

Molecular Dynamics Study of Melting and Freezing of Small Lennard-Jones Clusters

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The properties of small clusters of Lennard-Jones atoms were studied by using molecular dynamics simulations. Clusters containing from 13 to 147 atoms were found to undergo a transition, analogous to a melting transition for bulk materials, from a low-energy solidlike structure at low temperatures to a set of higher energy liquidlike structures at high temperatures. The transition creates noticeable features in plots of the equilibrium energy of clusters as a function of temperature, but the shapes of the curves depend on the size of the cluster and on whether a canonical ensemble or microcanonical ensemble is used for calculating the properties. The nonequilibrium energy as a function of temperature on heating or cooling at a finite rate can differ significantly from the equilibrium results. Coexistence among the minimum-energy structure, high-energy liquidlike structures, and typically one or more intermediate structures was observed over a range of temperatures. Results from potential energy minimization of fcc and icosahedral structures of various sizes indicate that a Lennard-Jones cluster must contain at least 5000 atoms before the fcc structure becomes more stable than the structure of the Mackay icosahedra.

Introduction

Over the past several years, the structures and properties of small clusters of atoms have been studied by using a variety of techniques. Some workers have proposed novel structures for clusters.¹⁻⁴ Others have performed systematic searches for potential energy minima for clusters of various sizes.⁵⁻⁷ The dynamics and thermodynamic properties of small clusters of Lennard-Jones atoms have been studied by means of Monte Carlo and molecular dynamics simulations.⁸⁻¹⁹ Supersonic jets have been used in conjunction with electron diffraction to study the structures of argon clusters containing from tens to thousands of atoms.^{4,16,17,20-23} Two striking results of these investigations are the fact that some small clusters of Lennard-Jones atoms at low temperatures are more stable in structures with icosahedral symmetry than those with crystalline symmetry and the observation that small clusters can undergo a phase change, much like the freezing and melting of a bulk material.

In 1962, Mackay presented a family of icosahedral structures as "a dense non-crystallographic packing of equal spheres".¹ In his report, Mackay showed that clusters containing certain "magic numbers" of identical atoms may form compact, nearly spherical structures with surfaces that are nearly close-packed. Each of these icosahedral structures is composed of 20 fused, distorted tetrahedra. For icosahedra containing at least 55 atoms, the packing within each tetrahedral unit is distorted face-centered cubic (fcc). Figure 1 depicts the first two Mackay icosahedra, containing 13 and 55 atoms. Larger icosahedra may be generated by building upon the 55-atom cluster.

Burton²⁴ reported in 1971 that 13- and 55-atom "spherical" fcc Lennard-Jones clusters are mechanically unstable and distort into compact, low-energy structures when allowed to relax.²⁵ These structures were found by Hoare and Pal to be Mackay icosahedra.²⁶ Hoare and Pal⁵ also established, for clusters of up to 60 atoms, that small icosahedral and other "pseudocrystalline" clusters of Lennard-Jones atoms are more stable at zero temperature than fcc clusters of the same size.

Farges and colleagues^{16,17} have performed molecular dynamics simulations in which small liquidlike Lennard-Jones clusters, containing from 7 to 143 atoms, were cooled until they became solidlike. When cooled, clusters of from 20 to about 50 atoms were found to form "polyicosahedral" structures, that is, structures containing two or more interpenetrating 13-atom icosahedra. Such polyicosahedral structures are qualitatively different from the Mackay icosahedra containing more than 13 atoms, which each contain only a single 13-atom icosahedron located at the center of the cluster. In the simulations of Farges et al., clusters larger than about 50 atoms displayed the icosahedral structure characteristic of the larger Mackay icosahedra. Interference functions calculated from these simulations were in qualitative agreement with those observed experimentally for argon clusters of comparable size.

Although small clusters of argon may have icosahedral symmetry, bulk solid argon is known to have the fcc crystal structure. Both experimental and theoretical studies have been performed^{17,21,22} to try to determine the size at which the crossover from icosahedral to crystalline ordering occurs. Farges and colleagues have used electron diffraction to study the structures of small argon clusters formed in supersonic jets.^{16,17,20} They reported a crossover from icosahedral to fcc ordering at a cluster size of about 750 atoms. Stein and co-workers^{21,22} have performed similar studies. Lee and Stein²² reported a crossover between a size of 1500 and 3500 atoms for clusters at somewhat colder

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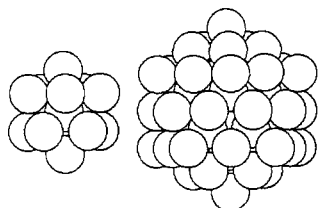


Figure 1. Mackay icosahedra containing 13 and 55 atoms.

temperatures than those of Farges et al. Lee and Stein²² also reported energy minimization calculations on Lennard-Jones systems that predicted a crossover at a system size of about 3000 atoms.

These theoretical and experimental results make it clear that the low-energy structures of small clusters of argon or Lennard-Jones atoms are more icosahedral than fcc-like. However, the true minimum-energy structures for clusters of more than 13 atoms are not known definitively, and it is unclear at what size the fcc structures become lower in energy than icosahedral structures.

Briant and Burton¹¹ have published an extensive molecular dynamics study of "melting" and "freezing" of Lennard-Jones clusters containing up to 100 atoms. In their study, solidlike clusters in the shapes of icosahedra or partial icosahedra were heated in steps from low temperature to temperatures at which atoms began to evaporate from the surface. Some of the findings they reported are the following:

(1) Sharp, first-order-like "melting", with a van der Waals-like loop in the energy as a function of temperature, was seen for clusters of as few as 7 atoms. We use the phrase "first-order-like" transition to refer to a significant change in the energy over a narrow temperature interval, suggestive of a broadened first-order transition. The low-temperature phase was solidlike with no diffusion; the high-temperature phase was liquidlike with a diffusion coefficient comparable to that of a bulk liquid.

(2) The melting transition was found to be reversible for clusters of 13 or fewer atoms. However, for a 55-atom cluster, melting did not appear to be reversible. That is, upon cooling, a liquid 55-atom cluster did not retrace its heating curve.

(3) A 13-atom cluster at a fixed energy near the melting transition was seen to make transitions back and forth between states of high and low potential energy.

Molecular dynamics simulations reported recently by Jellinek, Beck, and Berry¹⁹ indicate a first-order-like melting transition for a 13-atom cluster, without any loop. These workers also observed coexistence between liquidlike and solidlike states for the 13-atom system. The phrase "coexistence", as used by Jellinek et al., describes the observation that a cluster makes transitions from one type of structure to a distinctly different type of structure, spending a nonzero fraction of time in each structure. It corresponds in statistical thermodynamics to an ensemble that contains two distinct types of states for a cluster. Note that this use of the phrase coexistence differs from the usual one for coexistence of macroscopic phases, which corresponds to having two distinct phases simultaneously present in equilibrium in the same system. (Briant and Burton observed this same phenomenon—item (3) above—but did not use the term "coexistence" to describe it.) Monte Carlo studies of 13-atom Lennard-Jones clusters have been published by Etters and Kaelberer¹²⁻¹⁴ and Quirke and Sheng¹⁵ that dispute the first-order-like character of the transition. These studies indicate a "melting" transition, but one that appears to be more second-order-like than first-order-like. That is, the heat capacity undergoes a large change over a narrow temperature range, but the energy does not.

Blaisten-Barojas¹⁸ observed first-order-like transition for a 147-atom Lennard-Jones cluster in constant-temperature molecular dynamics simulations. No loop was observed in the energy vs. temperature curve.

These theoretical studies make it clear that some sort of structural and energetic phase transition takes place in small Lennard-Jones clusters, but its nature is still in doubt due in part to the conflicting results that have been reported.

In this paper, we report a molecular dynamics study of small Lennard-Jones clusters. This study was undertaken to help resolve the following issues:

(1) What is the nature of the phase transition seen for small clusters? What structural changes accompany this phase change? What is the equilibrium behavior of the energy as a function of temperature in the transition region? How do the properties of the transition depend on the size of the cluster?

(2) What are the minimum-energy structures of small Lennard-Jones clusters? How large must a cluster be before crystalline ordering of the low-temperature phase becomes more favorable than icosahedral ordering?

Our conclusions may be summarized as follows:

In constant-temperature simulations, small clusters containing from 13 to 147 atoms undergo an equilibrium structural transition as the temperature is increased, from a low-energy solidlike structure at low temperature to a set of higher energy liquidlike structures at high temperature, much like a melting transition of bulk materials. The transition is not a sharp one in that the solidlike and liquidlike structures and typically one or more intermediate structures coexist over a range of temperatures.

The equilibrium energy as a function of temperature rises from a lower value characteristic of the solidlike structures to a higher value characteristic of the liquidlike structures over this range of temperature. Various types of energy vs. temperature curves are obtained, depending on the size of the cluster. The shape of the curve is also significantly different for constant energy simulations (the microcanonical ensemble) and constant-temperature simulations (the canonical ensemble). This accounts for the discrepancy noted above between the Monte Carlo results of Etters and Kaelberer¹²⁻¹⁴ and the molecular dynamics results of Jellinek et al.¹⁹ When the clusters are heated and cooled too rapidly for equilibrium among the various structures to be achieved in the transition region, the transitions may appear to be irreversible and sharper than the equilibrium transition.

When the clusters are cooled too rapidly to fall into the structure of minimum energy, they either fall into a low-energy structure with characteristics similar to those of the minimum-energy structure, or they remain in the manifold of higher energy structures. The former behavior is analogous to imperfect crystallization and the latter to a glass transition.

The lowest energy structure observed for clusters of about 33 or fewer atoms is qualitatively different from that of larger clusters. (The exact size at which the change in structure takes place is not known with certainty but is somewhere between 33 and 38.) These results agree with those of Farges et al.^{4,16,17} who used the phrases polyicosahedral structure and multilayer icosahedral structure, respectively, to describe the smaller and larger clusters. The equilibrium energy as a function of temperature is also qualitatively different for the two size ranges.

Based on results obtained from energy minimization of clusters of various sizes and structures, it appears that a Lennard-Jones cluster at zero temperature must contain at least 5000 atoms before the fcc structure becomes more stable than that of the Mackay icosahedron.

Theoretical Framework

In this paper we investigate the properties of clusters of small numbers of atoms interacting with each other by means of the Lennard-Jones potential. We are interested in finding the minimum-energy structures of such clusters (i.e., the equilibrium structure at absolute zero temperature), the equilibrium energy and structural properties as functions of temperatures, and the observed energy and structural properties (which may differ from the equilibrium properties) as a function of temperature when the clusters are heated and cooled at finite rates, and in studying the phenomena of phase coexistence and phase transitions in these small clusters. The idea of "inherent structures", as defined by Stillinger and Weber,²⁷⁻²⁹ provides a unifying framework for

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discussing these features. In this section we will review the notion of inherent structures as applied to clusters, since it provides the conceptual framework we use in interpreting computer simulations on clusters.

The inherent structures formalism applied to clusters in a way of partitioning the $(3N - 6)$ -dimensional configuration space for the vibrations of a cluster of N particles into various regions. Within each region there is one and only one local minimum on the potential energy surface. A steepest descents minimization of the potential energy, starting from a point within one region, will lead to the unique local minimum in that region, and this minimization process is the basis for the partitioning of configuration space. The structure at the local minimum is the "inherent structure" throughout the corresponding region.

