Isomerization dynamics and ergodicity in Ar$_7$

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The isomerization dynamics of a model Ar$_7$ cluster, bound by the pairwise Lennard–Jones potential, are examined in the melting and liquid-like regions. We use molecular dynamics with frequent quenching to calculate the accumulated residence times and distribution of lifetimes in each of the four geometrical isomers as a function of the microcanonical energy. The residence times are compared with the ratios of the density of states associated with the isomers, evaluated by microcanonical Monte Carlo simulations, and are in good agreement. The distribution of lifetimes is found to be exponential (Poissonian) except at very short times. We propose and test a simple explanation for this behavior in terms of rapid recrossings of the dividing surface. The energy dependence of the individual isomerization rates is compared with the predictions of RRK theory through a knowledge of the transition states. We discuss the results in the light of a recent study that addressed the issue of ergodicity in this system. © 1997 American Institute of Physics. [S0021-9606(97)02144-2]

I. INTRODUCTION

The ergodic hypothesis is fundamental to statistical mechanics. A conservative classical system is ergodic if, starting from any given volume of phase space, every other region of phase space with the same energy is eventually reached. An ensemble of such systems is therefore distributed with uniform density over the energy hypersurface. This implies that a single system resides for the same time in equal volumes of phase space, and that the time average of a quantity over a sufficiently long dynamical trajectory can be replaced by the average over phase space.

Problems can arise in simulations if the system must overcome high barriers to reach other regions of phase space. If the total energy lies only slightly above a barrier, the length of a simulation required to obtain enough crossings for statistical sampling of all regions may be extremely long. Errors due to this so-called ‘quasi-ergodicity’ decrease as the length of the simulation increases, and disappear in the limit of an infinitely long simulation. Of course, molecular dynamics (MD) simulations are inherently nonergodic when the total energy lies below isomerization barriers since regions of phase space are then cut off from each other, although the dynamics within a connected region may still be ergodic. “Quasi-ergodicity” can also be a problem in Monte Carlo (MC) calculations, for example canonical Metropolis sampling at low temperatures. Here, slow barrier crossing can be accelerated by the jump-walking technique, in which jumps to higher temperature distributions are periodically attempted.

In a recent study, Seko and Takatsuka concluded that the dynamics of Ar$_7$-like clusters, modeled by a pairwise Lennard–Jones (LJ) potential, are not ergodic in the melting region. In particular, the accumulated residence times in geometrically distinct energy wells did not correspond to the density of states associated with these wells, and the distribution of lifetimes in the wells was not exponential. This paper re-examines these aspects of the dynamics, using rigorous microcanonical Monte Carlo sampling to evaluate the densities of states, which we find to be in good agreement with the dynamical simulations. The distribution of lifetimes is calculated to be exponential except at very short times, and we focus on the reasons for the deviation.

To aid our understanding of the dynamics, we have characterized the transition states that mediate the rearrangement processes. This also allows us to apply the rate theory of Rice, Ramsperger and Kassel (RRK) to estimate individual isomerization rates, which can then be compared with those obtained from the MD simulations.

II. FEATURES OF THE POTENTIAL ENERGY SURFACE

The LJ potential energy is

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

where \( r_{ij} \) is the distance between atoms \( i \) and \( j \). The well depth \( \varepsilon \) and pair separation \( \sigma \) at zero potential, together with the mass \( m \) of an atom, determine the time scale of the dynamics. Since the topology of the potential energy surface is not affected by the values of these parameters, there is no advantage in choosing values for which the dynamics are relatively fast; one would simply have to take correspondingly shorter time steps when integrating the equations of motion. All the present calculations were performed in reduced units where \( \varepsilon, \sigma, \) and \( m \) are taken as the units of the quantities they measure, defining \( \sqrt{\frac{m\sigma^2}{\varepsilon}} \) as the unit of time. For a physical perspective, however, we have converted the results using parameters appropriate to argon: \( \varepsilon=119.8 \text{ K}, \sigma=3.405 \text{ Å}, \) and \( m=39.948 \text{ amu}, \) which gives \( \sqrt{\frac{m\sigma^2}{\varepsilon}} = 2.156 \text{ ps}. \) We emphasize that since the LJ potential scales, the choice of absolute units has no effect whatsoever on any of our conclusions.

