An order parameter approach to coexistence in atomic clusters

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(Received 12 January 1995; accepted 13 March 1995)

We employ order parameters to investigate the dynamic equilibrium between the two lowest energy geometric isomers of LJ$_8$, between permutational isomers of the global minimum of LJ$_{14}$, and between solidlike, surface-melted, and liquidlike forms of LJ$_{55}$. For LJ$_{55}$ approximate analytical calculations which use only information derived from the potential energy surface can accurately model the equilibrium between the different forms. This approach provides a further illustration of how different regions of the potential energy surface influence the thermodynamics. Low-energy transition states are characterized to improve our understanding of the dynamics in the “surface-melted” phases. Finally, using a two state model, we consider the size dependence of the conditions necessary to produce an S-bend (Van der Waal’s loop) in the microcanonical caloric curve. © 1995 American Institute of Physics.

I. INTRODUCTION

Clusters occupy the intermediate size regime between atoms or molecules and bulk matter; they display similarities to and differences from both. Clusters are different from atoms and molecules in that stable geometries exist for (almost) any number, $N$, of component species and there are typically many possible geometric isomers for each value of $N$. Indeed, for Lennard-Jones (LJ) clusters the number of possible geometric isomers has been shown to rise exponentially with $N$. Clusters are different from bulk material in that a large fraction of the component particles are on the surface. Their finite size also causes “rounding” of thermodynamic properties. An understanding of clusters and how their properties evolve with size will provide new insight into both limits. This is especially true for the bulk, as clusters are of a size that makes calculations tractable which would not be possible for the bulk.

Bulk matter exhibits a first order melting transition at a single well-defined temperature. At this melting point, the free energies of the solid and liquid phases are equal and coexistence of the two phases in contact is possible. Above the transition temperature the superheated solid would be metastable and is not generally observed; below it, the liquid would be metastable and can sometimes be observed as a supercooled liquid. In this context the metastable phases correspond to local rather than global free energy minima.

In clusters, the melting transition occurs over a temperature range and coexistence can be said to occur when two states are thermodynamically stable at the same temperature. However, for clusters, coexistence refers to an ensemble of clusters, some of which are solidlike and some liquidlike. For the two states to be thermodynamically stable, they must be Helmholtz free energy minima in the canonical ensemble or entropy maxima in the microcanonical ensemble. However, this definition of coexistence has a practical problem, namely that a suitable order parameter needs to be found to distinguish solidlike and liquidlike clusters. In the canonical ensemble we expect to find Landau free energy minima for the solidlike and liquidlike states with a barrier between them. The order parameter must be a smooth function of the atomic coordinates, so that it passes through intermediate values during a transition between the two different regions of phase space.

The existence of such a free energy barrier has been predicted by a number of theoretical models. The first used a quantum density of states approach. It gave two Helmholtz free energy minima as a function of a rigidity parameter, and distinct stability limits for the solidlike and liquidlike states. However, since coexistence is observed in classical simulations, a classical explanation should be possible. One such approach uses capillarity theory, where the order parameter is effectively the dividing radius between solidlike and liquidlike regions of the cluster. Subsequently, Berry and Wales predicted Helmholtz free energy minima as a function of the defect density, using a model partition function based on a defective lattice.

Coexistence in clusters has been inferred from simulations in a number of ways. One approach, popularized by Berry and co-workers, is to associate coexistence with bimodality (or multimodality in some cases) in the probability distributions of the short-time averaged (STA) temperature in the microcanonical ensemble. By averaging the temperature over several vibrational periods, characteristic values can be identified for the solidlike and liquidlike states. In the microcanonical ensemble the liquidlike state has a lower characteristic temperature than the solidlike state because it is associated with high-lying wells on the potential energy surface (PES). If the STA temperature is followed along a molecular dynamics (MD) trajectory, it is observed to fluctuate between the values for the solidlike and liquidlike states, i.e., there is a dynamic equilibrium. The instantaneous temperature, though, is normally found to be unimodal, because it is subject to large fluctuations due to vibrational motion within the potential wells. The short-time averaging of the temperature reduces the vibrational noise. However, as the STA temperature is a dynamic property, the connection between multimodality in the STA temperature and thermodynamic stability is not obvious.

An alternative approach is to deduce coexistence from thermodynamic functions such as the caloric curve. For LJ$_{55}$ and LJ$_{147}$ extraction of the configurational density of states...
from histogram Monte Carlo simulations has conclusively shown that the microcanonical caloric curve (temperature as a function of energy) has an S-bend (Van der Waals loop).\(^9\) The two branches of the curve with positive slope correspond to local stability (a locus of entropy maxima), and the connecting branch with negative slope corresponds to instability and has a negative heat capacity. In this region there are two stable states. Regions of negative slope can only occur in microcanonical and isopotential ensembles of finite systems.\(^6,15\) Sufficient conditions for an S-bend were found by Berry and Wales in their work on a model partition function including defect interactions.\(^9\) Subsequently the necessary conditions to see two Landau free energy minima are two maxima in the configurational entropy for an S-bend in the isopotential caloric curve.\(^6,16\) However, there are many cases, such as LJ\(_{13}\), when bimodality is seen in the STA temperature distribution yet only an inflection is seen in the microcanonical caloric curve. One of the principal aims of this paper is to establish a connection between these observations.

Recently, Landau free energy barriers have been calculated directly from simulations for LJ clusters.\(^5\) The Landau free energy is given by

\[
A_L(Q) = A_c - kT \ln p_Q(Q),
\]

where \(A_L(Q)\) is the Landau free energy, \(p_Q(Q)\) is the canonical probability distribution function for the order parameter \(Q\), and \(A_c\) is the configurational part of the Helmholtz free energy. As \(A_c\) is independent of \(Q\), knowledge of \(p_Q(Q)\) is sufficient to calculate the Landau free energy barrier. Therefore the necessary conditions to see two Landau free energy minima are two maxima in \(p_Q(Q)\). For LJ\(_{52}\) the potential energy was found to be a suitable order parameter and for LJ\(_{147}\) a combination of the potential energy and a bond-order parameter was used.\(^6\) However, for LJ\(_{13}\) no free energy barrier was found. It was also shown that a Landau free energy barrier as a function of the potential energy is a necessary and sufficient condition for an S-bend in the isopotential ensemble and vice versa, and that an S-bend in the microcanonical ensemble is a sufficient condition for both these phenomena to be observed.\(^5\)

II. SHORT TIME AVERAGED ORDER PARAMETERS

Here we further develop the use of order parameters to investigate coexistence in finite systems and consider the possible use of a STA quantity, such as the STA temperature, as an order parameter. As the STA temperature is normally found from isoergic MD, it is necessary to extend the concept of order parameters to a “Landau entropy” in the microcanonical ensemble. Two maxima in the Landau entropy will indicate the presence of two thermodynamically stable states. The maxima will be separated by a Landau entropy well. The probability distribution function is

\[
p_Q(Q) = \frac{1}{\Omega(E)} \int \delta(Q' - Q) \delta(H - E) dq^e dp^e,
\]

where \(\Omega(E)\) is the energy density of states. \(\Omega(E)\) is related to the Landau density of states, \(\Omega_L(Q)\) by

\[
\Omega(E) = \int \Omega_L(Q) dQ.
\]

Consequently \(\Omega_L(Q)\) is

\[
\Omega_L(Q) = \int \delta(Q' - Q) \delta(H - E) dq^e dp^e.
\]

and we therefore define the Landau entropy as

\[
S_L(Q) = k \ln p_Q(Q) + S(E).
\]

As \(S\) is independent of \(Q\), we only need to know \(p_Q(Q)\) to find the Landau entropy well (if there is one), and the necessary condition for two Landau entropy maxima is the presence of two maxima in \(p_Q(Q)\). From this result, we can deduce that if the STA temperature is a valid order parameter, then bimodality does indeed indicate the presence of two Landau entropy maxima. However, in all previous work the order parameter has been a continuous function of the atomic coordinates so that it passes through intermediate values during a transition between the two states. Our thesis is that a STA quantity can act as a new kind of order parameter, i.e., one that is not a function of the instantaneous coordinates, and that for clusters an order parameter constructed from instantaneous coordinates is likely to be a less sensitive probe of coexistence than a STA order parameter.