A cluster at a general point in configuration space may be regarded as vibrationally excited from its inherent structure. The dynamical motion of the atoms in a cluster consists of vibrational motion of the N -particle configuration about its inherent structure and transitions from one inherent structure to another (together, of course, with any overall translation or rotation of the cluster). At the lowest energies, the motion takes place only in the region containing the absolute minimum of energy. At the highest energies, the motion will carry the system from one inherent structure to another quite rapidly, since the high kinetic energy enables the potential energy barriers between the regions to be overcome.

The equilibrium statistical thermodynamics of a cluster, either at a given temperature with the canonical ensemble or at a given energy with the microcanonical ensemble, can be expressed in terms of integrals over these various regions. For the canonical ensemble, a canonical partition function and hence a free energy for each of the separate regions can be defined, and the total canonical partition function and free energy can be expressed in terms of the contributions from each region. Similarly, for the microcanonical ensemble, a microcanonical partition function and hence an entropy can be defined for each separate region, and the total microcanonical partition function and total entropy can be expressed in terms of the contributions from each region.

At any temperature (in a canonical ensemble) or at any energy (in a microcanonical ensemble), the fraction of the systems in an ensemble that have each inherent structure is determined by a distribution function calculable from the quantities discussed in the previous paragraph. However, since there are a finite number of particles in the system, it is not necessarily true that the distribution among inherent structures and the resulting average thermodynamic properties are independent of the ensemble used. For example, the average energy of a cluster as a function of temperature in a canonical ensemble need not be the same as the energy as a function of average temperature (defined in terms of the average kinetic energy) in a microcanonical ensemble. Under most circumstances, if the cluster contains a large enough number of particles (and hence has a large number of mechanical degrees of freedom), it will be approximately true that calculated properties are independent of the ensemble used. However, when the cluster is in or near a phase transition, the ensemble dependence can be significant. This will become clearer when we discuss a simple model calculation in a later section of this paper.

The empirical basis for the notion of a phase transition in a cluster of finite size comes from two types of observations in computer simulations of clusters. The first observation is that the energy of a cluster as a function of temperature can undergo abrupt changes of value¹⁹ or of slope¹²⁻¹⁵ at certain temperatures on heating or cooling or display behavior reminiscent of a van der Waals loop.¹¹ These phenomena are superficially analogous to first-order and second-order thermodynamic transitions. However, a proper interpretation of these observations requires consideration of (1) the effects of finite system size on broadening the transition; (2) the fact that the broadening of the transition might be dependent on which ensemble is used; and (3) the possibility that the quantities calculated in the simulations might not actually

correspond to equilibrium values. The second type of observation that suggests the existence of a phase transition in clusters is that a cluster may spontaneously make drastic changes in its structure or potential energy during the course of a simulation. For example, in molecular dynamics runs on a 13-atom Lennard-Jones cluster, Jellinek et al.¹⁹ observed the cluster switching from liquidlike states of higher potential energy to solidlike states of lower potential energy and back, provided the total energy was within a certain range. For lower energies, only the solidlike states were observed, and for higher energies, only the liquidlike states were observed. The two types of states had distinctly different properties, and it is not unreasonable to refer to each of these groups of states as phases. Following Jellinek et al.,¹⁹ we shall use the term "coexistence" to refer to the phenomenon of transitions back and forth between two or more types of states.

The concept of a phase transition or phase change can be interpreted by using the ideas of inherent structures. A "phase" corresponds to a set of inherent structures, and different phases are different sets of inherent structures with distinctly different properties. The inherent structures corresponding to one phase are presumably adjacent to one another in configuration space, and there are boundaries in configuration space between the various phases. In a simulation of a cluster under conditions where it can undergo a phase transition, the dynamical motion (in the case of constant energy molecular dynamics) or the stochastic motion (in the case of Monte Carlo simulations) is such that the cluster spends a long time in one set of states before crossing a boundary and entering another phase. If the different sets of inherent structures have different properties, such as significantly different potential energies, the transitions will be noticeable in the results of the simulation. In order for a cluster to exhibit phase transitions, therefore, it seems likely that its inherent structures must be of two or more distinct types with distinctly different potential energies.

The spectrum of potential energies for the inherent structures of a cluster is then obviously of interest in understanding the phase transition behavior. This "spectrum" is merely the set of values of the potential energy at all the local minima on the potential energy surface. There will be a lowest value, corresponding to the absolute minimum energy, and then a set of many "excited" states. If there are significant gaps in the spectrum, then it appears possible that the types of behavior discussed above could take place. Moreover, if the states on either side of a gap have other properties that are different, such as different packings of the atoms and/or different barriers between inherent structures within the set of states, then the different phases might have different structural and dynamical properties as well as different energies. On the other hand, if there are no gaps in the spectrum and no sharp distinctions among the properties of various groups of states, then phase transition behavior is unlikely.

A distinctly different conceptual framework, based on quantum mechanics, for the discussion of phase transitions in clusters has been proposed by Berry, Jellinek, and Natanson.^{30,31} It assumes that the energy eigenvalues of a cluster are continuous functions of a parameter, γ , measuring the nonrigidity of a cluster. Each of the various phases of a cluster is interpreted as a group of quantum states, with the same value of γ , that is thermodynamically stable. An approximate theory based on this conceptual framework predicts that different phases can coexist over a range of temperatures, with the relative populations of the phases being governed by a temperature-dependent equilibrium constant. The approximate theory also predicts that the equilibrium constant K for the solid-liquid transition of a cluster is a discontinuous function of temperature. Below a temperature T_f it is zero. At T_f it jumps discontinuously to a nonzero value. Then it increases continuously until a temperature T_m , at which it jumps discontinuously to infinity.

The conceptual framework based on the use of inherent

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structures differs in several ways from that of Berry et al. The former is classical, and the latter is quantum mechanical. The former interprets each phase as corresponding to a region of configuration space. The latter interprets each phase as corresponding to a group of quantum mechanical energy eigenstates, whose classical analogue would be a region of phase space. Finally, the former will always predict that the equilibrium constants are continuous functions of temperature, since they are given by the ratios of finite-dimensional integrals over the various finite regions of configuration space and the integrands are continuous functions of temperature. The latter, on the other hand, predicts that the equilibrium constants are discontinuous functions of temperature.

The prediction of discontinuous equilibrium constants implies that the equilibrium energy of a cluster as a function of temperature should have two jump discontinuities, at T_f and T_m . Quantitative estimates of the magnitudes of these jumps for Lennard-Jones clusters of the size range studied in this paper have not been made. However, in the present work and in the previous published simulation work of which we are aware, such discontinuities have not been observed in equilibrium data. All of the results presented in this paper and the previously published results on small Lennard-Jones clusters appear to be consistent with the conceptual framework based on inherent structures, the interpretation of phases as groups of inherent structures of similar energy, and the existence of equilibrium constants that are continuous functions of temperature.

The last phenomenon of interest in this work is the behavior of clusters on heating and cooling at finite rates in computer simulations. If the temperature is changed slowly enough and if the motion is ergodic, then the system can equilibrate at each temperature and the equilibrium properties as a function of temperature can be obtained. In principle, slow cooling all the way to absolute zero will allow the true minimum-energy inherent structure to be determined. In the region of temperature or energy where a phase transition takes place, the system is most likely to be out of equilibrium, since the characteristic times for transition from one phase to another can be very long. At low energies or temperatures, the motion of the system is most likely not to be ergodic, because of the potential energy barriers between inherent structures.

Simulation Method

We have performed the following types of calculations on Lennard-Jones clusters of various sizes: (1) slow cooling runs using the constant temperature molecular dynamics method to study the phase transition and to attempt to determine the absolute minimum-energy structure; (2) slow heating runs to check on the reversibility of the transition and to check for equilibration at temperatures in the transition region; (3) constant-energy and constant-temperature calculations in the transition region to study coexistence of phases; (4) energy minimization calculations starting with various structures appearing in the previous types of calculations to study the spectrum of energies for inherent structures; and (5) energy minimization calculations starting with various icosahedral and microcrystalline structures in a further attempt to locate absolute minimum-energy structures as a function of cluster size.

In all of our molecular dynamics (MD) simulations, we used the velocity form of the Verlet algorithm³² and a truncated and shifted Lennard-Jones potential

$$u(r) = u_{LJ}(r) - u_{LJ}(r_c), \quad r < r_c \\ = 0, \quad r > r_c \quad (1)$$

where

$$u_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (2)$$

The value used for r_c was 6.0σ . At this distance, $u_{LJ}(r_c) = -8.6 \times 10^{-5}\epsilon$, where ϵ is the depth of the potential well. A time step

of 0.01τ , where $\tau = \sigma(m/\epsilon)^{1/2}$, was used. Temperatures and energies reported in this paper are in reduced units, i.e., units of ϵ/k and ϵ , respectively, where k is the Boltzmann constant. All simulations were performed on a Floating Point Systems array processor with a DEC PDP 11/34A host computer.

The simulations were performed at temperatures low enough that evaporation of atoms from the clusters generally did not occur, except for the smallest systems and the highest temperatures.

To study the freezing transition, the following procedure was adopted. First, a sphere of from 13 to 309 atoms was carved out of a bulk equilibrated Lennard-Jones liquid. Next, this cluster was equilibrated at a temperature above its melting temperature with the constant-temperature molecular dynamics method, which uses stochastic collisions;³³ i.e., at random times, particles chosen at random would be assigned new velocities picked at random from a Boltzmann distribution with a specified temperature, representing the temperature of a hypothetical external heat bath. The data of Briant and Burton gave some indication of appropriate temperatures at which to equilibrate the liquidlike clusters. After equilibration, the clusters were cooled by stochastic collisions with a bath temperature that decreased linearly with time until a temperature of zero was reached. The rate of cooling was varied by varying the rate at which the bath temperature decreased. Heating runs were performed by starting with the atoms in a low potential energy structure with zero kinetic energy and performing molecular dynamics calculations using stochastic collisions with a heat bath whose temperature increased with time. The stochastic collision frequency was from 0.28 to 2.3 collisions per atom per τ , depending on system size.

The stochastic collision technique, when combined with molecular dynamics, gives trajectories whose time averages are canonical ensemble averages with a temperature equal to that of the heat bath, provided the bath temperature is constant and the runs are long enough for the system to equilibrate.³³ In cooling and heating runs, therefore, the calculated properties as a function of the bath temperature will be true equilibrium properties, provided the cooling rate is slow enough that the system equilibrates at each temperature. If equilibrium is achieved at a particular cooling rate at a particular temperature, then a second cooling run at the same rate will give the same results at that temperature; heating at the same rate will give the same results at that temperature, and cooling at slower rates will also give the same results. These three types of reproducibility will be taken as evidence that equilibrium is achieved, although they are by no means a guarantee.

If the identical zero temperature structure is achieved in two or more cooling runs for a given cluster size, then this structure is a good candidate for the true minimum-energy structure (barring ergodicity problems). In the following, the zero temperature structure obtained from slow cooling will be referred to as the "apparent minimum energy structure" if the same structure was achieved in two or more MD cooling runs and if no other lower energy structure was obtained from the simulations or from direct construction of likely candidate structures.

To investigate the phenomenon of coexistence for clusters containing up to 147 atoms, we performed simulations both at constant energy and at constant temperature. The constant-energy simulations were done in one of the following two ways: (1) a velocity randomly selected from a Boltzmann distribution was given to each atom in a zero temperature cluster to bring the cluster's total energy to a given value; or (2) the velocities of the atoms of a liquid cluster were rescaled to bring the cluster's energy to a given value. The cluster was then allowed to evolve at constant energy, using the conventional MD method. It was found that for a given total energy, both method 1 and method 2 yielded essentially the same results, once any transients due to the initial state had vanished. The constant-temperature coexistence simulations were done by starting with a set of particle positions and temperatures obtained during a heating or cooling run at or near the temperature of interest and then performing molecular dy-

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namics calculations with the bath temperature set at the desired value.