It is well known that Lennard–Jones potentials have only four geometrically distinct isomers. We label these 1 to 4 in order of increasing...
potential energy (Table I). A systematic search of the potential energy surface by eigenvector-following found 12 true transition states, in agreement with Tsai and Jordan. Six of these transition states are for degenerate rearrangements (i.e., permutational isomerizations of the same structure), and the remaining six interconnect the four geometrical isomers, as summarized in Table II.

In microcanonical (constant energy) molecular dynamics simulations the cluster behaves like a solid at low energies, vibrating within a single well on the potential energy surface. At high energies, rapid isomerizations are observed, and the dynamics appear liquid-like. Between the intermediate energies of about ~14.5e and ~13.0e large amplitude vibrations within a well occur between infrequent isomerizations as the cluster melts.

We note that this cluster does not exhibit a Van der Waals loop in its microcanonical caloric curve. However, solid-like and liquid-like states can be said to coexist over a finite range of total energy in terms of a double maximum in the Landau entropy constructed from the short-time-averaged temperature. The present study is concerned with the dynamics of isomerization in the liquid-like and solid-like states can be said to coexist over a finite range of total energy in terms of a double maximum in solid-like and liquid-like states can be said to coexist over a finite range of total energy in terms of a double maximum in its microcanonical caloric curve. However, we note that this cluster does not exhibit a Van der Waals loop in its microcanonical caloric curve. However, solid-like and liquid-like states can be said to coexist over a finite range of total energy in terms of a double maximum in the Landau entropy constructed from the short-time-averaged temperature. The present study is concerned with the dynamics of isomerization in the liquid-like and melting regions from energies of ~14.505e to ~11.005e. Tables I and II show that all four geometries are accessible in this range, although barrier crossing may be slow at the lower energies.

### III. DISTRIBUTION OF RESIDENCE TIMES

We have simulated the cluster’s trajectory through phase space using constant energy MD with an adaptive step-size

Bulirsch-Stoer algorithm to integrate the classical equations of motion. This approach offers high integration speed and good conservation of the total energy (a typical standard deviation in this work was 1 part in 10^6 with a drift in the mean value of less than 1 part in 10^16). The atoms were initially assigned random velocities, scaled to give the desired total energy, subject to the constraints of zero overall linear and angular momenta.

To determine the potential well (isomer) in which the cluster resides at a particular point in time, we employed quenching. The simulation is suspended, and the potential energy is minimized with respect to the atomic positions. One way to do this is by following the path of steepest descent: \( \mathbf{q} \leftarrow \nabla V(\mathbf{q}) \), where \( \mathbf{q} \) is the N-dimensional vector in nuclear configuration space and N is the number of atoms. The simulation is then resumed from the point before the quench. Instead of steepest descent, we used conjugate gradient minimization, which gives very similar results, and is much faster. When two successive quenches give different energies, they must bracket the boundary between the basins of attraction of the two minima.

If quenching is frequent enough, as discussed below, we can estimate the isomerization rate from the time between changes in the quench energy.

For a unimolecular event such as the escape of a cluster from a particular potential well, we expect the waiting time \( \tau \) before the event occurs to have a Poissonian distribution, i.e., proportional to \( e^{-k\tau} \), where \( k \) is the (first-order) rate constant for the process. We can produce a histogram of lifetimes for a particular well by frequently quenching an MD trajectory.

### TABLE I. The four geometrically distinct minima of LJ 7.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Energy/( e )</th>
<th>Point group</th>
<th>( \bar{V}/\sqrt{e/m\sigma^2} )</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-16.505</td>
<td>( D_{5h} )</td>
<td>1.638</td>
<td>Pentagonal bipyramid</td>
</tr>
<tr>
<td>2</td>
<td>-15.935</td>
<td>( C_{3v} )</td>
<td>1.599</td>
<td>Capped octahedron</td>
</tr>
<tr>
<td>3</td>
<td>-15.593</td>
<td>( C_{3v} )</td>
<td>1.511</td>
<td>Tricapped tetrahedron</td>
</tr>
<tr>
<td>4</td>
<td>-15.533</td>
<td>( C_2 )</td>
<td>1.509</td>
<td>Bicapped trigonal bipyramid</td>
</tr>
</tbody>
</table>

### TABLE II. Transition states for nondegenerate (upper part of table) and degenerate rearrangements. \( \bar{V} \) is the geometric mean normal mode harmonic frequency for the 3N-7 = 14 modes with positive force constants, and \( \nu_{\text{max}} \) is the single imaginary frequency.