In a MD simulation, when the phase point moves between two regions a STA quantity will have an intermediate value because it is an average over a segment of the trajectory that includes the two regions and the transition state. Furthermore, if the transition between the states occurs on a time scale much shorter than that for short time averaging, then the probability that the cluster will be in the transition region is overestimated by the STA quantity, for it effectively assumes the cluster has been in the transition region for the whole of averaging period. As the time taken to move between the two regions increases relative to the averaging period, the probability that the STA quantity has an intermediate value is expected to approach from above the probability that the cluster is in the transition state region. Therefore, the probability that the STA quantity has an intermediate value is an upper bound to the true probability that the cluster is in the transition state region and the depth of any Landau entropy wells will be underestimated, i.e., STA order parameters should not produce spurious entropy wells.

The probability distribution of a STA quantity cannot be framed in terms of the phase space integral of Eq. (2), because each value of a STA order quantity is associated with a line on the phase space hypersurface (which cannot be defined independently of the dynamics) rather than a point. However, in practice these phase space integrals are rarely used. Instead, using the fact that the time average is equivalent to the ensemble average for an ergodic system, and assuming ergodicity, the integrals are done by averaging over a set of points. For a STA quantity, the only difference is that the average is over a set of lines. We can write \(p_Q\) as...
values of the temperature are associated with vibrational motion within a potential well, not passage between the two states, and therefore the instantaneous temperature is an unsuitable order parameter. Instantaneous coordinates will only work well when the values of the order parameter for the two states are so well separated that vibrational noise will not take the parameter into the transition region. Such a separation occurs for \( \text{LJ}_{55} \), which has bimodal instantaneous potential energy and energy distributions in the canonical ensemble.\(^6_{,14}\)

This analysis has served to give a unified picture of coexistence in clusters, by relating bimodality in STA temperature distributions to thermodynamic stability. This is especially important as the STA temperature is the most sensitive indicator of coexistence in clusters that has been found. It also suggests a variational method to find the depth of the well in the Landau entropy appropriate to the microcanonical ensemble. As a STA order parameter will give only a lower bound to the size of the entropy well, the averaging period can be varied to find the greatest depth which gives a lower bound to the true well depth. This procedure will be illustrated quantitatively for \( \text{LJ}_{13} \) in Sec. VI and \( \text{LJ}_{55} \) in Sec. VIII. Order parameters will also be used to investigate the dynamic equilibrium between the two lowest energy geometric isomers of \( \text{LJ}_8 \) in Sec. V, and between permutational isomers of \( \text{LJ}_{14} \) in Sec. VII.

### III. S-BENDS AND SIZE DEPENDENCE

Here, building upon previous work,\(^{16}\) we consider the conditions for an \( S \)-bend in the microcanonical caloric curve using a two state model. If an order parameter exists which can distinguish between different regions of phase space, we can write the density of states, \( \Omega \), as a sum over these regions, \( \Omega = \Sigma \Omega_i \). Using the definition of entropy, \( S = k \ln \Omega \), and temperature, \( T = (\partial E/\partial S)_{N,V} \) gives

\[
\frac{1}{T} = k \sum_i \frac{\Omega_i}{\Omega} \left( \frac{\partial \ln \Omega_i}{\partial E} \right)_{N,V} = \sum_i \frac{p_i}{T_i},
\]

where \( p_i \) is the probability of the phase point lying in region \( i \) and \( T_i \) is defined by \( 1/T_i = k(\partial \ln \Omega_i/\partial E)_{N,V} \). From this equation it follows that

\[
\left( \frac{\partial T}{\partial E} \right)_{N,V} = T^2 \sum_i \frac{p_i}{T_i} \left( \frac{\partial T_i}{\partial E} \right)_{N,V} - \frac{1}{T^2} \left( \frac{\partial p_i}{\partial E} \right)_{N,V},
\]

where the probabilities and their derivatives obey \( \Sigma p_i = 1 \) and \( \Sigma_i (\partial p_i/\partial E)_{N,V} = 0 \). For a two state system, this expression becomes

\[
\left( \frac{\partial T}{\partial E} \right)_{N,V} = T^2 \left( \frac{\partial p_1}{\partial E} \right)_{N,V} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) + T^2 \left[ \frac{p_1}{T_1} \left( \frac{\partial T_1}{\partial E} \right)_{N,V} + \frac{p_2}{T_2} \left( \frac{\partial T_2}{\partial E} \right)_{N,V} \right].
\]

The first term in this expression is negative and the second positive. To exhibit an \( S \)-bend, the caloric curve must have a region of negative slope, and therefore the following inequality must be satisfied for some range of energy:
\[
\left( \frac{\partial p_2}{\partial E} \right)_{N,V} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) + p_1 \left( \frac{\partial T_1}{\partial E} \right)_{N,V} + p_2 \left( \frac{\partial T_2}{\partial E} \right)_{N,V} .
\]

(10)

If we assume both regions behave harmonically, then \( T_1 = \alpha E \) and \( T_2 = \alpha (E - \Delta) \), where \( \Delta \) is the potential energy difference between the minima of the two regions. This assumption gives

\[
\left( \frac{\partial p_2}{\partial E} \right)_{N,V} \left( \frac{1}{E-\Delta} - \frac{1}{E} \right) > p_1 \left( \frac{\partial T_1}{\partial E} \right)_{N,V} + p_2 \left( \frac{\partial T_2}{\partial E} \right)_{N,V} .
\]

(11)

so

\[
\left( \frac{\partial p_2}{\partial E} \right)_{N,V} \Delta > p_1 \left( 1 - \frac{\Delta}{E} \right) + p_2 \left( 1 - \frac{\Delta}{E} \right)^{-1} ,
\]

\[
> 1 + \frac{\Delta}{E} (p_2 - p_1) + O \left( \frac{\Delta^2}{E} \right).
\]

(12)

In the middle of the coexistence region where \( p_1 = p_2 = 1/2 \), neglecting second-order terms in \( (\Delta/E) \) gives

\[
\left( \frac{\partial p_2}{\partial E} \right)_{N,V} \Delta > 1 .
\]

(13)

This equation was previously derived by Bixon and Jortner\(^{17} \) using the kinetic temperature, \( T_K = (E_K)/(3N-6)k \). We now continue the analysis, first noting that

\[
\left( \frac{\partial p_i}{\partial E} \right)_{N,V} = \frac{1}{\Omega_i} \left( \frac{\partial \Omega}{\partial E} \right)_{N,V} - \Omega_i \left( \frac{\partial \Omega}{\partial E} \right)_{N,V} ,
\]

\[
= \frac{p_i}{k} \left( \frac{1}{T_i} - \frac{1}{T} \right) .
\]