For both types of simulation, the system's potential energy was monitored as a function of time in an attempt to find abrupt changes associated with a phase transition. In addition, for the constant-energy simulations, plots of potential energy as a function of kinetic temperature were made by using the data from these simulations. Such plots helped to demonstrate whether or not there was a clear separation in energy among the various states observed. In both cases the data plotted were averages over 1 to 10τ .

A brief digression is in order concerning some important distinctions between simulations performed at constant energy and at constant temperature. The constant-energy simulations of a 13-atom cluster performed by Jellinek et al. were performed in an ensemble having constant energy, zero center of mass momentum, and zero angular momentum about the center of mass. In any constant-energy MD simulation, these three quantities will be conserved, although the latter two will not necessarily be zero, depending on the initial conditions. In constant-temperature simulations that employ stochastic collisions, this is not the case. The center of mass velocity and total angular momentum are in general not zero but fluctuate about zero as a result of the stochastic collisions.

For this reason, even single-phase energy vs. temperature curves obtained in constant-energy and constant-temperature MD simulations should not be expected to agree. To compare energy vs. temperature data obtained from constant-temperature simulations to similar data obtained from constant-energy simulations (with zero center of mass momentum and angular momentum), one can add $3kT$ to the energy in a constant energy simulation, where T in the case is $2/(3N-6)$ times the time-averaged kinetic energy. The quantity $3kT$ represents a contribution to the kinetic energy of $1/2 kT$ for each of three translational and three rotational degrees of freedom (with vibrational-rotational coupling assumed to be weak). This procedure has been followed in calculations appearing later in this paper that are based on a simple model for phase transitions in different ensembles.

In the constant-energy simulations we performed to study coexistence, the clusters in general had overall translational and rotational motion. The contribution to the kinetic energy from this motion was subtracted from the total energy to give the energy values reported in this paper.

At various times during many of the MD runs, the atomic coordinates were saved and later used as the starting point for a potential energy minimization calculation. Observation and structural analysis of these configurations gave information about the inherent structures of the various states attained by the clusters. Such information was useful for interpreting data from the heating and cooling runs as well as the runs that were performed to study coexistence among different phases. In addition, energy minimization runs were performed on larger clusters in an effort to find the most stable zero temperature structure as a function of cluster size. Clusters with both icosahedral and crystalline structure were constructed and energy minimized. The full, untruncated Lennard-Jones potential was used. These calculations were performed on a VAX 11/750 and MicroVAX II.

Structural Analysis Technique

To analyze the structural changes accompanying melting and freezing, we have used a generalization of a technique first used by Blaisten-Farójas¹⁸ for decomposing the first two peaks of the pair correlation function. In this technique, pairs of atoms are classified by (i) whether or not they are near-neighbors, (ii) the number of near-neighbors they have in common, and (iii) the near-neighbor relationships among the shared neighbors. Two atoms are said to be near-neighbors if they are within a specified cutoff distance of each other. We typically used a cutoff distance of 1.4σ in our analyses, which is roughly the distance to the first minimum in the pair correlation function of a solidlike cluster.

A graphical shorthand provides a convenient way of representing the possible types of pairs of atoms (Figure 2). Although this nomenclature is reminiscent of that used in graph theory, here

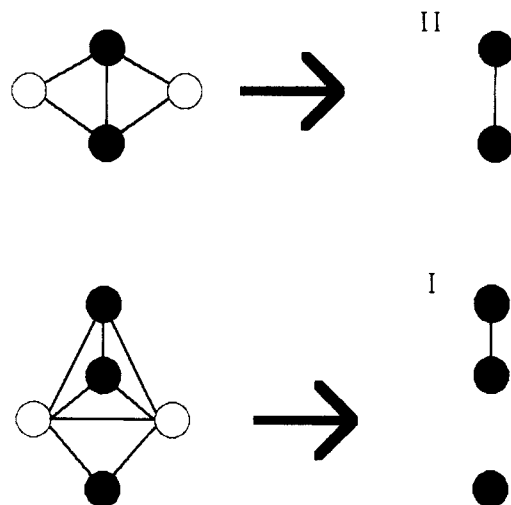


Figure 2. Diagrammatic nomenclature for structural analysis technique. Nearest-neighbors are connected by lines ("bonds").

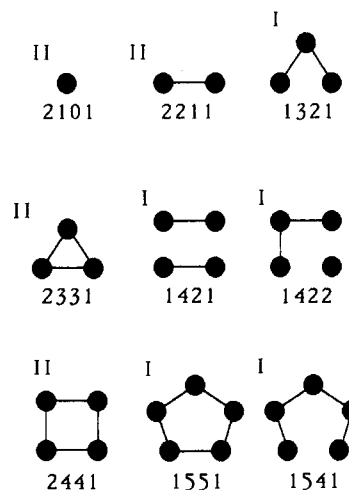


Figure 3. Common diagrams in dense atomic systems.

the diagrams represent physical structures rather than integrals. In a particular diagram, white circles represent atoms in the pair of interest ("root pair"), while black circles represent near-neighbors that these atoms have in common. Atoms that are near-neighbors of each other, as determined by the specified cutoff distance, are connected by lines ("bonds"). Note that two white circles appear in every diagram of this type, and that, by definition, each white circle is bonded to each black circle. Hence, for the sake of neatness and brevity, we can eliminate the white circles from the diagram, with their presence to be understood. This is not sufficient, however, to distinguish between cases where two diagrams are identical except for the bonding between the atoms in the root pair. To distinguish between these two cases, we label a diagram as type I if the atoms making up the root pair are directly connected by a bond or type II if they are not.

For referring to diagrams in the text, we introduce a more compact nomenclature as follows. We can characterize each of the diagrams by a sequence of four integers. The first integer, either 1 or 2, indicates the diagram "type", that is, whether or not the atoms comprising the root pair are near-neighbors. The second integer represents the number of near-neighbors shared by the root pair. The third integer represents the number of bonds among the shared neighbors. These three numbers are not sufficient to characterize a diagram uniquely, so a fourth integer, whose value is arbitrary as long as it is used consistently, is added to provide a unique correspondence between numbers and diagrams. Some diagrams that are prevalent in the systems we have studied are depicted in Figure 3.

Each of the various phases of a dense bulk Lennard-Jones system has its own signature in the diagrams that characterize

TABLE I: Normalized Abundances of Pairs in Bulk Systems^a

pair	crystal		liquid		nucleated solid
	fcc	hcp	equilibrium	supercooled	
2211	2.00	1.50	1.05	0.99	1.52
2101	1.00	1.50	1.61	1.59	1.42
1421	1.00	0.50	0.02	0.03	0.48
2441	0.50	0.50	0.05	0.10	0.40
1422	0	0.50	0.05	0.07	0.29
2331	0	0.17	0.70	0.81	0.22
1551	0	0	0.17	0.26	0.002
1541	0	0	0.16	0.22	0.09
1321	0	0	0.05	0.02	0.01
2321	0	0	0.14	0.09	0.04
1311	0	0	0.03	0.02	0.03

^aNormalized abundances of selected diagrams in various bulk Lennard-Jones systems. Quantities are normalized such that the total number of type I pairs is unity. (The latter three columns are from simulation data for 500-atom systems in periodic boundary conditions.)

TABLE II: Normalized Abundances of Pairs in Clusters^a

pair	local icos		multilayer icos		face-centd cubic	
	N = 13 icos	N = 19 dbl icos	N = 55 icos	N = 147 icos	N = 55 fcc	N = 147 fcc
2211	0	0.07	0.64	0.99	1.83	1.45
2101	0.14	0.32	0.97	1.12	0.79	0.68
1421	0	0	0	0.17	0.83	0.67
2441	0	0	0.26	0.34	0.29	0.28
1422	0	0	0.38	0.39	0	0
2331	0.71	0.81	0.38	0.26	0	0
1541	0	0	0	0	0	0
1551	0.29	0.34	0.10	0.05	0	0
1321	0.71	0.59	0.26	0.13	0	0
2321	0	0	0	0	0.33	0.16
1311	0	0	0.26	0.26	0.17	0.11

^aNormalized abundances of selected diagrams for clusters of various sizes and structures, illustrating local icosahedral order, multilayer icosahedral order, and fcc order. Quantities are normalized such that the total number of type I pairs is unity. (The 19-atom cluster is composed of two interpenetrating 13-atom icosahedra. The other clusters are either Mackay icosahedra or fcc cuboctahedra.)

its local structure. For example, four diagrams are represented in a perfect bulk fcc crystal: 2211, 2101, 1421, and 2441, in the ratios 4:2:2:1. A bulk hcp crystal contains 1422 and 2331 pairs in addition to these four (with overall ratios 9:9:3:3:1 for 2211, 2101, 1421, 2441, 1422, and 2331 pairs, respectively). For a more disordered system, such as a Lennard-Jones liquid, a much greater number of different diagrams appears. The 1421, 1422, and 2441 pairs are present in considerably less abundance than for the close-packed crystalline systems, but 2331 pairs are in greater abundance, and 1551 and 1541 pairs, which are not present in perfect fcc or hcp crystals, are relatively numerous in the liquid. The latter three types of pairs become still more numerous in supercooled liquids and glasses. Table I displays the relative abundances of various diagrams found in bulk systems. These quantities are normalized in each case to make the total number of type I pairs unity.

Clusters with crystalline structure contain the same types of pairs present in bulk crystals, along with additional pairs involving atoms on the clusters' surfaces. By contrast, Mackay icosahedra contain 1551 pairs, which are not present in either fcc or hcp clusters. The larger Mackay icosahedra (of 55 atoms or more) are, however, composed of twinned, distorted fcc tetrahedra. Types of pairs not found in fcc systems can appear only where these tetrahedra meet. The sizes of the tetrahedra and thus the local fcc character of the Mackay icosahedra increase with increasing cluster size. The abundances of the various types of pairs in cuboctahedral fcc and icosahedral clusters for various sizes are shown in Table II.

In this study, we have observed two distinct types of order in the lowest energy structures of clusters containing from 13 to 147 atoms. We shall use the terms "local icosahedral order" and "multilayer icosahedral order" to describe these two types of

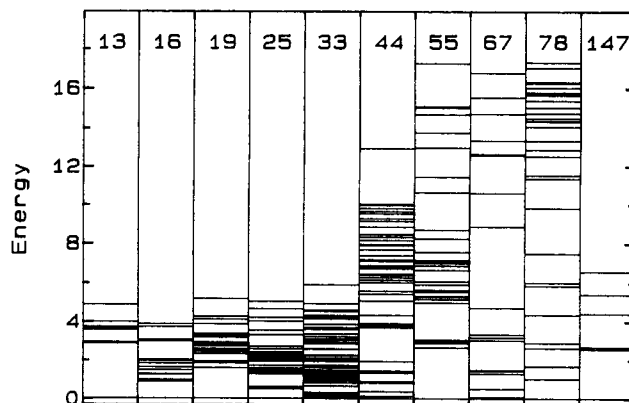


Figure 4. Local energy minima found for clusters containing 13 to 147 atoms. For each cluster size, the zero of energy is taken to be the energy of the apparent ground state. For clusters containing 55 or more atoms, we found minima of higher energy that are not shown.

structure. The latter term has already been used by Farges and co-workers.^{4,17} We define these terms as follows. By local icosahedral order we mean order characteristic of the 13-atom icosahedron, namely the presence of 2331 and 1551 pairs in the absence of 1421, 1422, and 2441 pairs. For a system to have local icosahedral structure as we have defined it, it need not contain a complete 13-atom icosahedron, but only the principal structural motifs characteristic of the icosahedron. By multilayer icosahedral order we mean order characteristic of the larger Mackay icosahedra (of 55 or more atoms), namely the presence of 1422 and 2441 pairs (as well as perhaps 1421 pairs) along with a relatively small but nonzero number of 2331 and 1551 pairs. In a later section we shall present results of this structural analysis technique as applied to clusters at both high and low temperatures.

