deepens with increasing temperature. This is due to the boundary conditions artificially constraining the particles to positions near the minimum of the potential and does not correspond to a physically realizable state for a free cluster at nonzero temperature. Further decrease of the box size compresses the cluster and hence the interparticle distances, forcing the atoms into the repulsive-core region of the potential. As a result, the energy increases rapidly. The important observation is that there exists a region of stability, where the system properties are not affected by the artificial constraint of the box.

Above the liquid-gas transition temperature, there is *no* region where the internal energy is independent of the enclosing volume, as indicated by the curve at $kT/\epsilon = 0.1735$ (21 K for argon) in Fig. 11. As the radius of the box increases beyond 0.8σ, the cluster expands and the energy rapidly approaches zero. The cluster is simply not bound and the atoms distribute themselves

TABLE I. Equilibrium vector locations (x, y, z) of each atom, at $kT/\epsilon = 0.0083$ for cluster sizes $N = 3$ to $N = 13$.

N = atom number	3	5	7	9	11	13
1	(0.0, 0.0, 0.0)	(0.0, 0.0, 0.0)	(0.0, 0.0, 0.0)	(0.0, 0.0, 0.0)	(0.0, 0.0, 0.0)	(0.0, 0.0, 0.0)
2	(1.12, 0.0, 0.0)	(1.11, 0.19, 0.04)	(−0.74, −0.65, −0.50)	(1.03, −0.27, 0.35)	(0.75, −0.47, −0.64)	(0.39, 1.00, 0.14)
3	(0.56, 0.97, 0.0)	(0.42, 0.97, −0.36)	(0.57, −1.68, 0.06)	(−0.98, 0.07, −0.52)	(−0.64, 0.52, 0.73)	(−0.39, −1.00, −0.14)
4		(0.41, 0.73, 0.73)	(−0.38, −1.69, −0.47)	(0.84, 0.07, −0.71)	(0.08, 1.11, 0.05)	(0.72, −0.79, −0.09)
5		(0.60, 0.02, −0.93)	(0.81, −0.63, 0.35)	(−0.10, 0.70, −0.85)	(0.09, −1.10, 0.06)	(−0.73, 0.80, 0.09)
6			(−0.21, −0.99, 0.37)	(0.13, −0.88, 0.66)	(0.99, 0.48, −0.11)	(0.10, −0.44, −0.98)
7			(0.31, −0.87, −0.60)	(−0.11, −0.38, −1.07)	(0.47, 0.50, 0.89)	(−0.12, 0.43, 0.99)
8				(0.53, −0.95, −0.38)	(0.88, −0.45, 0.48)	(0.99, −0.68, 0.84)
9				(−0.57, −0.94, −0.21)	(−0.79, 0.61, −0.43)	(−0.10, 0.68, −0.84)
10					(0.24, 0.54, −0.92)	(0.90, 0.09, 0.60)
11					(−0.11, −0.45, 0.99)	(−0.90, −0.09, −0.60)
12						(0.91, 0.24, −0.53)
13						(−0.91, −0.24, 0.52)

more or less uniformly in the interior of the box. The important observation is that, above the transition temperature, the system behaves like a gas constrained by the enclosing volume of the boundary condition.

IV. DISCUSSION CONCLUSIONS

It has been emphasized that the nature of the surface boundary conditions, imposed on small aggregates, is of central importance in deducing the systems properties. Our position is that free-surface boundary conditions are mandatory in investigating the thermodynamics of stable clusters. It is not our objective to deduce the distortion to system properties introduced by artificial boundaries. It has been common practice in previous works[5-7] to use some sort of boundary condition to enclose the cluster in a well-defined volume. It is then argued that this artificially imposed condition does not appreciably affect system properties.

We have explored the effects of box boundary conditions, which are summarized in Fig. 11 for $N=3$. It is clear that for $T<T_B(N)$ there is a critical box size, such that larger boxes will not affect system properties. Moreover, free-surface boundary conditions (infinitely large box) give identical results. This information confirms that clusters with free-surface boundary conditions are sufficiently metastable below $T_B(N)$ to calculate meaningful thermodynamic properties. The increase in critical box size with temperature indicates that the clusters undergo substantial thermal expansion. For $T>T_B(N)$, Fig. 11 shows that *all* finite box sizes seriously affect predicted
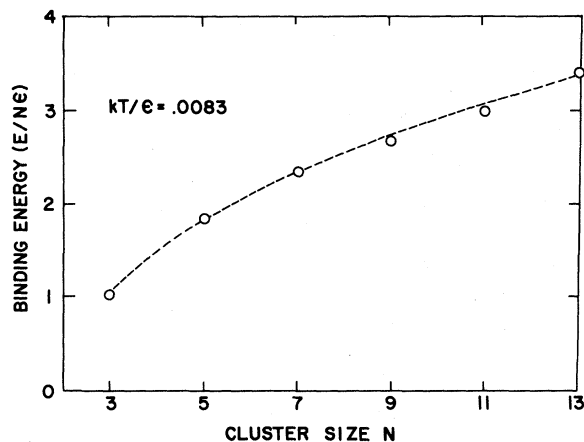
system properties. The energy approaches zero as the box size becomes large and the particle distribution inside the box is nearly uniform. The temperature at which such behavior first appears is identical to the liquid-gas transition temperature, predicted in Sec. II and displayed in Fig. 2. To summarize, there is no metastable bound state for $T>T_B(N)$. The results discussed in connection with Fig. 11 qualitatively apply to all cluster sizes investigated.