<table>
<thead>
<tr>
<th>Transition state</th>
<th>Energy/( e )</th>
<th>Point group</th>
<th>Connected minima</th>
<th>( \bar{V}/\sqrt{e/m\sigma^2} )</th>
<th>( \nu_{\text{max}}/\sqrt{e/m\sigma^2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-15.445</td>
<td>( C_1 )</td>
<td>1, 2</td>
<td>1.668</td>
<td>0.503</td>
</tr>
<tr>
<td>2</td>
<td>-15.320</td>
<td>( C_1 )</td>
<td>2, 3</td>
<td>1.625</td>
<td>0.501</td>
</tr>
<tr>
<td>3</td>
<td>-15.283</td>
<td>( C_1 )</td>
<td>2, 4</td>
<td>1.620</td>
<td>0.503</td>
</tr>
<tr>
<td>4</td>
<td>-15.033</td>
<td>( C_1 )</td>
<td>1, 3</td>
<td>1.530</td>
<td>0.411</td>
</tr>
<tr>
<td>5</td>
<td>-15.026</td>
<td>( C_1 )</td>
<td>1, 4</td>
<td>1.533</td>
<td>0.210</td>
</tr>
<tr>
<td>6</td>
<td>-14.597</td>
<td>( C_1 )</td>
<td>1, 4</td>
<td>1.529</td>
<td>0.414</td>
</tr>
<tr>
<td>7</td>
<td>-15.098</td>
<td>( C_{2v} )</td>
<td>2, 2</td>
<td>1.632</td>
<td>0.283</td>
</tr>
<tr>
<td>8</td>
<td>-14.816</td>
<td>( C_1 )</td>
<td>4, 4</td>
<td>1.572</td>
<td>0.366</td>
</tr>
<tr>
<td>9</td>
<td>-14.811</td>
<td>( C_{2v} )</td>
<td>4, 4</td>
<td>1.576</td>
<td>0.355</td>
</tr>
<tr>
<td>10</td>
<td>-14.568</td>
<td>( C_{2v} )</td>
<td>3, 3</td>
<td>1.525</td>
<td>0.202</td>
</tr>
<tr>
<td>11</td>
<td>-14.549</td>
<td>( C_1 )</td>
<td>4, 4</td>
<td>1.526</td>
<td>0.186</td>
</tr>
<tr>
<td>12</td>
<td>-12.549</td>
<td>( D_{5h} )</td>
<td>3, 3</td>
<td>0.863</td>
<td>0.318</td>
</tr>
</tbody>
</table>
noting when the energy of the quenched geometry changes, and counting how many times the lifetimes fall within a series of time “bins.” We chose to quench every 0.0464 reduced time units (equivalent to 0.1 ps for Ar). The harmonic normal mode periods of the system, derived from the eigenvalues of the Hessian matrix at the minima, range from 0.38 to 1.78 reduced units (0.8–3.8 ps for Ar), so we are quenching several times within a typical vibrational period.

We have run trajectories for $0.278 \times 10^9$ reduced time units (0.6 $\mu$s for Ar) at energies ranging from $-14.505 \varepsilon$ to $-11.005 \varepsilon$ in intervals of 0.5 $\varepsilon$. At the lowest energy, isomerizations were not frequent enough to gather reliable lifetime statistics, but for the other trajectories, the distribution of lifetimes in wells of a particular geometry was always found to be exponential except at very short lifetimes. Figure 1 shows the distribution of lifetimes of isomer 2 at an energy of $-13.505 \varepsilon$ (in the melting region). Despite the inevitable noise, the data are clearly well represented by a simple exponential decay after the initial oscillation, as shown in the figure. The peak and trough at very short lifetimes have already been observed at higher energies by Amar and Berry. We have now run longer trajectories and gather more statistics, showing that this behavior persists in the melting region. Seko and Takatsuka noticed the trough at short lifetimes and the cap of the octahedron.