(14)

Therefore, using Eq. (7),

\[
\left( \frac{\partial p_2}{\partial E} \right)_{N,V} = \frac{p_1 p_2}{k} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) = \frac{p_1 p_2}{ak} \frac{\Delta}{E(E-\Delta)} .
\]

(15)

Substituting this result into Eq. (11) and rearranging gives

\[
\left( p_1 - \frac{p_1 p_2}{ak} \right) \Delta^2 / E > 2 p_1 \Delta / E + 1 < 0 .
\]

(16)

Taking the middle of the coexistence region, where \( p_1 = p_2 = 1/2 \) and \( E = E_{1/2} \),

\[
\left( 1 - \frac{1}{2ak} \right) \Delta^2 / E_{1/2} > 2 \Delta / E_{1/2} + 2 > 0 .
\]

(17)

As this quadratic has negative curvature for all realistic values of \( a \), the above inequality has a physically meaningful solution when \( (\Delta/E_{1/2}) \) is greater than the larger root of the quadratic. This solution is

\[
\Delta / E_{1/2} = (1/4ak - 1/2)^{1/2} - 1 .
\]

(18)

For an \( N \)-atom cluster the density of states for a single harmonic minimum is\(^{18} \)

\[
\Omega(E) = \frac{E^{3N-7}}{(3N-6)! \prod_{j=1}^{x} \nu_j} .
\]

(19)

Therefore,

\[
\frac{1}{\alpha} = \left( \frac{\partial E}{\partial T} \right)_{N,V} = (3N-7)k .
\]

(20)

Hence,

\[
\frac{\Delta}{E_{1/2}} > 2 \left( \frac{(3N-8)^{1/2} - 1}{(3N-9)k} \right) \approx \frac{2}{\sqrt{3N}} \quad \text{for large } N .
\]

(21)

A similar relationship can be derived for the \( N \) dependence of \( S \)-bends in the isothermal curve of the isopotential ensemble. In this case

\[
\left( \frac{\partial E}{\partial T} \right)_{N,V} = \left( \frac{3N}{2} - 4 \right) k ,
\]

(22)

where \( E \) is the potential energy and \( T \) is the isopotential temperature. Hence,

\[
\frac{\Delta}{E_{1/2}} > 2 \sqrt{\frac{2}{3N}} \quad \text{for large } N .
\]

(23)

As \( E_{1/2} < E_{1/2}/\sqrt{2} \), this confirms that an \( S \)-bend is more likely in the isopotential ensemble than the microcanonical ensemble.

From Eq. (21) it is clear that for a series of clusters with similar values of \( \Delta/E_{1/2} \), an \( S \)-bend will become more likely as the size increases (Fig. 2). This result is in good agreement with simulations of icosahedral Lennard-Jones\(^{14} \) and cuboctahedral gold clusters.\(^{19} \)

In the bulk limit the above model predicts the caloric curve will be vertical at \( E_{1/2} \) (Fig. 2), which is clearly at variance with the expected behavior for a bulk first-order phase transition. This difference arises because we have not allowed for the cluster dividing into distinct solidlike and liquidlike regions, which would contribute a term of the form \( \Omega(x)^{1-x} \Omega(y) \) to the density of states, where \( x \) is the fraction of the cluster that is liquidlike. Such phase separation does not occur for small clusters because the energy of the dividing surface makes it unfavorable, but for the bulk the interface is a negligible fraction of the total energy. The size at which
two forces are collinear, there is also no transfer of angular momentum. The effect of the box is to restrict the phase space considered to bound clusters. The time step used was 0.004 65 reduced time units, which is equivalent to 1 × 10^{-14} s for Ar.

The relative root-mean-square interatomic separation $\delta$ was used to assess the degree of melting. It is defined as

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

where the angle brackets indicate that an average is taken over the whole trajectory. Lindemann’s criterion states that melting is expected when $\delta$ becomes greater than about 0.1.

The kinetic temperature was calculated from

$$T_K = \frac{2E_K}{k\kappa},$$

by taking the mean of $T_K$ over the whole trajectory. The kinetic temperature differs slightly from the thermodynamic temperature for a cluster containing 55 atoms. STA temperatures were found by averaging $T_K$ over 500 time steps. The same averaging period was used for the STA order parameters. Quenching was performed using a conjugate gradient technique. The specific details of the MD runs and the order parameters used are given in the relevant sections.

Cluster isomerizations are unimolecular reactions, and so Rice–Ramsperger–Kassel–Marcus (RRKM) theory was used to give further insight into the observed dynamics of the cluster. Assuming that the reorganization of energy among the vibrational modes is facile, the rate constant, $k(E)$, is given by

$$k(E) = \frac{\sigma G^* (E - E_{\text{ts}})}{h \Omega (E - E_{\text{min}})},$$

where $G^* (E - E_{\text{ts}})$ is the phase volume associated with the transition state, $\Omega (E - E_{\text{min}})$ is the density of states for the minimum, and $\sigma$ is the reaction path degeneracy. $\sigma$ is $h_{\text{min}}/h_{\text{ts}}$ or $2h_{\text{min}}/h_{\text{ts}}$ for nondegenerate and degenerate rearrangements, respectively, where $h$ is the order of the point group. A degenerate rearrangement connects permutational isomers and a nondegenerate rearrangement connects geometric isomers. $\Omega (E)$ and $G^* (E - E_{\text{ts}})$ can be calculated within the harmonic approximation if the energies and normal mode frequencies of the minima and transition state are known. This approximation gives for the rate constant,

$$k(E) = \sigma \left( \frac{E - E_{\text{ts}}}{E - E_{\text{min}}} \right)^{\kappa - 1} \frac{\prod_{j=1}^{\kappa} \nu_{j}^{\text{min}}}{\prod_{j=1}^{\kappa} \nu_{j}^{\text{ts}}},$$

where $\kappa$ is the number of nonzero vibrational frequencies for the minimum. The harmonic approximation is likely to lead to a significant error in the absolute values for the rate constants, but the relative values should be useful in comparing the rearrangement mechanisms.

V. LJ₈

LJ₈ has a featureless caloric curve and a unimodal STA temperature distribution for all energies in the melting

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There are two low energy minima, the capped pentagonal bipyramid (CPBP) and the dodecahedron, with very similar energies. The dynamic equilibrium between these two isomers allows the cluster to melt without visiting any other high energy minima. This equilibrium has very little effect on the caloric curve because the temperatures associated with both isomers at a given total energy are very similar. The rise in Lindemann’s $\delta$, which signals the onset of melting, occurs when the dodecahedron is first seen from quenching.

The energies of some of the lower energy minima and transition states are given in Tables I and II, and the three lowest energy rearrangements are depicted in Fig. 3. The two main types of rearrangement mechanism seen for this cluster are Lipscomb’s diamond–square–diamond (DSD) process and Johnson’s edge-bridging process (EBP). The $AB$ and $BB$ rearrangements allow LJ8 to explore all its permutational isomers. The RRKM rate calculations predict that the $AB$ rearrangement will be the first to occur as the energy is increased.