The very close agreement between our work, in the limit of 0 K, and that of Hoare and Pal[14] was presented in Sec. III. The structure specifications, bond lengths, and binding energies agree almost exactly, for all cluster sizes. Finite-temperature calculations cannot be compared because their work is limited to 0 K. This remarkable agreement is further evidence that the Monte Carlo method, with free-surface boundary conditions, is accurately simulating system properties.

Evidence indicating the existence of solid, liquid, and gaseous phases for these clusters comes from the observation of atomic positions. By following the position changes with succeeding configurations, the part of phase space preferred by the atoms implies the state of matter. The details of the position-change observations were presented in Sec. III. In addition, the solid-liquid

FIG. 10. Binding energy per atom, in units of ϵ, as a function of N, the number of atoms contained in the clusters. The temperature is $kT/\epsilon=0.0083$.
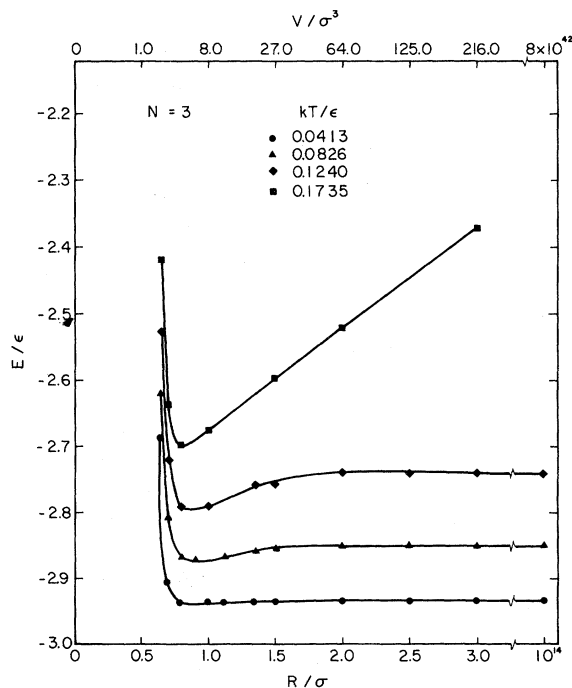
FIG. 11. Average potential energy as a function of box size for $N=3$ at different temperatures.

transition is characterized by an abrupt change in
the width of peaks in the bond length distributions,
as depicted for $N = 13$ in Fig. 9. These changes
are accompanied by an abrupt change in the in-
ternal energy. Since these effects all occur at
the same temperature, for a given cluster, the
evidence is that a major structural change occurs
within the cluster—the resulting disorder cor-
responding to the entropy increase during melting.
Similar results are obtained for smaller clusters,
except the abrupt changes near the melting tem-
perature become more diffuse.

Evidence for the liquid-to-gas transition is based
primarily upon the observation that above $T_B(N)$
the clusters do not form a stable bound state. The
density and binding energy decrease monotonically
toward zero as the number of configurations gen-
erated is increased. This result is based upon
free-surface boundary conditions. If box boundary
conditions are imposed, the atoms distribute
themselves approximately uniformly throughout
the enclosed volume, and the energy of the cluster
is a function of the box volume. For example, see
the curve at $kT/\epsilon = 0.1735$ in Fig. 11.