We propose that the initial peak is simply due to rapid recrossings of the transition state while the cluster is undergoing rearrangement. These recrossings do not constitute genuine isomerizations, and are really due to the sensitivity of quenching to the precise starting point when the structure is near a transition state. Quenching defines a hypersurface in configuration space that passes through the transition state and separates the two minima. This surface is not flat, but is a function of all the vibrational coordinates of the cluster, and these change as a transition takes place. The trajectory is therefore likely to recross different parts of the surface when the transition to occur in the first place. The dip in the distribution of lifetimes in Fig. 1 lasts just over 1.5 reduced units, which is probably an underestimate of the true period. We have checked that the recrossings are not a quirk of the conjugate gradient algorithm by rerunning some of the simulations using eigenvector-following instead; the results were very similar.

We would expect the majority of trajectories that visit an isomer only briefly, to return to the same well from which they came. The last well should not only be of the same geometry as the one preceding the visit, but should also be the same permutational isomer of this structure. We have tested this proposal by calculating the percentage of trajectories that return to the same permutational isomer after visiting isomer 2 (the capped octahedron) as a function of the time associated with the visit. Figure 2 shows the results. Over 70% of visits shorter than 0.232 reduced time units returned to the same permutational isomer, compared with typically 10% at longer lifetimes, supporting our suggestion.

We now turn to the trough at short lifetimes in the distribution in Fig. 1. To obtain a perfectly exponential distribution of lifetimes, the probability density of escape from a given well would have to be constant in time, right from the point that the system enters that well. Isomerization occurs when sufficient energy accumulates in a particular degree of freedom to carry the system over a transition state. A uniform escape probability therefore implies a random distribution of the energy within the vibrational modes of the cluster. This is unlikely to be the case when a cluster has just entered a well, since the energy must be unevenly distributed for the transition to occur in the first place. The dip in the distribution of lifetimes in Fig. 1 lasts just over 1.5 reduced units (3 ps for Ar). As mentioned above, the harmonic normal mode periods lie between 0.38 and 1.78 reduced units, so the duration of the dip is of the order of a molecular vibration. It
seems reasonable, therefore, that exponential behavior is recovered only after this delay, since some motion is required to redistribute the energy. This is consistent with the concept of a transport process in configuration space, an approach currently being pursued by Takatsuka and Seko.\textsuperscript{17}

We conclude this section by noting that the overall distribution of lifetimes in any basin\textsuperscript{3} is not expected to be exponential. Each well has its own decay constant, so the overall distribution is a sum of exponentials with different exponents. At high energies it is possible that this distribution may approach exponential behavior because the rate constants for isomerizations become similar when the total energy lies high above the potential energy surface (the barriers are then less important).

### IV. ACCUMULATED RESIDENCE TIMES

If the dynamics are ergodic then the total time that a cluster spends in a particular well is proportional to the density of states associated with that well at a given total energy. Denoting the density of states at energy $E$ for isomer $i$ by $\Omega_i(E)$, and the time associated with that isomer during a simulation at the same energy by $t_i(E)$, the ergodicity condition is

$$
\frac{t_i(E)}{\sum_j t_j(E)} = \frac{\Omega_i(E)}{\sum_i \Omega_i(E)}. \tag{2}
$$

The microcanonical density of states is given by

$$
\Omega(E) = C \int \int \delta[H(q,p) - E] d\mathbf{p} d\mathbf{q}, \tag{3}
$$

where $\mathbf{p}$ is the $3N$-dimensional momentum space vector, $C$ is a constant, and (for a homogeneous system)

$$
H = \frac{1}{2m} \sum_{i=1}^{3N} p_i^2 + V(q) \tag{4}
$$
is the classical Hamiltonian. The momentum integral in Eq. (3) can be done analytically, giving\textsuperscript{18}

$$
\Omega(E) = C' \int [E - V(q)]^{(\kappa-2)/2} \Theta[E - V(q)] d\mathbf{q}, \tag{5}
$$