In order to study the dynamic equilibrium between the CPBP and the dodecahedron, an order parameter, $Q$, was constructed that distinguishes between them and which varies smoothly along the reaction path connecting them. $Q$ in reduced units is

$$Q = (20.8 + E_c) \left( \sum_{a=1,2,3} I_a - 13.615 \right), \quad (30)$$

where $E_c$ is the potential energy, and $I_a$ are the principal moments of inertia. The dodecahedron has a smaller value of $\sum I_a$, because of its more compact structure. 13.615, the value of $\sum I_a$ for the transition state $AB$, is subtracted from $\sum I_a$ so that $Q$ is negative for the dodecahedron and positive for the CPBP. The energy dependent term was included so that for any of the higher energy minima, $Q$ has a larger value than for the CPBP. 20.8$\epsilon$ is added to $E_c$ to shift the zero of this term to a value of $E_c$ just below the lowest possible potential energy and so make the term always positive and more sensitive to the differences in potential energy between the minima. Figure 4 shows the variation of the order parameter along a set of reaction paths between the low energy minima. The paths were calculated using eigenvector following.

### Table I. Low energy minima of LJ8.

<table>
<thead>
<tr>
<th>Description</th>
<th>Point group</th>
<th>Energy/$\epsilon$</th>
<th>$Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Capped pentagonal bipyramid</td>
<td>$C_s$</td>
<td>-19.821489</td>
<td>0.2631</td>
</tr>
<tr>
<td>B Dodecahedron</td>
<td>$D_{2d}$</td>
<td>-19.765298</td>
<td>-0.4608</td>
</tr>
<tr>
<td>C Bicapped octahedron</td>
<td>$C_{2v}$</td>
<td>-19.189311</td>
<td>1.1562</td>
</tr>
<tr>
<td>D Bicapped octahedron</td>
<td>$D_{3d}$</td>
<td>-19.169280</td>
<td>2.1499</td>
</tr>
<tr>
<td>E Stellated tetrahedron</td>
<td>$T_d$</td>
<td>-18.976056</td>
<td>0.9183</td>
</tr>
</tbody>
</table>

### Table II. Low energy transition states of LJ8. The transition states are labeled by the two minima they connect.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Point group</th>
<th>Energy/$\epsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$AB$ DSD</td>
<td>$C_1$</td>
<td>-19.281244</td>
</tr>
<tr>
<td>$AA$ EBP</td>
<td>$C_1$</td>
<td>-19.159274</td>
</tr>
<tr>
<td>$BB$ DSD</td>
<td>$C_{2v}$</td>
<td>-18.926304</td>
</tr>
<tr>
<td>$BE$ double DSD</td>
<td>$C_{2v}$</td>
<td>-18.707532</td>
</tr>
<tr>
<td>$AD$ DSD</td>
<td>$C_1$</td>
<td>-18.694706</td>
</tr>
<tr>
<td>$AA$ 3 atom pop-in, pop-out</td>
<td>$C_2$</td>
<td>-18.420172</td>
</tr>
<tr>
<td>$BC$ EBP+DSD</td>
<td>$C_1$</td>
<td>-18.372695</td>
</tr>
</tbody>
</table>

FIG. 3. The three lowest energy rearrangements of LJ8 given in Table II. (a) $AB$; (b) $AA$, and (c) $BB$. The graphics were produced with Mathematica (Ref. 30) using a cutoff of 1.3$\sigma$ for triangulation. The left-hand frame shows the lower energy minimum, the middle frame the transition state with the transition vector superimposed, and the right-hand frame the higher energy minimum.

FIG. 4. Plot of $Q$ against distance along the reaction path for the rearrangements given in Table II. The reaction paths were calculated using eigenvector-following (Ref. 33). Details of the calculation of $S$ can be found in Ref. 33.
MD runs of 2.5×10^6 time steps were performed at energies from 2.40 to 1.90 e atom^−1. The lowest energy run was initiated from the CPBP. Short time averages were taken of Q and the kinetic temperature. At low energies the STA Q distribution is unimodal at a value corresponding to the CPBP. Between 2.32 e atom^−1 and 2.125 e atom^−1, there is a second peak at lower Q in the STA Q distribution due to the dodecahedron [Figs. 5(a) and 6(a)]. In contrast, instantaneous Q distributions are unimodal. In this energy range both isomers correspond to Landau entropy maxima, which are separated by a Landau entropy well [Fig. 5(b)]. At higher energies the two peaks merge to form a single peak because the time scale for rearrangement between the two isomers is of the order of the averaging period, and some small peaks appear at higher Q and lower temperature in the STA distributions due to some of the higher energy minima.

The mean and standard deviation of STA Q and temperature were calculated for each peak in the STA Q distribution, along with the integrated probabilities. The values of Q for both isomers increase with total energy [Fig. 6(a)], because of the increase in the average E and the expansion of the cluster as the total energy is increased. The mean STA temperature for the dodecahedron is always slightly lower [Fig. 6(b)]. This result is consistent with the slightly higher potential energy of the dodecahedron compared to the CPBP and has no significant effect on the caloric curve. As can be seen from Fig. 5(c), the STA temperature distributions for the two structures overlap and so the overall STA distribution is unimodal with a shoulder at low temperature due to the dodecahedron. The probability of the cluster being associated with the dodecahedron is always lower than the corresponding probability for the CPBP [Fig. 6(c)], because it has higher symmetry than the CPBP and so fewer permutational isomers. This lower probability causes the dodecahedron to have a significantly lower Landau entropy [Figs. 5(b) and 6(d)]. In contrast to results obtained for conventional instantaneous order parameters, the Landau entropy well depths are monotonically decreasing with energy [Fig. 6(d)]. The large well depths at low energy are due to the low transition rate between the two structures. For infinite time MD runs, the well depths would diverge as the energy tends to the energy of the transition state AB from above.

VI. LJ 13

LJ 13 has a bimodal STA temperature distribution for a range of energy. The two peaks correspond to solidlike and liquidlike clusters. We calculated the depth of the Landau entropy well for LJ 13 using the STA temperature as an order parameter, paying particular attention to the effect of the averaging period. This calculation was done at a total energy of 2.36 e atom^−1, where the probabilities of observing the solidlike and liquidlike states are approximately equal. All the STA distributions were calculated from the same MD run of 2×10^6 time steps (20 ns for Ar). The depth of the entropy well was calculated from the distributions using Eq. (5). From Fig. 7, it can be seen that there is a broad maximum in the well depth as a function of averaging period. The well is shallower for shorter averaging periods because the STA temperature becomes more sensitive to the vibrational fluctuations in the kinetic energy which broaden the distributions for each state. For longer averaging periods the well is shallower because the temperature is averaged over both states. The maximum value for the depth of the entropy well was 0.90 k.
VII. LJ14

In contrast to LJ13, LJ14 has a featureless caloric curve and a unimodal STA temperature distribution is seen for all energies. These results have been ascribed to the existence of low-lying degenerate rearrangements of the global minimum, the singly capped icosahedron. The Lindemann δ rises to a value of 0.25 before other minima are seen from quenching at \(-2.63\) e atom\(^{-1}\). By Lindemann’s criterion this implies that the cluster melts without visiting any other geometric isomers. For this cluster there is a gradual increase in the nonrigid properties of a single geometric isomer as it becomes increasingly easy for it to transform between its permutational isomers, rather than a transition from solidlike to liquidlike minima.