Results and Conclusions

Melting, Freezing, and Coexistence. The energies of the inherent structures found for the small clusters help provide a unified interpretation of the dynamics results for the various system sizes. The "spectra" of local energy minima for several different cluster sizes are shown in Figure 4. In this figure, the energy of the most stable structure found for each system size is set to zero, and energies of other local minima are expressed with respect to this state. The most stable structure of a given system was assumed to be the structure of lowest energy into which such a system was observed to freeze upon slow cooling, unless a structure of lower energy was constructed by different means. The energies depicted in Figure 4 are local minima found as a result of quenching configurations from a variety of different MD runs, including constant-energy and constant-temperature runs, as well as heating and cooling runs. For systems of 55 or more atoms there are local minima of higher energy that are not shown in Figure 4. These correspond to inherent structures of liquidlike or glasslike states.

A caveat should be noted here. The method of energy minimization of configurations generated in our simulations by no means constitutes an exhaustive search for local energy minima. However, all of the minima we have found do correspond to states actually achievable by systems undergoing fairly realistic dynamical motion, as opposed to minima that might have low energies but not be accessible because of large kinetic barriers. It is conceivable that there are local minima in the gaps between the lowest energy structure observed and what appear in Figure 4 to be the lowest lying excited states. On the other hand, all of our data concerning the separation between the lowest energy structure, its low-lying excitations, and higher energy states for the various cluster sizes are consistent with the dynamical behavior exhibited by the simulated clusters.

The clusters of various sizes fell into natural groups depending on their melting and freezing behavior and the structure of the low-temperature phase. Each of these groups will be discussed separately.

Magic Numbers: $N = 13$. The energy spectrum for the 13-atom system (Figure 4) indicates that the minimum-energy

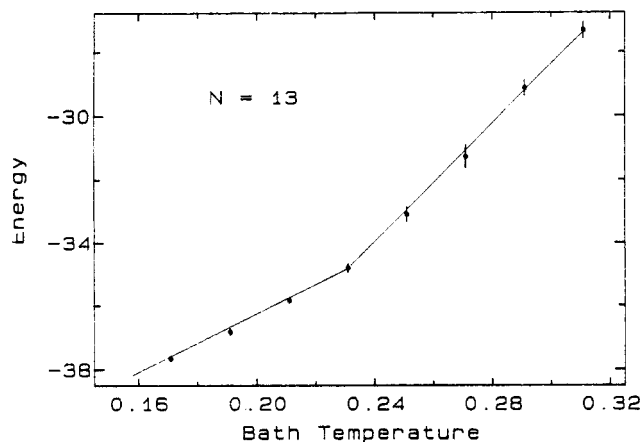


Figure 5. Energy as a function of bath temperature for a 13-atom cluster. Values are expressed in reduced units. Each data point represents the average energy over a temperature interval of $0.02\epsilon/k$ as the bath temperature is raised at a rate of $1.0 \times 10^{-5}\epsilon/k$ per τ .

structure for this system—the icosahedron—is quite stable relative to local minima of higher energy. It appears that the lowest lying excitation of the 13-atom icosahedron is part of the high-energy manifold of inherent structures characteristic of the liquidlike phase rather than a distinct structure intermediate between the icosahedron and liquidlike states. This is not the case for larger icosahedra, for which distinct intermediate states were observed. Hoare and McInnes have found 988 different local energy minima for the 13-atom system.⁷ By energy minimization of solidlike and liquidlike 13-atom clusters, we have found 9 minima, a small fraction of this number. However, our results agree with those of Hoare and McInnes for the magnitude of the energy gap between the icosahedron and its first excitation, giving us some confidence that there are no minima in this gap that we have missed. The gap suggests that there are (at least) two phases for the 13-atom cluster.

A plot of the energy as a function of bath temperature obtained by slowly heating a 13-atom icosahedron from zero temperature is depicted in Figure 5. Note that the slope of the curve changes sharply over a narrow temperature range, while the value of the energy does not abruptly change. The conditions of this simulation approximate the conditions of a canonical ensemble. In a true canonical ensemble, however, the bath temperature remains at a fixed value, while in the simulation, the bath temperature was slowly changed (at a rate of $1.0 \times 10^{-5}\epsilon/k$ per τ).

For the 13-atom system, evidence of coexistence of two distinctly different phases was seen over a wide range of energies and temperatures. Figure 6 depicts a typical coexistence run at constant energy for this system size. The cluster's potential energy fluctuates within two narrow and well-separated ranges and only occasionally jumps abruptly from one range to another. For simulations of duration 500τ , similar such evidence of coexistence was seen for cluster energies between -35.6ϵ and -25.5ϵ in the constant-energy simulations, and for reduced bath temperatures between 0.23 and 0.32 in the constant-temperature simulations. At temperatures higher than 0.32 in the constant-temperature simulations the cluster would begin to evaporate.

The lowest temperature at which coexistence was observed in the constant-temperature (canonical ensemble) simulations coincides with the abrupt change in heat capacity evident in Figure 5. Thus, the distinct feature in the heating curve, which has the superficial appearance of a second-order-like transition, corresponds to a boundary between a low-temperature region, in which the cluster adopts only the lowest energy inherent structure, and an intermediate temperature region in which two phases coexist. A high-temperature region, containing *only* the higher temperature phase, cannot be observed in the constant-temperature simulations due to evaporation.

Our results for the equilibrium energy as a function of temperature for the 13-atom system agree with the Monte Carlo data of Etters and Kaelberer¹² as well as the data of Quirke and

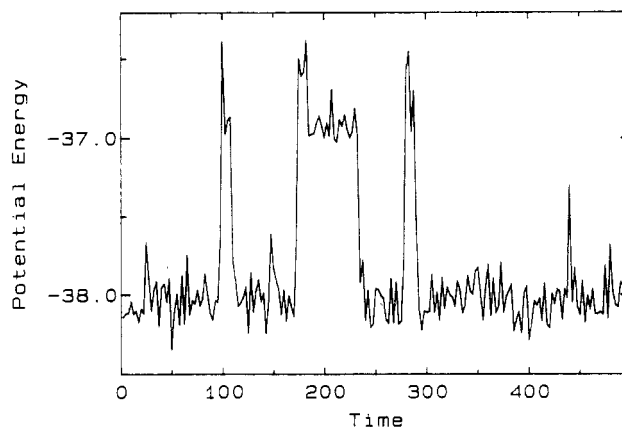


Figure 6. Coexistence run for a 13-atom system at an energy of -33.5ϵ . Time and potential energy are expressed in reduced units.

Sheng,¹⁵ which correspond to a canonical ensemble. They are in apparent disagreement with the constant-energy MD data of Jellinek et al.,¹⁹ which correspond to a microcanonical ensemble, in two respects. First, the results of Jellinek et al. for the energy as a function of temperature are quite different in the coexistence region and display an inflection point. Second, the range of temperatures over which they observed coexistence is much smaller than the range over which we observed it. In what follows, we shall present calculations based on a simple model that indicate that this apparent disagreement arises from the difference between the canonical and microcanonical ensembles.

Coexistence between a solidlike and liquidlike phase can be regarded as a chemical equilibrium:



At constant temperature in the canonical ensemble, the relative amount of time spent in each of the two phases is determined by the difference in their free energies. At constant energy in the microcanonical ensemble, the relative amount of time spent in each of the phases is determined by the difference in their entropies. If $E(T)$ or $T(E)$ is known for each of the two phases, and if the free energy difference is known at a given temperature or the entropy difference is known at a given energy, then the relative amount of time spent in each of the two phases can be calculated for either ensemble. If one assumes that these are the only two phases present, then the energy at any temperature in the canonical ensemble is given by

$$E_{\text{eq}}(T) = x_{\text{sol}}(T) E_{\text{sol}}(T) + x_{\text{liq}}(T) E_{\text{liq}}(T) \quad (3)$$

or the temperature at any energy in the microcanonical ensemble is given by

$$T_{\text{eq}}(E) = x_{\text{sol}}(E) T_{\text{sol}}(E) + x_{\text{liq}}(E) T_{\text{liq}}(E) \quad (4)$$

where x_{sol} and x_{liq} represent the fraction of time spent in the solidlike and liquidlike phases, respectively. (The temperature appearing in this equation is the kinetic temperature, defined for the constant-energy case as $2/(3N - 6)$ times the kinetic energy divided by Boltzmann's constant, and not the thermodynamic temperature, defined as the derivative of the total energy with regard to entropy. Equation 4 is derived from the equation for the average kinetic energy for coexisting phases.)

To predict the equilibrium $T(E)$ or $E(T)$ curve for a 13-atom cluster based on the above model, we need to know the thermodynamic properties of each phase. Because our constant-temperature data did not provide the energy as a function of temperature for a purely liquidlike phase, due to the onset of evaporation, we have used the data of Jellinek et al.

The solidlike and liquidlike $T(E)$ curves were assumed to be linear. It was found that least-squares fits to what Jellinek et al. claimed were single-phase data in the high-energy region resulted in a predicted equilibrium curve that disagreed significantly with the equilibrium curve that they found. It appears that there was a small amount of the solidlike phase still in coexistence with the liquidlike phase at the highest energy they studied, about -26.8ϵ .

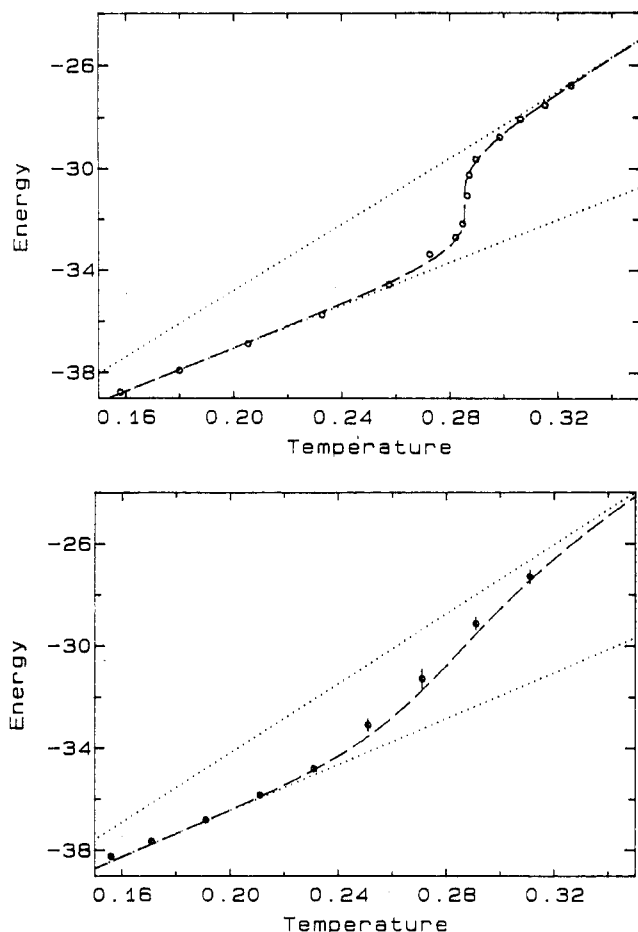


Figure 7. (a) Comparison of calculated microcanonical energy-temperature curve with constant energy MD data of Jellinek et al. for a 13-atom system (from ref 19). (b) Comparison of calculated canonical energy-temperature curve with our constant temperature MD data for a 13-atom system. In both (a) and (b), points are MD data; dotted curves correspond to the two states assumed in the model; dashed curve is the equilibrium curve predicted by the model. In (a) the equations for the single-phase lines are (in reduced units, with $k = 1$) $T_{\text{sol}} = 1.0815 + 0.02379E$ and $T_{\text{liq}} = 0.7352 + 0.01538E$. The energy at which the entropies of the two phases are equal was determined graphically to be $E = -31.8$. In (b) the equations for the single-phase lines are $E_{\text{sol}} = -45.46 + 45.03T$ and $E_{\text{liq}} = -47.79 + 68.00T$. The single-phase curves in (b) were obtained from those in (a) by expressing the energy in terms of the temperature and adding $3T$ to account for rotational and translational degrees of freedom present in constant-temperature simulations that are not present in constant-energy simulations.