where $\Theta(x) = 1$ for $x > 0$ and zero otherwise. $\kappa$ is the number of independent components of $\mathbf{p}$ and is equal to $3N - 6$ for this system in which the total linear and angular momenta are constant at zero. The above form for the momentum integral assumes that the vibrational modes are well coupled so that the energy is randomized amongst them. We expect this to be the case for the homogeneous and strongly anharmonic LJ$_7$ cluster, and we shall see that the MD data are consistent with this assumption. Special care must be taken when studying systems that have degrees of freedom with very different time scales or weakly coupled modes. Examples of such systems are the trapped molecule clusters He$_8$I$_2$ and Ar$_8$I$_2$ which have been examined recently using a modified microcanonical Monte Carlo method.\textsuperscript{19}

Equation (5) could be evaluated by brute force MC by generating random configurations $\mathbf{q}$ and weighting each by $[E - V(q)]^{(\kappa-2)/2} \Theta[E - V(q)]$. To evaluate the density of states associated with each minimum, every configuration could be assigned to one of the four isomers by quenching, allowing the integral in Eq. (5) to be restricted to each of the isomers in turn.\textsuperscript{3} The problem lies in generating the random configurations. If the components of $\mathbf{q}$ are completely random, the overwhelming majority of resulting configurations would have $V(\mathbf{q}) > E$ and therefore zero weight. It is difficult to devise a method for choosing evenly distributed configurations that make significant contributions to the integral. Building up a configuration by placing one atom at a time with restrictions dependent on those already placed may have introduced a bias in previous work.\textsuperscript{3}

We have evaluated Eq. (5) using Metropolis importance sampling\textsuperscript{20} to obtain a microcanonical distribution in configuration space.\textsuperscript{21} Starting from a configuration $\mathbf{q}$, a new configuration $\mathbf{q}'$ is generated by moving a randomly chosen atom to a random position within a box of length $\delta l$ centered on its old position. The move is accepted with probability

$$
\pi(\mathbf{q} \rightarrow \mathbf{q}') = \min \left[ 1, \frac{[E - V(\mathbf{q}')]^{(\kappa-2)/2} \Theta[E - V(\mathbf{q}')]}{[E - V(\mathbf{q})]^{(\kappa-2)/2} \Theta[E - V(\mathbf{q})]} \right]. \tag{6}
$$

If a move is rejected, the old configuration is counted again. This scheme generates a Markov chain which rigorously reproduces the microcanonical ensemble whilst not involving any dynamics. We chose $\delta l = 0.2a$, which gave an acceptance rate between 25% and 50%. At high energies, evaporation can become a problem. Since we are not interested in the dissociation of an atom from the cluster, moves were...
automatically rejected if they took an atom outside a radius of 2σ from the center of mass. This radius is larger than the most extreme atomic excursions observed in the MD simulations, and the proportion of moves rejected in this way was never greater than 2 in 10^6, so we do not expect this constraint to affect the results.

Evaluating the ratio of densities of states for Eq. (2) is now simply a matter of using quenching to determine the ratio of samples associated with each isomer. Since successive configurations are highly correlated, it is more efficient to sample once every 1000 steps. This provides a better coverage of configuration space, and reduces the computation time required for convergence, as the majority of the computational effort is spent performing the quenches. The convergence of the ratios at $E = -12.505\varepsilon$ is shown in Fig. 3 as an example. Table III lists the results for $E$ ranging from $-14.505\varepsilon$ to $-11.505\varepsilon$ with 10^6 samples at each energy.

The fractional accumulated residence times on the left-hand side of Eq. (2) are easily calculated from the quench data obtained from the MD simulations of the previous section (each of duration 0.6 μs with quenching every 0.1 ps for the Ar parameters). The convergence of the occupation statistics at $E = -12.505\varepsilon$ is shown in Fig. 4, and the results as a function of energy are listed in Table IV. They are largely in agreement with the MD results of Seko and Takatsuka, and the small discrepancies can probably be attributed to the different quenching method.