The low energy minima and transition states are given in

<table>
<thead>
<tr>
<th>Description</th>
<th>Point group</th>
<th>Energy/e</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>capped icosahedron</td>
<td>C(_{3v})</td>
</tr>
<tr>
<td>B</td>
<td>capped decahedron</td>
<td>C(_{2v})</td>
</tr>
<tr>
<td>C</td>
<td>bicapped defective icosahedron</td>
<td>C(_r)</td>
</tr>
<tr>
<td>D</td>
<td>bicapped defective icosahedron</td>
<td>C(_r)</td>
</tr>
<tr>
<td>E</td>
<td>bicapped defective icosahedron</td>
<td>C(_1)</td>
</tr>
</tbody>
</table>

FIG. 6. (a) Plot of the mean values of STA \(Q\) for the CPBP and dodecahedron as a function of energy. The dashed line without error bars is the overall mean value of \(Q\). (b) Plot of the mean values of the STA temperature for the CPBP and dodecahedron. The dashed line is the mean temperature for the run. (c) Plot of the probability of the cluster being in the potential well of the CPBP and the dodecahedron. (d) Plot of the heights of the Landau entropy maxima measured with respect to the bottom of the Landau entropy well (solid lines) and the Landau entropy difference (dashed line) between the CPBP and the dodecahedron as a function of energy.

FIG. 7. Plot of the average well depth in the Landau entropy against the averaging period for the STA temperature. The results are for a MD run at \(-2.36\) e atom\(^{-1}\) of 2x10\(^6\) time steps for LJ13.
Tables III and IV, respectively, and the mechanisms of the four lowest energy rearrangements are shown in Fig. 8. The lowest energy rearrangement is an edge-bridging process which allows the capping atom to diffuse over the surface of the cluster. If this alone were responsible for the rise in $\delta$, the cluster could hardly be said to have melted, because this process only allows the cluster to explore a small fraction of the possible permutational isomers. The two other degenerate rearrangements involve intershell exchange between the capping atom and the surface layer, allowing a much greater exploration of the possible permutational isomers. They resemble mechanisms reported in theoretical studies of metal fcc $\{100\}$ surfaces.\textsuperscript{34,35} The other low energy rearrangement is nondegenerate and involves a cooperative multiple diamond–square ($\text{DS}$) mechanism. This allows permutation of surface atoms without intershell exchange. Interestingly, the steepest descent path away from the transition state $AB$ does not lead directly to the capped icosahedron but instead to transition state $AA1$. Steepest descent reaction paths which connect two transition states are not as uncommon as might be thought and have been reported for a number of systems.\textsuperscript{36} None of these four rearrangements involve exchange of the core atom, and so they do not allow the exploration of all possible permutational isomers of the capped icosahedron.

RRKM calculations have been performed using Eq. (29) to obtain rate constants for the six lowest energy rearrangements given in Table III. The results are shown in Fig. 9. They predict that as the energy of the cluster is increased, the edge-bridging mechanism via transition state $AA1$ will be the first to occur. The two “pop-in, pop-out” mechanisms will occur next. The rate is greater for the higher energy rearrangement of the two, because the vibrational contribution to the rate constant is larger. The corresponding transition state is more “open,” has a lower average vibrational frequency and so has a broader transition state valley. The multiple DS process has a much lower rate than the above three because of the narrowness of its transition state valley. The multiple DS process has a much lower rate than the above three because of the narrowness of its transition state valley. For LJ$\text{13}$ a similar multiple DS is a low energy degenerate rearrangement of the icosahedron, but the observed melting behavior—there is a coexistence of solidlike and liquidlike states rather than a gradual softening of the solidlike state—suggests it is of little dynamical significance. It is probably generally true that such multiple DS processes will not have a significant role in the dynamics of a cluster because of

![Fig. 8](image.png)

**TABLE IV.** Low energy transition states of LJ$\text{14}$. The transition states are labeled by the two minima they connect.

<table>
<thead>
<tr>
<th>Mechanism Point group</th>
<th>Energy/(e)</th>
<th>(\Pi^* \nu_i/\Pi_{\nu_i}^{-1} \nu_i)</th>
<th>(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$AA1$ EBP $C_{2v}$</td>
<td>-47.092 180</td>
<td>17.286 2 2</td>
<td>2</td>
</tr>
<tr>
<td>$AB$ pentuple DS $C_2$</td>
<td>-46.148 501</td>
<td>15.881 6 2</td>
<td>6</td>
</tr>
<tr>
<td>$AA2$ 2 atom pop-in, pop-out $C_2$</td>
<td>-45.950 087</td>
<td>100.544 7 8</td>
<td>8</td>
</tr>
<tr>
<td>$AA3$ 3 atom pop-in, pop-out $C_2$</td>
<td>-45.840 234</td>
<td>462.387 9 10</td>
<td>10</td>
</tr>
<tr>
<td>$AE$ 2 atom pop-out $C_1$</td>
<td>-45.326 842</td>
<td>32.099 9 8</td>
<td>8</td>
</tr>
<tr>
<td>$AA4$ pentuple DSD $C_s$</td>
<td>-45.005 943</td>
<td>24.270 9 10</td>
<td>10</td>
</tr>
</tbody>
</table>

![Fig. 9](image.png)

**FIG. 9.** Plot of the RRKM rate as a function of energy for the six lowest energy rearrangements given in Table IV. The horizontal line at 1 ns$^{-1}$ is the threshold rate for observing the rearrangements on the time scale of our simulation. The rate has been converted into ns$^{-1}$ using values of \(e\) and \(\sigma\) appropriate for Ar.
the narrowness of their transition state valleys, unless other rearrangements with broader valleys are too high in energy to contribute.

We have probed the melting dynamics of LJ$_{14}$ using an order parameter that can distinguish between permutational isomers, and by monitoring intershell exchange. We use the distance index, $d$, employed by Sugano,\textsuperscript{37} which is defined as

$$d = \frac{1}{2} \| A - A_0 \|^2,$$

where $A$ is the adjacency matrix whose elements $A_{ij}$ are given by

$$A_{ij} = \begin{cases} 1, & \text{if } r_{ij} < r_0 \\ 0, & \text{otherwise} \end{cases},$$

and $A_0$ is the initial adjacency matrix. This index gives a measure of the number of nearest neighbor contacts that have to be broken and formed to transform between two configurations. Consequently, $d$ does not allow us to distinguish all $2.91 \times 10^{10}$ permutational isomers of the capped icosahedron, but is a measure of permutational order, i.e., how far away the cluster is from the initial permutation in the space of all permutations. As $d$ is discrete and nonunique, it cannot be used to calculate entropy well depths between different permutational isomers. If only the edge-bridging mechanism is "feasible,"\textsuperscript{38} the value of $d$ cannot exceed six. The pop-in, pop-out mechanisms entail much larger values of $d$ and can be differentiated from the multiple DS by the intershell exchange.

MD trajectories, equivalent to 10 ns for Ar, were performed for energies between $-3.3$ and $-2.1$ $\epsilon$ atom$^{-1}$. The atoms farthest from and nearest to the center of mass were followed throughout the run and the proportion of time each atom spent in these positions calculated. $d$ was always calculated with respect to the initial configuration. The cutoff, $r_0$, used in the construction of the adjacency matrix was $1.5 \sigma$. A smaller value led to $d$ being too sensitive to the changes in nearest-neighbor distances due to vibrational motion.