This is confirmed by the fact that we have seen evidence of coexistence of the icosahedron and liquidlike states in constant-energy dynamics for energies as high as -25.4ϵ . When the $T(E)$ curve for the liquidlike phase was slightly modified to account for this, good agreement was obtained between the predicted and observed equilibrium curve (Figure 7a).

To make the connection with the canonical ensemble, we assumed that the $T(E)$, or equivalently $E(T)$, curves for the individual phases are the same for the canonical and microcanonical (with constant center of mass momentum and angular momentum) ensembles, once proper account is made for the differing number of degrees of freedom in the two cases. With this assumption, the chemical equilibrium model predicted an equilibrium $E(T)$ curve for the 13-atom system in a canonical ensemble that gave reasonable agreement with our data and with the Monte Carlo data of others^{12,15} (Figure 7b). Thus the two types of simulation data for the 13-atom cluster are in fact consistent with each other and consistent with a simple equilibrium constant model for a cluster with two phases.

Larger Magic Numbers: $N = 55, 147$, and 309. Energies as functions of temperature are shown in Figure 8 for heating and cooling simulations of 55- and 147-atom clusters. Both of these

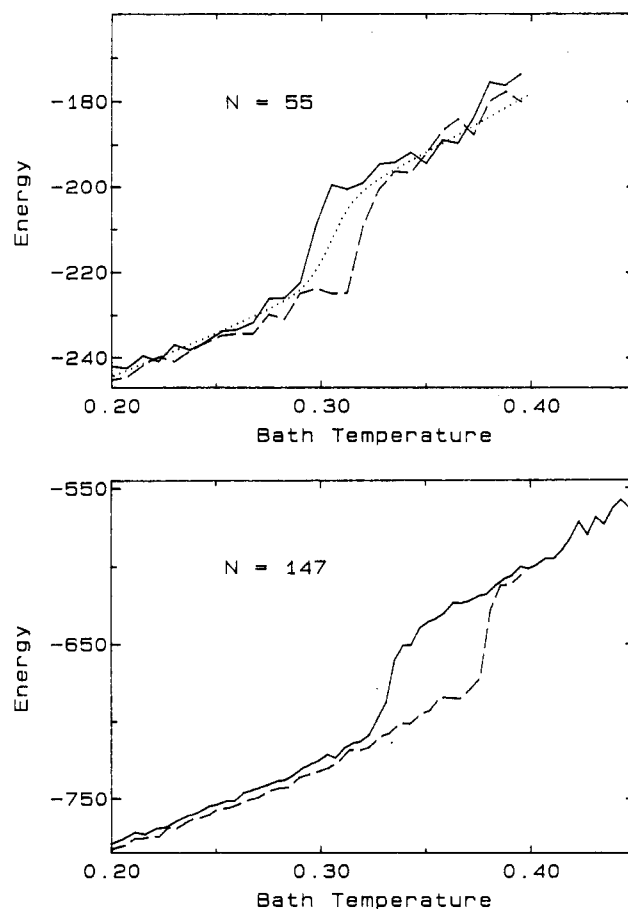


Figure 8. Heating and cooling curves for (a) 55- and (b) 147-atom clusters. Solid lines are cooling curves; dashed lines are heating curves. Dotted line in (a) depicts equilibrium curve predicted by a three-state model. (See text for description of model.)

systems were observed to undergo sharp freezing transitions upon cooling and similar sharp melting transitions upon heating. The hysteresis indicates that these first-order-like transitions do not represent the equilibrium behavior. At the cooling rates used in these runs, the 55-atom cluster froze into a perfect Mackay icosahedron in two separate simulations. No lower energy structures were observed for the 55-atom cluster in the simulations or were obtained by direct construction. Therefore the apparent minimum energy structure for the 55-atom Lennard-Jones cluster is indeed the perfect Mackay icosahedron. Only one cooling run was performed for the 147-atom cluster. This cluster froze into an icosahedron with a single defect—a misplaced vertex atom. This type of defect appears to be the first excitation of the icosahedron as shown in Figure 4. In the heating runs, the initial configurations were Mackay icosahedra. For this reason, the heating and cooling curves for the 147-atom system do not coincide at low temperature.

When cooled at the same rate as the 147-atom system, a liquidlike 309-atom system froze into a structure that had some of the gross features of the Mackay icosahedron of this size, but that was highly defective. Slower cooling for such a large system size would have consumed an unreasonable amount of computer time and was therefore not attempted.

The cooling rates used for these systems were 5.0×10^{-5} ($N = 55$) and 1.0×10^{-5} ($N = 147$) reduced temperature units per τ . Using values of the Lennard-Jones parameters appropriate to argon ($\sigma = 3.4 \text{ \AA}$; $\epsilon/k = 120 \text{ K}$),³⁴ these rates are 2.79×10^9 and $5.58 \times 10^8 \text{ K/s}$.³⁵ For cooling rates significantly faster than

(34) Michels, A.; Wijker, H. U. B.; Wijker, H. K. *Physica* **1949**, *15*, 627.

(35) For the 147-atom system, the cooling rate reported above was used to cool the cluster from a reduced temperature of 0.45 to a temperature of 0.25, after which the system was cooled at 2.5 times this rate until zero temperature was reached. Freezing took place at a temperature of about 0.32. The 309-atom system was cooled only to a temperature of 0.34, with the freezing transition taking place at a temperature of about 0.40.

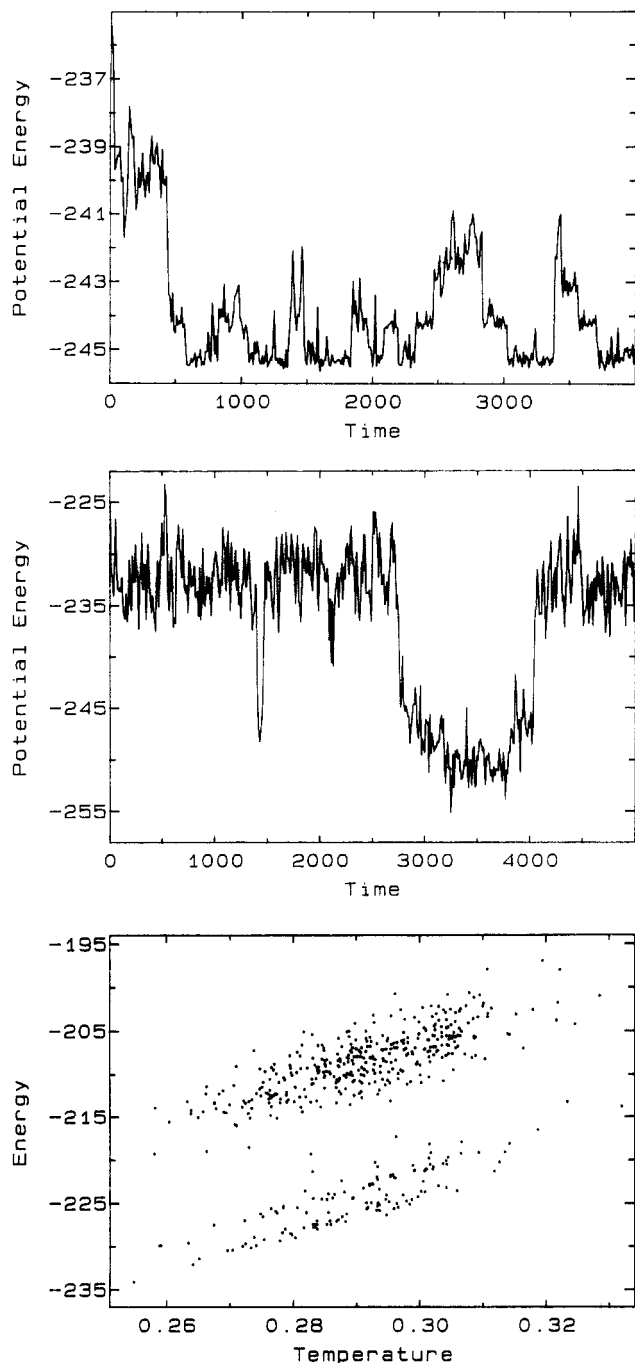


Figure 9. Coexistence data for the 55-atom cluster. (a) Constant energy, $E = -219.6$; (b) constant temperature, $T_{\text{bath}} = 0.29$; (c) energy as a function of kinetic temperature for run depicted in (b). Each point represents an average over 10τ .

these, 55- and 147-atom clusters froze into defective structures having considerably higher energies than perfect icosahedra.

The 55- and 147-atom systems display the large gap between the lowest energy structure observed and its first excitation seen for the 13-atom case. For these larger systems, however, the first few excitations of the icosahedra are clearly distinct, in energy and in structure, from liquidlike states. Coexistence runs indicate that for the 55-atom system these low-lying excitations can coexist in equilibrium with either the icosahedron or the liquidlike state or both. We shall focus principally on the 55-atom cluster in the remainder of this section.

Figure 9a provides a striking example of coexistence of the apparent minimum energy structure and its low-lying excitations in the 55-atom cluster. The regions of differing potential energy in this figure correspond to (in order of increasing potential energy) the 55-atom icosahedron, the icosahedron with one or two misplaced vertex atoms, the icosahedron with one misplaced vertex

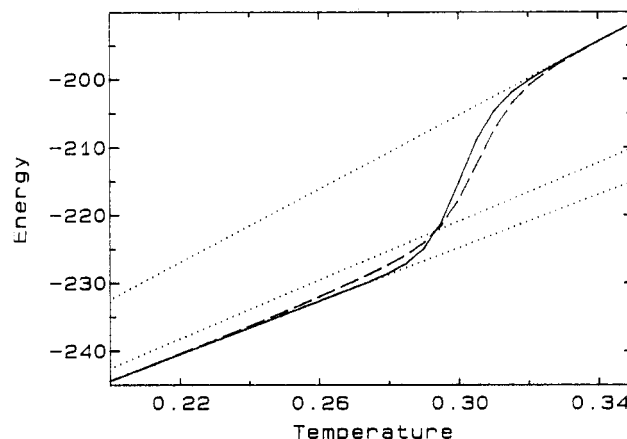


Figure 10. Calculated equilibrium curves for the 55-atom canonical system. Dashed curves are predictions based on the two-state model; solid curves are predictions based on the three-state model; dotted curves correspond to the three states assumed in the model.

atom and one misplaced edge atom, the icosahedron with four misplaced vertex atoms, and the liquidlike phase, which existed only near the beginning of the run. For this run, the liquidlike states should not be regarded as in coexistence with the other states since the system never reentered liquidlike structures from any of the other structures.