Figure 5 compares the MD residence fractions with the MC density of states ratios. The agreement is good, and is consistent with ergodic dynamics in this energy range on the time scale we have investigated. The analogous results of Seko and Takatsuka, plotted in Fig. 6, do not show agreement even outside the melting region. We suggest that this may be due to a bias in their algorithm for generating random configurations for the density of states calculations, and also possibly because of an inadequate number of samples (50 000 without importance sampling).

The interesting dominance of isomer 4 at high energies is easily explained by the data in Table I. In the harmonic approximation, the density of states of geometrical isomer $i$ is

$$\Omega_i(E) = \frac{2N!}{h_i^{(PG)} (3N-7)! (h \bar{\nu})^{N-6}},$$

where $E_i$ is the potential energy at the minimum, $\bar{\nu}$ is the geometric mean frequency, and $h_i^{(PG)}$ is the order of the point group of the isomer. The factor $2N!/h_i^{(PG)}$ accounts for the number of permutational isomers. From Table I we see that the lower symmetry and lower mean vibrational frequency of isomer 4 cause it to have a larger density of states at high energy. Physically this corresponds to a larger number of identical wells with smaller curvature, i.e., "wider."

**FIG. 3.** Example of the convergence of the density of states ratios for the four isomers in the microcanonical MC calculation. The energy is $-12.505\varepsilon$.

**FIG. 4.** Example of the convergence of the accumulated residence times of the four isomers in the MD simulations. The energy is $-12.505\varepsilon$. The trajectory length corresponds to 0.6 μs for Ar.

**FIG. 5.** Results of the present work. Solid lines: percentage of MD trajectory associated with isomers 1 to 4. Dashed lines: percentage of the density of states associated with isomers 1 to 4.
Having counted the number of transitions between the isomers and calculated the accumulated residence times, the unimolecular rate constant for an individual isomerization process is easily obtained by dividing the number of transitions by the total residence time in the first isomer. Table V gives the rate constant matrix at a series of energies. Each row of the matrix lists the isomerization rates from one isomer to each of the four. The results are consistent with those of Amar and Berry, although we expect the new results to be better converged since our simulations are far longer; we obtained considerable variation in the rates when they were calculated from portions of the long trajectory of the size used in the previous study.

It is interesting to note that there are significant rates between isomers 3 and 4 in Table V in spite of the fact that none of the transition states in Table II links these minima. Further searches starting from parts of the trajectory where quenching changes from one well to the other failed to find a new transition state. However, if the quench interval is decreased, the number of 3→4 transitions decreases, in contrast to other rates which appear to increase, presumably due to the detection of more rapid recrossings. This indicates that the 3→4 transitions are actually going via an intermediate, and that there is no saddle directly between them. This illustrates the dilemma pointed out by Amar and Berry: frequent quenching is desirable in order to detect all transitions, yet it has the effect of counting recrossings, which are not true isomerizations. Thus it is not clear whether the “true” rates are overestimated or underestimated. We feel that our choice of quenching interval is a sensible compromise; several quenches are made within a typical oscillation, but the interval is not so small that the atoms hardly have a chance to move.

Equipped with the transition states for the various processes (Table II) we can compare the rates from MD with those predicted by simple RRK theory, which uses the harmonic approximation for the density of states at the minimum and transition state, and assumes rapid randomization of vibrational energy. The rate constant is given by

$$k(E) = \frac{\hbar^{(PG)}}{\hbar^{(PG)*}} \prod_{i=1}^{3N-6} \frac{E-E_i}{\hbar^{(PG)} \hbar^{(PG)*} \prod_{i=1}^{3N-7} \nu_i}$$

where $\hbar^{(PG)}$ and $\hbar^{(PG)*}$ are the order of the point group of the minimum and of the transition state (their ratio accounts for the “path degeneracy”$^{23}$), $\nu$ and $\nu^*$ are the real normal mode frequencies of the two species.

### Table V. Frequencies of transitions between isomers for $-14.505 \leq E \leq -11.005$ from MD. The entry in row $i$ and column $j$ is the isomerization rate from isomer $i$ to $j$ in ns$^{-1}$. The simulations were each of length 0.6 μs with quenching every 0.1 ps.