From Table V, it can be seen that diffusion of the capping atom over the surface begins at $-3.1$ $\epsilon$ atom$^{-1}$, intershell exchange between the surface atoms and the capping atom at $-2.9$ $\epsilon$ atom$^{-1}$, and exchange between the core and surface atoms at $-2.6$ $\epsilon$ atom$^{-1}$. These results confirm the order predicted from RRKM theory. The core atom of the capped icosahedron is least mobile because there are no de-

TABLE V. Values of some dynamical properties for the MD trajectories of LJ$_{14}$. The number of exchanges in an upper limit because some of the "exchanges" may be due to vibrational motion.

<table>
<thead>
<tr>
<th>Energy/ $\epsilon$ atom$^{-1}$</th>
<th>Final value of $d$</th>
<th>Atoms visiting cap site</th>
<th>Surface-cap exchanges</th>
<th>Atoms visiting core site</th>
<th>Core-surface exchanges</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-3.3$</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0.02</td>
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<td>$-3.2$</td>
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<td>0</td>
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<td>$-3.1$</td>
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</tr>
<tr>
<td>$-3.0$</td>
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<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0.08</td>
</tr>
<tr>
<td>$-2.9$</td>
<td>46</td>
<td>13</td>
<td>36</td>
<td>1</td>
<td>0</td>
<td>0.22</td>
</tr>
<tr>
<td>$-2.8$</td>
<td>33</td>
<td>13</td>
<td>217</td>
<td>1</td>
<td>0</td>
<td>0.25</td>
</tr>
<tr>
<td>$-2.7$</td>
<td>35</td>
<td>13</td>
<td>675</td>
<td>1</td>
<td>0</td>
<td>0.26</td>
</tr>
<tr>
<td>$-2.6$</td>
<td>46</td>
<td>14</td>
<td>1509</td>
<td>4</td>
<td>17</td>
<td>0.28</td>
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<tr>
<td>$-2.5$</td>
<td>48</td>
<td>14</td>
<td>2679</td>
<td>6</td>
<td>45</td>
<td>0.29</td>
</tr>
<tr>
<td>$-2.4$</td>
<td>45</td>
<td>14</td>
<td>4232</td>
<td>14</td>
<td>262</td>
<td>0.30</td>
</tr>
<tr>
<td>$-2.3$</td>
<td>45</td>
<td>14</td>
<td>5394</td>
<td>14</td>
<td>680</td>
<td>0.31</td>
</tr>
<tr>
<td>$-2.2$</td>
<td>42</td>
<td>14</td>
<td>6057</td>
<td>14</td>
<td>1084</td>
<td>0.31</td>
</tr>
<tr>
<td>$-2.1$</td>
<td>44</td>
<td>14</td>
<td>6523</td>
<td>14</td>
<td>1637</td>
<td>0.32</td>
</tr>
</tbody>
</table>

FIG. 10. Plots of $d$ along a $10^4$ time step segment of a trajectory at an energy of (a) $2.9$ $\epsilon$ atom$^{-1}$, (b) $2.7$ $\epsilon$ atom$^{-1}$, and (c) $2.4$ $\epsilon$ atom$^{-1}$. (a) and (c) are equivalent to 0.01 ns and (b) to 0.008 ns for Ar. (a) shows steps in $d$ of magnitude 2 corresponding to edge-bridging rearrangements. (b) shows a large rise in $d$ at time step 460 due to an intershell exchange. (c) shows the very rapid diffusion found at high energy.
generate rearrangements allowing exchange of the core atom; the cluster must pass through a higher energy minimum for exchange to occur. There is a large jump in $\delta$ accompanying the onset of surface-cap intershell exchange (Table V). The behavior of $d$ along trajectories at different energies is shown in Fig. 10. The value of $d$ is subject to fluctuations of one and sometimes two units because of vibrational motion. The increase in diffusion with energy is apparent from Fig. 10.

We have shown that the rise in Lindemann’s $\delta$ associated with the capped icosahedron alone is due to diffusion of the cap atom and surface-cap intershell exchange. Although complete permutational disorder is not possible because of the immobile core of the capped icosahedron, $\delta$ is a reasonable guide to the degree of melting. The activation energy for diffusion is different for each of the three icosahedral shells, and can be explained by reference to the minima and transition states on the PES. This behavior is a precursor to the surface melting behavior seen for larger clusters.20

VIII. LJ55

Surface-melted clusters were first reported by Nauchitel and Pertsin.39 This phenomenon has recently been characterized for Lennard-Jones clusters.20 From MD simulations diffusion constants have been calculated for the different icosahedral shells of the cluster for a range of magic and nonmagic clusters. Below the cluster melting energy, significant diffusion constants were found for the surface layers while the core of the cluster remained rigid. For magic number clusters, following the STA total energy along an isothermal MD trajectory in the above energy region showed that the cluster spent a period of time in one region of phase space with a characteristic energy, and then jumped to a different region of phase space.21 Three well-defined STA energy bands were seen for LJ55 and at least four for LJ147. Quenching for LJ55 showed the lowest STA energy band was associated with the icosahedron, the middle band with minima containing one vacancy in the outer shell and a single capping atom on the surface, and the highest band with icosahedral minima with two vacancies in the surface shell and two capping atoms on the surface. The capping atoms and vacancies were observed to diffuse across the surface, the latter more slowly. From the STA energy bands Kunz and Berry inferred that the solid and surface-melted states coexisted. These states were previously noted by Honneycutt and Andersen40 and Stillinger and Stillinger,41 but were not connected with surface-melting.

Kunz and Berry also extended an analytical theory for the melting of clusters9 to allow for surface melting. From this they showed that if the vibrational entropy was sufficiently nonlinear in the number of capping atoms, there would be a stable state in the canonical ensemble corresponding to the surface-melted states as well as the solidlike and homogeneously melted liquidlike states. From a limited sample of minima of LJ55, they found evidence that the vibrational entropy became saturated for states with three capping atoms, and thus concluded that LJ55 satisfied the above condition. However, this result is at variance with Ref. 10, where $\log \nu^{\cos} / \nu^{\cos}$ was calculated for a sample of over a thousand minima. This function showed a linear increase with the energy of the minimum up to $-268\epsilon$ where there was a sharp jump due to the lower frequencies associated with the liquidlike minima. Kunz and Berry were also puzzled by the results of Labastie and Whetten for LJ55,14 where no evidence for surface melting was seen, and suggested that the statistical methods employed in the latter study might be the cause of this perceived difference. However, we see no reason why the coexistence seen in STA properties should be visible in the thermodynamic functions that Labastie and Whetten calculated.

In recent work by Lynden-Bell and Wales,6 the potential energy was found to be the most effective order parameter to distinguish between the solidlike and liquidlike states, and was used to calculate a Landau free energy barrier between them. Two Landau free energy minima were found in the reduced temperature range 0.29–0.31.

In the present study, the STA temperature is being used as an order parameter to distinguish between the solidlike, surface-melted, and liquidlike states. The STA temperature reflects the minimum energy of the wells with which the cluster is associated, where high temperatures correspond to low energy minima. Thus we expect that the STA temperature bands will be related to peaks in the energy distribution of the minima. (This distribution is shown in Fig. 6 of Ref. 6.) Therefore the STA temperature can be used to elucidate the connection between the observed behavior and the inherent structures22 (local minima) of the PES and to understand their effect on thermodynamic properties such as the caloric curve. The minima on the PES of LJ55 can be divided into six energy ranges as in Table VI. It is expected that ranges I, II, III, and VI make up the solidlike state, the two surface-melted states, and the liquidlike state, respectively.