For runs performed at higher energies, and for some of the constant temperature runs, coexistence was seen among the perfect icosahedron, the liquidlike phase, and one or more states of intermediate potential energy. Figure 9, parts b and c, depicts potential energy as a function of time and total energy as a function of internal temperature for a 55-atom system at a bath temperature of 0.29. Figure 9c clearly illustrates the presence of a state intermediate between the icosahedron and higher energy liquidlike states, with its own separate energy vs. temperature curve. This intermediate state was the icosahedron with a single misplaced vertex atom, which appears to be the first excitation of the icosahedron.

For constant-temperature simulations as long as 5000τ , evidence of coexistence was seen between temperatures of 0.280 and 0.315. Below the lower temperature, only the perfect icosahedron was observed, and above the upper temperature only liquidlike structures, with inherent structures of energy greater than the simple excitations of the icosahedron, were observed. When coexistence was observed, one of the phases always consisted of these simple excitations. The solid icosahedron was observed for temperatures as high as 0.31 and the liquidlike states were observed for temperatures as low as 0.29. The temperature range over which coexistence was observed approximately coincides with the range in which hysteresis is observed in the heating and cooling curves of Figure 8a.

In constant-energy simulations as long as 5000τ , coexistence was seen between energies of -231.9ϵ and -210.1ϵ . In the lower part of this range (below -219.6ϵ), coexistence was seen only between the icosahedron and its simple excitations. At the upper end of this range, coexistence was seen only between liquidlike states and simple excitations of the icosahedron, but not the icosahedron itself.

The most prevalent intermediate state in the simulations was the first excitation of the icosahedron, corresponding to a misplaced vertex atom. Using the data depicted in Figure 9c, we were able to calculate the thermodynamic properties of this state and predict the shape of the equilibrium $E(T)$ curve based on a three-state model (a generalization of the model used for the 13-atom system). Such a curve is compared in Figure 10 with predictions of a two-state model, in which only the icosahedron and liquidlike states were assumed to exist. The presence of the intermediate state broadens the transition significantly, especially on the low-temperature end. The dotted curve in Figure 8a depicts the $E(T)$ curve predicted by the three-state model.

Both the two-state and three-state models predict a significant

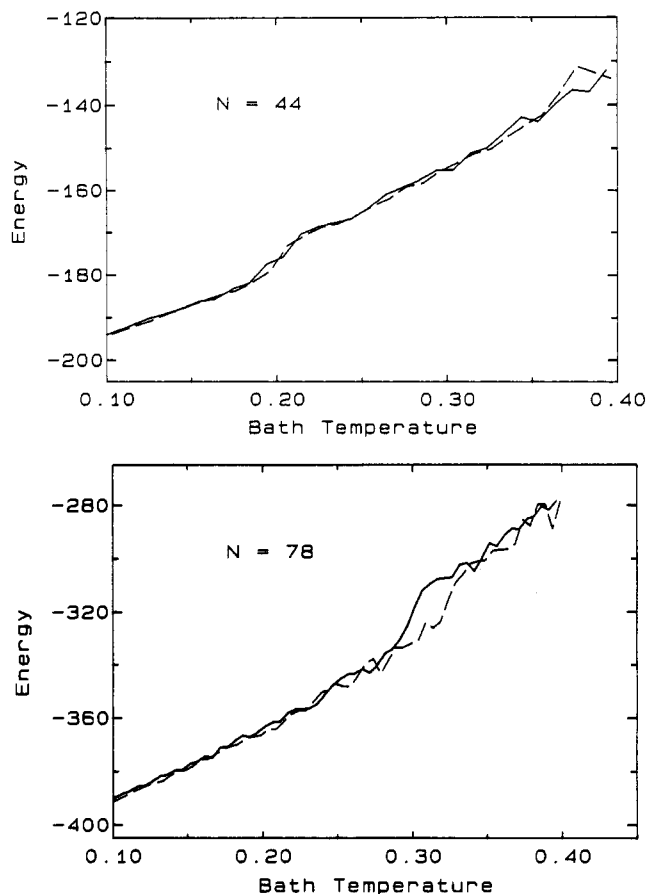


Figure 11. Heating and cooling curves for (a) 44- and (b) 78-atom clusters. Solid curves are cooling curves; dashed curves are heating curves.

van der Waals-like loop in the $T(E)$ curve for a 55-atom system in the microcanonical ensemble; i.e., the function contains a maximum, an inflection point, and a minimum. Our constant-energy simulation data can neither confirm nor contradict the presence of this feature, due to noise in the data.

Only a small number of coexistence runs was performed for the 147-atom system. For simulations lasting up to 5000τ , coexistence was seen only between a liquidlike state and various highly disordered solidlike states, but not the perfect icosahedron. It is possible that, for appropriate energies or temperatures, coexistence between a liquidlike state and the perfect icosahedron does occur, but is likely that runs of longer duration would be required to see this behavior.

Nonmagic Numbers: $44 \leq N < 147$. The cooling rates for which 55- and 147-atom clusters fell into the Mackay icosahedron or its first excitation were used in cooling runs for clusters of comparable size containing nonmagic numbers of atoms. Clusters of 44, 67, 78, and 100 atoms displayed fairly sharp freezing transitions that were first-order-like in appearance, although not as sharp as the transitions seen for the 55- and 147-atom clusters. (The data are shown for the 44- and 78-atom clusters in Figure 11. The behavior of the 67- and 100-atom systems was similar to that of the 78-atom system.) Except for the 44-atom case, these systems displayed hysteresis in their cooling and heating curves, indicating that equilibrium was not achieved in the transition region. Repeated cooling runs for these four sizes led to different inherent structures with slightly different energies at zero temperature, indicating lack of equilibration at low temperatures. This appears to be due to the fact that there is no single deep energy well in configuration space into which any of these systems can fall upon freezing. (See the spectra of inherent structure energies in Figure 4.)

Although none of the nonmagic number clusters containing 44 atoms or more froze into the same structure in two separate cooling runs, the structures obtained in two runs for a given cluster size

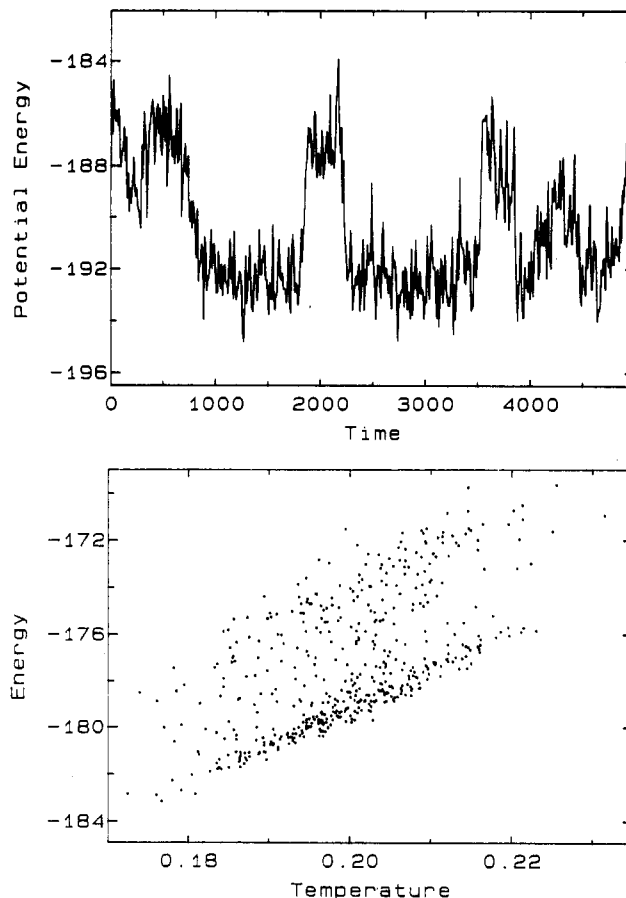


Figure 12. Constant-temperature coexistence data for a 44-atom cluster. (a) Potential energy as a function of time for $T_{\text{bath}} = 0.20$; (b) energy as a function of kinetic temperature for run depicted in (a). Each point represents an average over 10τ .

were similar and differed only slightly in energy. Based on observation of the gross features of these low-temperature clusters, it appears that clusters in this size range assume structures similar to the Mackay icosahedra, inasmuch as it is possible. The structural analysis technique described above demonstrates that these clusters are characterized by multilayer icosahedral order. The low-temperature structures typically consist of a core Mackay icosahedron (of 13 or 55 atoms) with surplus atoms clumped together on the surface. When a sufficiently large number of excess atoms are on the surface, the atoms appear to form an incomplete layer appropriate to the next larger Mackay icosahedron. Farges and co-workers have noted similar structures in their simulated clusters of comparable size.^{4,17}

Figure 4 illustrates that the gap between the lowest energy structure observed and its low-lying excitations is smaller for the 44-, 67-, and 78-atom clusters than for the Mackay icosahedra. (Inherent structure studies were not performed for the 100-atom system.) The large gap in energy between a Mackay icosahedron and its low-lying excitations is a consequence of the icosahedron's closely packed surfaces. For the clusters containing nonmagic numbers of atoms, the surfaces of the lowest energy structures observed are not as closely packed, because there are insufficient atoms to form a complete outer layer; thus, displacing a surface atom on a nonmagic number cluster does not in general require as much energy as does displacing an atom on the surface of a complete Mackay icosahedron. As a result, the nonmagic number clusters have excitations of lower energy.

Among the larger ($44 \leq N < 147$) clusters containing nonmagic numbers of atoms, coexistence was studied only for the 44-atom system. The data display evidence of coexistence among more than two structures (Figure 12). In Figure 12b, regions corresponding to the lowest energy structure observed and to disordered states of high potential energy can be distinguished, but the data also indicate the presence of a large number of intermediate states.

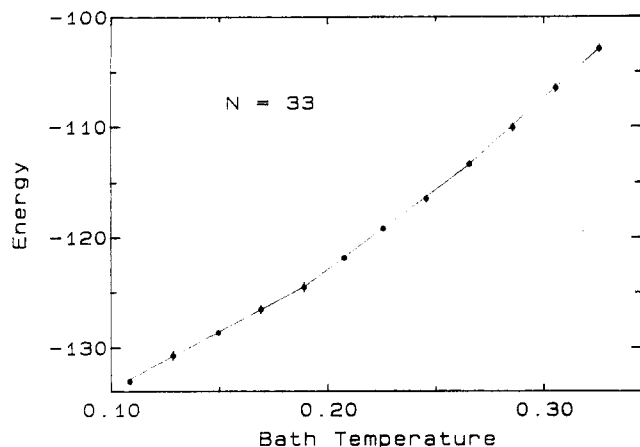


Figure 13. Energy as a function of bath temperature for a 33-atom cluster.

Nonmagic Numbers: $13 \leq N \leq 33$. Cooling and heating runs performed for clusters of 33 or fewer atoms containing nonmagic numbers of atoms displayed qualitatively different behavior from that of the larger systems. This is illustrated in Figure 13 which depicts a slow heating curve for the 33-atom system. There is no abrupt change in either the heat capacity or the energy as the temperature is increased. Slow cooling and heating for 16-, 19-, and 25-atom systems displayed sharper changes in the heat capacity than for the 33-atom case, but no sharp changes in the energy over a narrow temperature range as was seen in systems of 44 or more atoms.