A direct comparison of our results with recent
molecular dynamics (MD) calculations on argon[6]
is not possible because there are no cluster sizes
in common. However, we believe the artificial
boundary conditions used in that work interfere
with the intrinsic behavior of the cluster. An ex-
ample illustrates the point. McGinty[6] confines
the clusters to a spherical box of radius propor-
tional to $N^{1/3}$. According to this formula, the box
volume for $N = 3$ would be $52\sigma^3$. It is obvious from
Fig. 11 that, for any argon temperature $T > 15$ K
($kT/\epsilon > 0.125$), this small box size would interfere
with the cluster's behavior. In order to make
comparisons with the MD work,[6] we have extrapo-
lated our results for smaller clusters to $N = 15$.
Figure 2 shows that $T_B(15) \simeq 50$ K for argon
($kT/\epsilon = 0.4167$). There is no evidence of gaseous
state above 50 K in the MD results[6] because the
small confining volume acts to hold the cluster
together, resulting in a well-defined internal en-
ergy. It is wrong to construe properties, derived
in this manner, as that of a stable bound-state
cluster. Above T_B, the MD results must cor-
respond instead to an artificially constrained gas.
Other points of disagreement are that no sharp
solid-fluid phase transition is observed, contrary
to the evidence summarized in Figs. 1 and 9 and
to Burton[7]; nor do the energies agree well. At
25 K our results give $E/N\epsilon = -2.85$ for $N = 13$, al-
most identical to the MD[6] results for $N = 15$
($E/N\epsilon = -2.82$). Again, an extrapolation of Fig. 1
to $N = 15$ indicates that we would claim a sub-
stantially greater binding energy.

In the limit of 0 K, the normal-mode bond lengths
and internal energy, calculated by Burton[1,5] for
argon with $N = 13$, do not agree with our results
and consequently, not with Hoare and Pal[14] either.
Since thermodynamic properties are calculated
using the 0-K normal-mode frequencies, which
in turn depend upon the 0-K bond lengths, the
numerical accuracy of Burton's work is open to
question. Based upon our results, the normal-
mode calculations above $T_B(N)$ are surely meaning-
less. The anomalous behavior reported[5] for the
entropy and free energy, at temperatures in ex-
cess of $T_B(\infty)$, is undoubtedly an artifact of the
attempt to use normal-mode methods in a fluid
regime. The situation is even more critical than
this, however. A simple calculation shows[16] that
a harmonic normal-mode analysis is valid only if
$\langle |\vec{u}_i| \rangle < 0.06R_m$, where $R_m \simeq 1.12\sigma$ is the nearest-
neighbor separation. An inspection of Fig. 9
shows that, with $N = 13$, $\langle |\vec{u}_2| \rangle \simeq 0.06R_m$ at an argon
temperature $T = 33$ K, the normal-mode analysis
is, therefore, not justifiable unless $T < 33$ K.
More precise limits of validity necessitate a de-
tailed calculation of anharmonic contributions.
As shown in Fig. 3, the bond length distribution
and hence the frequency spectrum are temperature
dependent even at the lowest temperatures. Pre-
vious works have not been capable of accounting
for this effect.[5]

In conclusion, we again emphasize the impor-
tance of a correct description of the boundary
conditions. If artificial boundaries are used, they
must not be allowed to interfere with the dynam-
ical behavior of the aggregate.

One of the more surprising results of this work
is the slow rate at which system properties ap-
proach bulk behavior as the cluster size is in-
creased. This is particularly evident in Figs. 2
and 9 for the liquid-gas transition and the binding
energy per atom, as a function of N.

The biased random-walk method has proved to
be a valuable tool, particularly in determining
the structures of small aggregates at different
temperatures, the existence and character of
solid-liquid and gas-liquid phase transitions, and
in providing a basis for calculating other prop-
erties, such as specific heats, free energies,
entropies, etc. Calculations of these latter quanti-
ties are in progress.

A valid criticism of this and all other work cited
herein is the neglect of zero-point motion. Al-
though it is of negligible importance for Xe and
Kr, its neglect introduces calculational errors
on the order of 10% for some argon properties at
low temperatures.[17] At higher temperatures,
thermal effects tend to mask out the zero-point
motion.

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[12] The liquid-to-gas phenomenon observed for small clusters occurs under somewhat different circumstances than is normally the case with a bulk sample. The quantity $T_B(\infty)$, quoted here for argon, is measured at one atmosphere of pressure, although the liquid-to-gas transition may occur at any pressure between the critical point and the triple point. Incidentally, the triple-point temperature of argon is approximately 83 K. The boundary condition imposed on the clusters is, however, equivalent to zero external pressure. Under such circumstances the phase diagram for bulk argon shows that the liquid state does not exist and the transition occurs by sublimation from a solid to a gaseous phase. On the other hand, the clusters investigated in this work definitely exhibit a liquidlike phase. We suspect that for finite aggregates with a free-surface boundary condition, the temperature interval over which the liquid state exists will diminish to zero in the limit of very large N, leading asymptotically to established bulk behavior. The qualitative aspects of this discussion apply equally well to krypton and xenon.

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