MD runs of $2.5 \times 10^6$ time steps were performed at 23 energies around the coexistence region. The STA temperature distributions were calculated for each energy. At low energies the distribution is unimodal. It becomes bimodal at 48.193$\epsilon$, and trimodal at 49.183$\epsilon$. This multimodality implies that the surface-melted states are thermodynamically stable. At 60.238$\epsilon$ a much broader peak appears at lower temperature. Figure 11(a) shows trimodal behaviour due to dynamic coexistence between the solid and the two surface-melted states. Figure 11(b) shows bimodal behavior due to dynamic coexistence between the liquidlike and solid/surface-melted states. The shoulders of the high-temperature peak are the remnants of the trimodal behavior seen at lower energies.

<table>
<thead>
<tr>
<th>Region</th>
<th>Lower energy bound/\epsilon</th>
<th>Higher energy bound/\epsilon</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>−279.248 47</td>
<td>−279.248 47</td>
</tr>
<tr>
<td>II</td>
<td>−276.604 29</td>
<td>−276.199 35</td>
</tr>
<tr>
<td>III</td>
<td>−274.500 00</td>
<td>−273.000 00</td>
</tr>
<tr>
<td>IV</td>
<td>−273.000 00</td>
<td>−271.500 00</td>
</tr>
<tr>
<td>V</td>
<td>−271.500 00</td>
<td>−268.840 00</td>
</tr>
<tr>
<td>VI</td>
<td>−268.840 00</td>
<td>...</td>
</tr>
</tbody>
</table>

TABLE VI. Division of the PES into energy ranges. There are no minima with energies between regions I and II, and II and III.
The peaks have merged because the greater vibrational energy has broadened the distributions for each state. These STA temperature results are in good agreement with Kunz and Berry’s work on LJ55 in the canonical ensemble. Quenching was performed from the run at $254.243 \epsilon$ to test the hypothesis that the three peaks in the STA temperature distribution were due to the first three peaks in the distribution of the potential energy minima. A quench was performed if the short-time-averaged temperature was within a temperature range around the maximum of any of the three peaks. The results, given in Table VII, unequivocally show the correspondence between the STA temperature peaks and the different energy ranges of potential energy minima.

Some of the quenched structures in energy ranges II and III were examined further. A selection of these minima are shown in Fig. 12 and their energies are given in Table VIII. Range II consists of icosahedral-based structures with a vacancy in a five-coordinate vertex site and a single cap atom. There are eleven such structures, four with the cap in the center of a triangular face [Fig. 12(a)] and seven with the cap in an off-center site [Fig. 12(b)]. These structures have been reported previously in a study using a more sophisticated potential to represent Ar.41 Range III consists of structures with two vertex vacancies and two cap atoms [Figs. 12(b), 12(i), and 12(j)], and structures with a vacancy in a six-coordinate edge site and a single capping atom [Fig. 12(g)]. The lower energy structures have the two cap atoms paired, either on the same face [Figs. 12(c) and 12(d)] or straddling two faces [Figs. 12(e) and 12(f)]. We also examined some minima corresponding to range IV. We found structures with three cap atoms, as well as some with combined edge and vertex vacancies and two capping atoms [Fig. 12(k)] and distorted icosahedra [Fig. 12(l)].

The STA temperature distribution was partitioned according to its peaks, and the mean and standard deviation of the temperature were calculated for each, along with the integrated probabilities. The two surface-melted states can be clearly seen in the STA temperatures in Fig. 13(a), but they have only a small effect on the caloric curve. They cause it to bend gradually away from the temperature corresponding to the icosahedron. In the language of Eq. (21), the value of $\Delta/E_1^{1/2}$ is too small for surface melting to cause a significant feature in the caloric curve. From the probabilities [Fig. 13(b)] it can be seen that, despite their length, some of the MD runs have not achieved ergodicity in the energy range $47–55 \epsilon$, because the passage between solidlike and surface-melted states is infrequent on the time scale of the run. Lindemann’s $\delta$ begins to rise at the onset of the surface-melting.

Thermodynamic properties can be predicted from a rep-
representative sample of minima on the PES using a harmonic superposition approximation.\textsuperscript{10,43} Such a sample can be obtained from a high energy MD run with regular quenching. The total density of states, $\Omega(E)$, can be written as a sum over the known minima, each weighted by $\gamma(E')$, where $\gamma(E')$ is the number of quenches to minimum $s$. This analysis gives\textsuperscript{10}

$$
\Omega(E) \approx \sum_{E_s^0 < E} \gamma(E') \left( \frac{E - E_s^0}{E' - E_s^0} \right)^{k-1},
$$

where $E'$ is the energy of the MD run. The use of $\gamma(E')$, which takes into account the fact that as the energy increases, we have an increasingly small fraction of the total number of minima at that energy. In the derivation of the formula it is assumed that the density of states for minimum $s$ at energy $E'$ is proportional to $\gamma(E')$. It is easy, therefore, to see the contribution that a subset of minima on the PES makes to the density of states by restricting the sum in Eq. (32) to those minima. That subset of minima can be defined by any suitable order parameter. Hence, the density of states of region $i$ of the PES, $\Omega_i$, is

$$
\Omega_i \approx \sum_{E_s^0 < E} \gamma(E') \left( \frac{E - E_s^0}{E' - E_s^0} \right)^{k-1}.
$$

From $\Omega_i(E)$ we can work out all the thermodynamic properties of region $i$, such as the temperature, heat capacity, and Helmholtz free energy.

For $\text{LJ}_{55}$, it is instructive to calculate the contribution of minima in the energy ranges given in Table VI to $\Omega(E)$. These calculations may help to explain why there is no peak in the STA temperature distributions corresponding to states in energy range IV. A sample of 989 minima produced from a MD run at 64.748$\varepsilon$ is used in the calculations.\textsuperscript{10} Plotted in Fig. 14(a) is the function

$$
\phi(E) = \ln \Omega_i - \ln c - 2.89E,
$$

where $c$ is the proportionality constant in Eq. (32). A multiple of the energy has been subtracted to show more clearly the main features in the density of states. 2.89$\varepsilon^{-1}$ is the value of the inverse temperature at an energy corresponding to the minimum in the total $\phi(E)$. The double maximum in the total $\phi(E)$ is equivalent to two points of inflection in $\ln \Omega(E)$, a result which has previously been observed by Labastie and Whetten\textsuperscript{14} and is the necessary and sufficient condition for an $S$-bend in the microcanonical caloric curve.\textsuperscript{16} This double maximum is due to the competition between the solidlike/surface-melted state and the liquidlike state, and in particular the very sharp rise in the liquidlike