When cooling runs were repeated with different initial configurations, it was found that clusters of 16, 19, and 25 atoms froze into the same low-temperature states in the two different runs. The 33-atom system, on the other hand, did not.

The energies of the inherent structures for these systems help explain this behavior (Figure 4). For the 33-atom system there is virtually a continuum of local energy minima from the lowest energy structure observed upward. Because there are no clear gaps between the low-lying states for this system, phase change behavior appears unlikely, in agreement with the data obtained from slow heating. Inherent structures found for the 16-, 19-, and 25-atom systems indicate that the lowest lying excitations for these clusters are at least 0.49ϵ above the apparent minimum-energy structures. While these gaps are much smaller than the gaps found for the Mackay icosahedra, they are larger than for the 33-atom case.

The low-temperature structures of some of the smaller clusters are depicted in Figure 14; these structures were obtained from slow cooling runs. For 16, 19, and 25 (but not 33) atoms, these structures are apparent minimum-energy structures. Based only on gross features, it is clear that these structures are qualitatively different from the structures of the larger clusters. (For example, contrast these clusters with the 55-atom icosahedron in Figure 1.) Subunits of local fivefold symmetry are prevalent in these structures, although there is not necessarily any overall fivefold symmetry. These clusters are characterized by a large amount of local icosahedral order as defined in the previous section.

Of the smaller clusters containing nonmagic numbers of atoms, coexistence runs were performed for 19-, 25-, and 33-atom clusters. Coexistence among at least three states was indicated by the constant-energy data obtained for all three systems, as well as by the constant-temperature data for the 19-atom system. For the 25- and 33-atom systems, the constant-temperature data were less clear, and it was difficult to distinguish transitions among different types of structure from noise. In light of the energy minima found for these systems, this behavior is not surprising. The very small gaps between local energy minima for the 33-atom system, and to a lesser extent for the 25-atom system, are consistent with the coexistence results. For the 19-atom system, on the other hand, the gap between the apparent minimum-energy structure and its first excitation is larger than for any other systems containing nonmagic numbers of atoms, and coexistence was clearly indicated

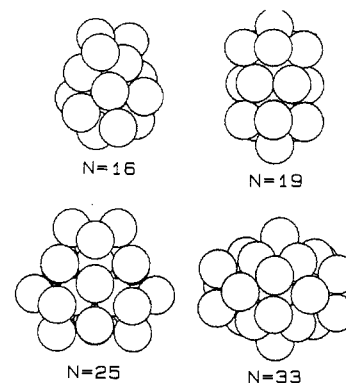


Figure 14. Structures of apparent ground states for clusters containing 16, 19, 25, and 33 atoms.

in both constant-energy and constant-temperature simulations.

The 19-, 25-, and 33-atom systems all appear to have coexistence ranges extending on the high-temperature side to temperatures at which evaporation begins to occur, and none of the heating or cooling curves for these systems give evidence of a one-phase liquidlike region at high temperatures.

Nonmagic Numbers: $33 < N < 44$. The results above show a qualitative difference between the lowest energy structures observed for the smaller (33 or fewer) and larger (44 or more) nonmagic number clusters. This was seen by Farges and co-workers^{4,16,17} in their MD simulations of Lennard-Jones clusters. They reported a crossover from what they called polyicosahedral structure by multilayer icosahedral structure at a cluster size of about 35 atoms. The term "polyicosahedral" was used to refer to clusters containing two or more interpenetrating 13-atom icosahedra. Our simulation results provide further evidence (although not proof) that the two types of structures seen by Farges et al. are the structures of the true minimum-energy structures for systems of the appropriate sizes.

We performed cooling runs for clusters in the crossover region containing 38, 39, and 41 atoms. For cooling at a rate of $5 \times 10^{-5}\epsilon/k$ per τ , the following results were obtained. Two independent cooling runs of a 38-atom system demonstrated behavior similar to that seen in systems of 33 and fewer atoms; i.e., a relatively smooth transition and a low-temperature phase with local icosahedral order (which means much the same as "polyicosahedral order" but which does not require the existence of two or more complete 13-atom icosahedra). Although the low-temperature structures obtained from the cooling runs were both characterized by local icosahedral order, they were not identical. For the 39-atom system, two independent cooling runs demonstrated behavior characteristic of the larger systems; i.e., a first-order-like transition and a low-temperature phase whose appearance was that of an incomplete 55-atom icosahedron. In this case, the low-temperature structures obtained from the two runs were identical, indicating that the structure observed is the apparent minimum-energy structure. Of two cooling runs performed for a 41-atom system, one resulted in behavior characteristic of the smaller systems and the other in behavior characteristic of the larger systems.

Energy minimization results revealed that the locally icosahedral structures into which the 38- and 41-atom clusters froze are not the minimum-energy structures for these cluster sizes. After energy minimization, these cooled clusters had greater energies than clusters of the same size that were constructed by peeling surface atoms from a 55-atom icosahedron. In addition, the multilayer icosahedral 41-atom cluster was of lower energy than the locally icosahedral 41-atom cluster.³⁶

(36) For the 41-atom system, estimates of cluster free energies based on the simulation data indicate that, at the transition temperature, the locally icosahedral structure has a slightly lower free energy than the multilayer icosahedral structure, even though the latter is more stable at zero temperature. No transitions between the two types of structure were seen below the transition temperature, presumably because of poor kinetics.

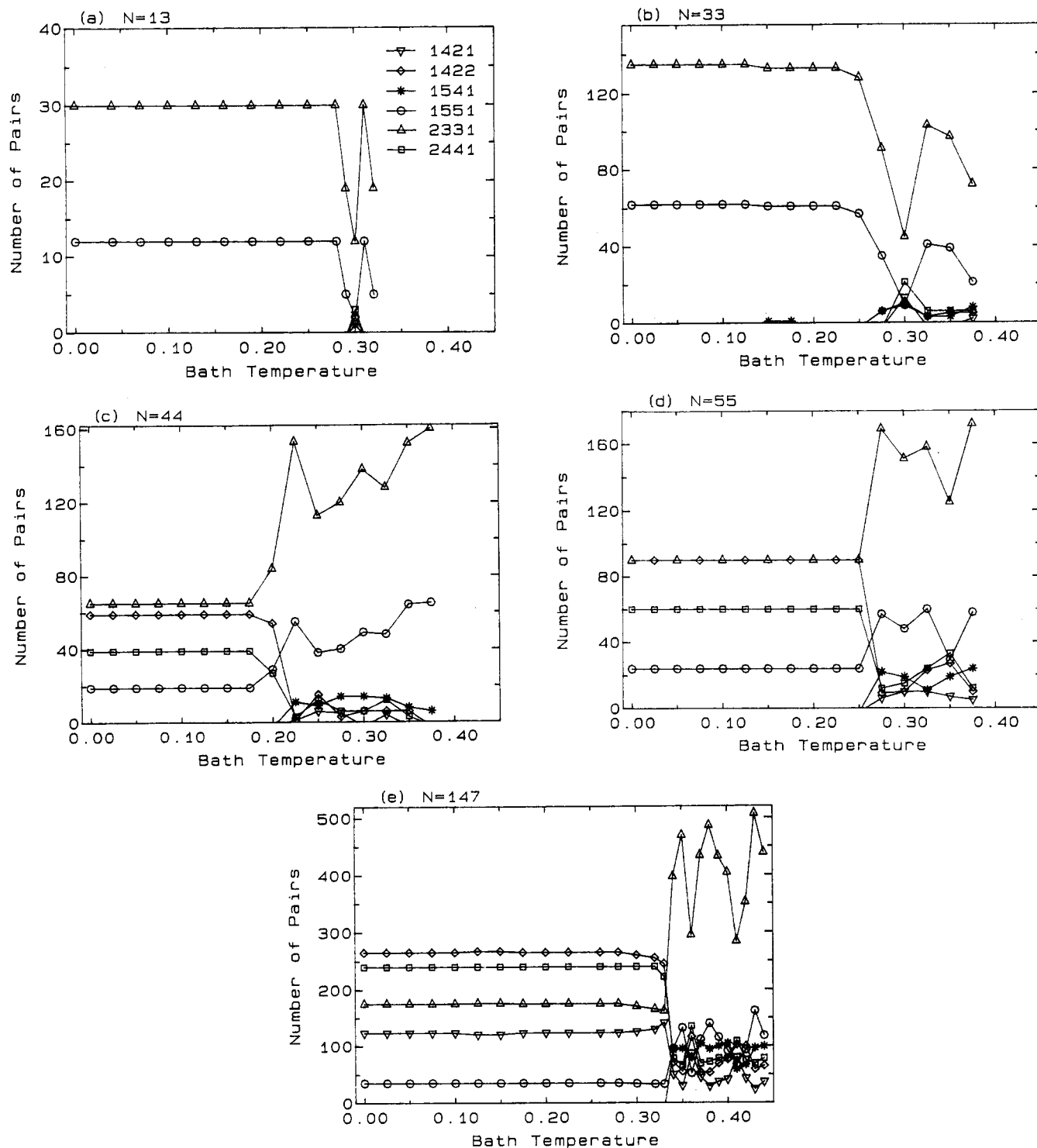


Figure 15. Abundances of selected pairs as functions of bath temperature for (a) 13-, (b) 33-, (c) 44-, (d) 55-, and (e) 147-atom systems. Points lying on the x axis are not shown for the sake of clarity.

For the 33-atom system, a locally icosahedral structure obtained from simulations has a lower energy than an energy-minimized 33-atom cluster constructed by peeling atoms from a 55-atom icosahedron. Thus, it appears that the crossover in the structure of the lowest energy structure observed occurs between system sizes of 33 and 38 atoms, in agreement with the results of Farges and co-workers.⁴

Structural Changes Accompanying Freezing. We have mentioned the qualitative differences in the structure of the low-temperature phase exhibited by the smaller ($13 \leq N \leq 33$) and larger ($44 \leq N \leq 147$) clusters. In this section we will make the comparison between the two cases somewhat more quantitative, making use of the structural analysis technique described above.

Figure 15 displays the relative abundances of various types of pairs of atoms as a function of temperature for clusters of 13, 33,

44, 55, and 147 atoms. Each graph was obtained from a single heating or cooling run. The configurations used in the analysis were energy minimized before being analyzed, in part to help eliminate apparent changes in structure due solely to density changes and in part to better distinguish among the different states in the coexistence region for the smaller systems.

Figure 15 illustrates the change in the nature of the freezing transition as the cluster size increases from 33 to 44 atoms. The final transition to the low-temperature structure for the 33-atom system is characterized by a rise in local icosahedral order; that is, a rise in the number of 2331 and 1551 pairs. The structure of the larger system, on the other hand, appears to undergo a discontinuous change in its structure upon freezing, into a state of less local icosahedral order and greater multilayer icosahedral order. All of the systems of 33 atoms or fewer that were studied

displayed behavior qualitatively similar to that for the 33-atom case. All of the systems of 44 atoms or more displayed the apparent discontinuous change in structure displayed by the 44-atom case.