### Table VIII. Energies of LJ\textsubscript{55} minima represented in Fig. 12.

<table>
<thead>
<tr>
<th>Description</th>
<th>Point group</th>
<th>Energy/$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>vertex vacancy+centered cap</td>
<td>$C_s$</td>
<td>-276.596 76</td>
</tr>
<tr>
<td>vertex vacancy+off-centered cap</td>
<td>$C_1$</td>
<td>-276.199 35</td>
</tr>
<tr>
<td>2 vertex vacancies+capping pair</td>
<td>$C_s$</td>
<td>-274.281 36</td>
</tr>
<tr>
<td>2 vertex vacancies+capping pair</td>
<td>$C_1$</td>
<td>-274.250 58</td>
</tr>
<tr>
<td>2 vertex vacancies+capping pair</td>
<td>$C_s$</td>
<td>-274.216 87</td>
</tr>
<tr>
<td>edge vacancy+centered cap</td>
<td>$C_s$</td>
<td>-274.136 72</td>
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</tr>
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<td>$C_s$</td>
<td>-273.832 34</td>
</tr>
<tr>
<td>2 vertex vacancies+2 caps</td>
<td>$C_1$</td>
<td>-273.826 03</td>
</tr>
<tr>
<td>fused vertex and edge vacancy+capping pair</td>
<td>$C_s$</td>
<td>-272.586 59</td>
</tr>
<tr>
<td>distorted icosahedron</td>
<td>$C_s$</td>
<td>-272.826 03</td>
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</tbody>
</table>

FIG. 13. (a) Plot of the temperature against energy for LJ\textsubscript{55}. The caloric curve has been split into contributions from regions of phase space corresponding to peaks in the STA temperature distribution. The overall caloric curve is represented by the dashed line without any error bars. (b) Plot of the probability of LJ\textsubscript{55} being in regions of phase space I, II, III, and VI characterized by their different STA temperatures. Above 60 $\varepsilon$ regions I–III were indistinguishable. The energy is measured relative to the energy of the global minimum icosahedron.
density of states due to the extremely large number of liquidlike minima and their lower average vibrational frequency. It can be seen from Fig. 14(a) that there is no point at which states with three capping atoms make a significant contribution to the density of states, and therefore the probability of the cluster being in such a well is always very low. This consequence arises simply because the liquidlike states become the dominant contributor to the density of states at an energy lower than that required for the density of states of minima with three capping atoms to compete.

The probability that the cluster is in region $i$ of the PES can also be calculated by this method, and is given by

$$p_i(E) = \frac{\Omega_i}{\Omega} \sum_{E_i^0 < E} \gamma(E') \left( \frac{E - E_i^0}{E' - E_i^0} \right)^{\kappa-1} \sum_{E_i^0 < E} \gamma(E') \left( \frac{E - E_i^0}{E' - E_i^0} \right)^{\kappa-1}. \quad (35)$$

This calculation has been done for the energy ranges of Table VI. The results [Fig. 14(b)] are in excellent agreement with the probabilities found by simulation, bearing in mind the error in the latter due to nonergodicity. In the ergodic region the two sets of results lie almost on top of each other. This correspondence confirms the utility of the harmonic superposition method\textsuperscript{10} not only in being able to reproduce thermodynamic properties, such as the $S$-bend in the microcanonical caloric curve,\textsuperscript{10} but also in elucidating the role of different parts of the PES in the thermodynamics. It also shows that the STA temperature is a suitable order parameter to distinguish regions of the PES with different potential energy.

In previous work\textsuperscript{38, 41} transition states were found from a sample of 402 minima.\textsuperscript{33} Here we examine some of the
It can be seen from Fig. 16 that the Landau entropy well melted state, and the liquidlike state are approximately equal. Energy the probabilities of observing the solidlike/surface-pop-out mechanisms energy of 6.374 \( \epsilon \)

FIG. 16. Plot of the average well depth in the Landau entropy against the averaging period for the STA temperature. The results are for a MD run of \( 2.5 \times 10^6 \) time steps at 6.374 \( \epsilon \) relative to the icosahedron energy of LJ. 55 transition states which are responsible for the dynamics of the surface-melted states and the transitions between the different states. Most of the low energy transition states are localised rearrangements, the majority of which are edge-bridging processes which allow the cap atoms of the surface-melted states to diffuse rapidly across the surface. In a previous study of the transition states of the icosahedron, some “pop-out” rearrangements for the formation of vertex and edge vacancies were illustrated. In Fig. 15 we show some other types of rearrangement. Information on these rearrangements is given in Table IX. Defect creation mechanisms are responsible for passage between the solidlike and surface-melted states [Figs. 15(a), 15(e), and 15(h)]. The capping pairs in the low energy minima of energy range III can move without splitting up in a mechanism that involves two cooperative edge-bridging processes [Fig. 15(b)]. As for LJ 14, surface-cap intershell exchange can occur by pop-in, pop-out mechanisms [Figs. 15(c) and 15(g)] without the cluster changing state. Mechanisms for the motion of the surface defects are shown in Figs. 15(d) and 15(f).

Finally, as for LJ 13, we calculated the Landau entropy well depth using the STA temperature as an order parameter for a range of averaging periods. The calculations were performed for the same MD run of \( 2.5 \times 10^6 \) time steps at a total energy of 63.374 \( \epsilon \) relative to the icosahedron energy. At this energy the probabilities of observing the solidlike/surface-melted state, and the liquidlike state are approximately equal. It can be seen from Fig. 16 that the Landau entropy well persists for much higher values of the averaging period than for LJ 13 because the residence times in each state are much longer. This persistence is due to the greater complexity of the PES for LJ 55. A liquidlike minimum is much less likely to be connected by a transition state to a solidlike minimum for LJ 55 than for LJ 13. For averaging periods of more than 500 time steps, the solidlike and surface-melted states can again be resolved in the higher temperature peak. This multimodality shows that the unimodality of the high temperature peak at an averaging period of 500 time steps was due to broadening of the temperature distributions for each state with the higher vibrational energy rather than to averaging over both states. Interestingly, the instantaneous temperature distribution is unimodal, in contrast to the canonical potential energy and energy distributions, which show bimodality over a range of temperature. The maximum value of the depth of the Landau entropy well is 3.3 \( k \), significantly higher than for LJ 13, as expected.

IX. Conclusions

We have shown the usefulness of order parameters based upon short time averages in elucidating coexistence in atomic clusters. Multimodality in order parameter probability distributions can be related to Landau entropy maxima in the microcanonical ensemble and hence thermodynamic stability. Landau entropy maxima are separated by Landau entropy wells. These entropy wells correspond to regions of phase space which connect two stable states and have a lower density of states; they are entropy bottlenecks. The advantage of using STA order parameters is that they are a more sensitive probe of coexistence in clusters; vibrational fluctuations in instantaneous order parameters can obscure coexistence. This advantage has been illustrated for LJ 8, where a geometric STA order parameter has been used to show that the two lowest energy isomers coexist. For LJ 14 cap diffusion and surface-cap exchange is responsible for the nonrigid behavior of the capped icosahedron and the rise in Lindemann’s \( \delta \). For LJ 55 the STA temperature distinguishes between coexisting solidlike, surface-melted, and liquidlike states. The dynamic equilibrium between these states has been related to the minima and transition states on the PES, and further insight into the thermodynamics has been provided by calculations using the harmonic superposition method.

S-bends in the microcanonical and isopotential ensembles imply that two states are thermodynamically stable.
In a two state model we have shown that an S-bend in the microcanonical ensemble is likely when the inequality $\Delta E_{1/2} > 2\sqrt{3N}$ is satisfied. Therefore, S-bends become more probable as the size of the cluster increases and when $\Delta E_{1/2}$ is large. The latter is the case when the two states are separated by a large energy gap and the lower energy state is as solidlike as possible and the higher energy state as liquidlike as possible. This situation occurs for the icosahedral magic number clusters.

ACKNOWLEDGMENTS

J. P. K. D. is grateful to the EPSRC for financial support and D. J. W. is a Royal Society Research Fellow.

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