Each of the clusters of 19 or more atoms that displayed local icosahedral ordering, as determined by the structural analysis method, was found to contain at least two interpenetrating 13-atom icosahedra. Based on energies and appearance, some of the zero temperature clusters of from 19 to 38 atoms generated in our MD cooling runs appear to be identical with or similar to polyicosahedral structures constructed by Farges et al.⁴

Glass Transition. In addition to the "slow" cooling runs reported above, that were designed to achieve low-temperature equilibrium structures, fast cooling runs were performed to determine whether or not small clusters undergo any process analogous to the glass transition of bulk materials. We found that clusters of 44 atoms or more, when cooled rapidly, have two additional types of behavior, which are analogous to imperfect crystallization and the glass transition.

For cooling rates slightly faster than those that allow the cluster to fall into its minimum-energy structure, the cluster may at some temperature change its structure abruptly and achieve a greater amount of multilayer icosahedral order. This type of ordering is also a characteristic of the lowest energy structures observed for clusters of this size, so this behavior is analogous to that of a supercooled liquid that crystallizes imperfectly on rapid cooling. This change in structure is usually accompanied by an abrupt drop in the energy over a range of temperatures, leading to a curve that resembles that of a broadened first-order transition.

For faster cooling rates, quite different behavior may be observed in that there is no abrupt increase in the amount of multilayer icosahedral order, and the cluster at low temperatures is characterized by a significant amount of local icosahedral order. When this takes place, the energy as a function of temperature usually (but not always) undergoes an abrupt change in slope at some temperature. This behavior is analogous to that observed in the glass transition of bulk liquids.

The basis for these two different types of behavior for clusters of 44 or more atoms is easily understood from the results discussed above about the nature of the local energy minima of these clusters. In particular, the lowest energy structures observed and one or more higher energy structures are similar to or identical with (complete or incomplete) Mackay icosahedra and have energies that are distinctly lower than those of the states populated at high temperatures. If the cooling rate is small enough for the system to fall into this low-energy manifold, the energy will drop abruptly. The system will then either eventually fall into the true minimum-energy state, in a way analogous to perfect crystallization of a bulk material, or it will remain in an excited state in this manifold, in a way analogous to imperfect crystallization. If the cooling rate is too fast for the system to fall into this manifold, the energy of the cluster remains high and does not drop abruptly, but the system falls out of equilibrium and the heat capacity drops when it is no longer able to make transitions from one state to another.

For smaller nonmagic number clusters (less than 33 atoms), it does not appear to be worthwhile to try to distinguish imperfect crystallization from a glass transition for rapidly cooled clusters. The equilibrium behavior of these clusters appears to generate cooling curves with the appearance of a glass transition, and the lowest energy states observed are locally icosahedral, like the glassy structures of the larger clusters.

The Onset of Crystalline Structure. A question relevant to the study of small clusters and to the transition from behavior characteristic of a finite system to behavior characteristic of the bulk is, At what size does a crystalline cluster become more stable than an icosahedral cluster? The somewhat inconclusive theoretical and experimental evidence relating to this question is reviewed in the Introduction of this paper.

We performed energy minimization of various clusters with a full Lennard-Jones potential to try to find the minimum cluster size for which the fcc structure is more stable than the Mackay

TABLE III: Binding Energies of Minimized Clusters^a

N	structure				
	icos	fcc sp	hcp sp	fcc oct	fcc cuboc
19	3.8242	3.6288	3.6340		
44	0.7202			4.6110	
55	5.0773	4.8778	4.9117		4.8778
87		5.2720	5.2500		
146		5.7782		5.7641	
147	5.9623	5.7828	5.8636		5.8121
309	6.4959	6.3779	6.3926		6.3805
1415	>7.2848	7.2470	7.2306		7.2311
3871	>7.6319	7.6265			
5083	>7.7108	>7.7120			

^a Binding energies of clusters of various structures after energy minimization. Values in this table are total binding energies divided by the number of atoms. The symbol > indicates that complete minimization did not take place. "Icosahedral" clusters containing nonmagic numbers of atoms were obtained from cooling runs.

icosahedron. The various types of clusters considered included (i) Mackay icosahedra and icosahedra-like clusters from cooling runs, (ii) "spherical" fcc clusters centered at a lattice point,³⁷ (iii) "spherical" hcp clusters centered at a point of packing,³⁷ (iv) octahedral fcc clusters (which have eight close-packed faces), and (v) cuboctahedral fcc clusters (which have magic numbers identical with those for the Mackay icosahedra).

The binding energies per atom for clusters of various structures and sizes appear in Table III. For the larger system sizes, energy minimization runs were carried out only long enough to determine the *relative* stabilities of the various clusters. In practice, this meant that for the larger system sizes, the most stable cluster was only partially minimized.

In a small cluster where a large fraction of the atoms is on the surface, one expects the energy of a cluster to be strongly dependent on the structure of its surface. And indeed, for some small system sizes, octahedral and/or cuboctahedral fcc clusters are more stable than spherical fcc clusters of the same size, even though the surface *areas* of the octahedral and cuboctahedral clusters are larger. At larger sizes, however, it appears that the surface area, rather than surface structure, becomes more important in determining the stability of clusters, and spherical fcc clusters become more stable than octahedral or cuboctahedral fcc clusters by the time the cluster size reaches 1415 atoms.

At this cluster size, a spherical fcc cluster was also found to be more stable than a spherical hcp cluster, although for some smaller sizes, hcp clusters were more stable. For the Lennard-Jones potential, the bulk hcp crystal is known to be more stable than the bulk fcc crystal,³⁸ so presumably there is a crossover from fcc to hcp structure at some system size above 1415 atoms, but this issue was not investigated. (The data indicate that there are multiple reversals in the relative stabilities of hcp and fcc spherical clusters for sizes up to 1415 atoms. It is possible that this behavior continues to larger system sizes.)

For clusters containing 3871 or fewer atoms, the Mackay icosahedra were found to be more stable than fcc structures (or any other structures that were minimized) in all cases. Complete energy minimization could not be performed for 5083-atom systems, but after partial minimization a spherical fcc cluster was more stable than an icosahedral cluster by 0.015% (a difference of about 6e out of 39200e total binding energy). However, based on the rates at which the energies were changing, the energy of the icosahedral cluster appeared to be approaching that of the fcc cluster, so we cannot say with confidence whether or not the fcc cluster is more stable for this system size.

Hence, we conclude that a Lennard-Jones cluster must contain at least 5000 atoms (and maybe more) before the fcc structure becomes more stable than that of the Mackay icosahedra. For the largest systems, we considered only clusters containing magic

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numbers of atoms, because it is not known a priori what the lowest energy "Mackay icosahedral" structure would be for a cluster containing a nonmagic number of atoms. It is possible that if such structures were considered, the crossover from icosahedral to fcc structure would occur at a smaller cluster size.

There are two likely reasons for the disagreement of our results with the experimental results of the Farges and Stein groups for the onset of fcc ordering in argon clusters. First, the clusters generated in the jets were at nonzero temperature, where entropy effects become relevant in determining stability. Our energy determinations were obviously at zero temperature. If fcc clusters have greater entropies than icosahedral clusters, then it is possible that the most stable structure for a cluster of, say, 1000 atoms could be icosahedral at zero temperature and fcc at some higher temperature.

A second and more probable reason for disagreement is that the Lennard-Jones potential is an inadequate potential for argon. The true pair potential for argon is known to a high degree of accuracy.^{39,40} One would have to use this potential along with a three-body potential⁴¹ to achieve a more definitive statement about the relative stabilities of icosahedral and fcc argon clusters as a function of cluster size.

The most reasonable explanation of the disagreement between our results and those of Lee and Stein,²² who claimed that fcc Lennard-Jones clusters become more stable than icosahedra at a size of about 3000 atoms, appears to be that their energy minimization procedure, which allowed relaxation only in the radial direction, resulted in incomplete minimization.

Summary

We have performed molecular dynamics simulations of clusters containing 13, 16, 19, 25, 33, 38, 39, 41, 44, 55, 67, 78, 100, 147, and 309 Lennard-Jones atoms to determine the equilibrium structure and thermodynamic properties of these clusters as functions of temperature. The studies included heating and cooling runs to obtain the energy as a function of temperature as well as coexistence studies in which the transition between different structures was observed in both constant-energy and constant-temperature molecular dynamics simulations. In addition, clusters of specified structures containing as many as 5083 atoms were subjected to energy minimization runs to determine the relative stability of various types of structure at zero temperature as a function of cluster size.

Based on the results reported in this paper, we infer the existence of three regimes for the most stable structure at zero temperature. These regimes are as follows.

The lowest energy states observed for Lennard-Jones clusters containing from 13 to 33 atoms are characterized by local icosahedral structure; i.e., structure characteristic of the 13-atom icosahedron. Clusters containing from 19 to 33 atoms contain at least two interpenetrating 13-atom icosahedra and are in this sense polyicosahedral.^{4,16,17}

The lowest energy structures that we have observed for clusters containing from 38 to about 5000 atoms are of structure similar to or identical with the Mackay icosahedra containing 55 or more atoms.

For a cluster size of 5083 atoms, the energies of a spherical fcc cluster and Mackay icosahedron are too close for us to determine their relative stabilities. Presumably, the fcc structure becomes more stable than the icosahedron for larger cluster sizes,

if not for this size. (Ultimately the hcp structure must become more stable since it is the most stable crystal form for the bulk Lennard-Jones substance.)

At nonzero temperatures, clusters were seen to form one or more structures in addition to the lowest energy structure. Clusters of at least 13 atoms form structures at high temperature that have the structural and dynamical properties of a liquid. All clusters studied undergo a phase transition in the sense that there is a range of temperatures and/or energies in which the clusters make transitions among very different types of states. In the vicinity of this melting transition, clusters of 13 to 55 atoms make transitions among the lowest energy state observed, high-temperature liquidlike states, and, with the possible exception of the 13-atom case, one or more intermediate states that can be described as low-lying excitations of the lowest energy state. We suspect that the 147-atom cluster also makes such transitions, but in our limited coexistence studies of this large system, we have observed only coexistence between the intermediate states and the liquidlike states.

The signature of the phase transition in the behavior of the equilibrium energy as a function of temperature in the canonical ensemble is different for clusters of different sizes. For clusters containing 44 or more atoms, there are three distinct temperature ranges. At low temperatures, only the minimum-energy structure appears to be present; at intermediate temperatures, the minimum-energy structure and liquidlike structures, as well as intermediate structures, coexist in equilibrium; at high temperatures, only liquidlike structures are observed. In these systems, the energy undergoes a large change over the relatively narrow intermediate range of temperatures in which coexistence is observed. For systems of 33 or fewer atoms, only two regimes are observed, corresponding to the low-temperature and intermediate-temperature regimes for the larger systems. The boundary between these two regimes is marked by a large change in the heat capacity over a narrow range of temperatures, much like the boundary between these two regimes for the larger systems. Because of the wide coexistence range for the smaller systems, evaporation occurs before high enough temperatures are reached that only liquidlike structures are observed. The different types of behavior in the transitions observed for the larger and smaller systems are correlated with the differences in the structures of the lowest energy structures observed.

The shapes of the equilibrium energy-temperature curves may be different in the microcanonical ensemble than in the canonical ensemble. In the case of the 13-atom system, the results in the two ensembles can be seen to be consistent through the use of a simple equilibrium constant model.

Note. After this work was submitted for publication, our attention was called to four papers by Berry et al.⁴²⁻⁴⁵ These papers, which had not yet been published when this paper was written, discuss additional work on phase transitions in microclusters that is directly related to the present paper.

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE84-10701 (H.C.A.) and through an NSF Graduate Fellowship (J.D.H.). It also benefited from the use of a departmental computing facility funded by the National Science Foundation through grant CHE83-12693.

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