<table>
<thead>
<tr>
<th>$E = -14.505$</th>
<th>$E = -12.505$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>4.461</td>
<td>0.055</td>
</tr>
<tr>
<td>0.000</td>
<td>15.790</td>
</tr>
<tr>
<td>0.000</td>
<td>19.563</td>
</tr>
<tr>
<td>$E = -14.005$</td>
<td>$E = -12.005$</td>
</tr>
<tr>
<td>0.008</td>
<td>2.008</td>
</tr>
<tr>
<td>19.344</td>
<td>0.508</td>
</tr>
<tr>
<td>1.204</td>
<td>71.390</td>
</tr>
<tr>
<td>1.333</td>
<td>60.191</td>
</tr>
<tr>
<td>$E = -13.505$</td>
<td>$E = -11.505$</td>
</tr>
<tr>
<td>0.005</td>
<td>9.693</td>
</tr>
<tr>
<td>42.329</td>
<td>2.411</td>
</tr>
<tr>
<td>5.022</td>
<td>118.358</td>
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<tr>
<td>5.776</td>
<td>105.051</td>
</tr>
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<td>$E = -13.005$</td>
<td>$E = -11.005$</td>
</tr>
<tr>
<td>0.020</td>
<td>25.522</td>
</tr>
<tr>
<td>67.899</td>
<td>7.423</td>
</tr>
<tr>
<td>10.893</td>
<td>178.766</td>
</tr>
<tr>
<td>10.508</td>
<td>141.211</td>
</tr>
</tbody>
</table>
frequencies of the minimum and transition state (available from the eigenvalues of the Hessian), \( N \) is the number of atoms (7), and \( E_0 \) and \( E_1 \) are the potential energy of the minimum and of the transition state. An extra factor of 2 must be included in Eq. (8) for degenerate rearrangements to account for flux in both directions through the transition state.

Figure 7 shows the rates from isomer 2 to each of the four as a function of energy. Table II shows that the relevant transition states are 1, 7, 2, and 3. The two sets of lines correspond to MD (solid) and RRK (dashed). Rate constants are notoriously difficult to predict, and the agreement between MD and RRK is quite good here. RRK predicts the correct order, i.e., \( 2 \rightarrow 4 \rightarrow 2 \rightarrow 1 \rightarrow 2 \rightarrow 3 \rightarrow 2 \rightarrow 2 \), and apart from the degenerate rearrangement, the rates themselves agree to within a factor of 2, RRK being systematically higher in each case.

VI. SUMMARY

We have used frequent quenching within microcanonical MD simulations to calculate the distribution of lifetimes for the four distinct geometrical isomers of a model \( \text{Ar}_7 \) cluster. The distribution was found to be exponential except for times shorter than a typical molecular vibration. At very short lifetimes there is an initial peak. We have shown that the majority of these short visits return to the previous permutational isomer. This is consistent with the suggestion that the peak is due to rapid recrossings of the transition state due to the sensitivity of quenching in this region. These recrossings do not constitute genuine isomerizations. After the initial peak, a trough is observed until exponential behavior is achieved after a period of the order of a molecular vibration. We suggest that this delay is due simply to the randomization of kinetic energy which is required for the subsequent Poissonian (exponential) distribution of lifetimes.

We then calculated the ratio of densities of states associated with each of the four isomers using Metropolis impor-

tance sampling of configuration space in the microcanonical ensemble. These ratios were compared with the fraction of time associated with each of the four isomers in the MD simulations. Good agreement was observed, consistent with ergodic dynamics in the energy range studied (\(-14.505 \epsilon \) to \(-11.005 \epsilon \)). Seko and Takatsuka\(^1\) have studied the same cluster, but concluded that the dynamics are nonergodic in the melting regime on the basis of a range of statistics. We note that the agreement between residence times and densities of states presented here is at variance with the latter study, and have put forward explanations for the discrepancies. Although our results suggest that the system does behave ergodically on the relatively long time scales considered, they certainly do not prove this, and there is scope for further investigation of this question.

Finally, we used the accumulated residence times and transition frequencies to construct the rate matrix for isomerization at a series of energies. Having characterized the transition states for the various processes, we compared the predictions of RRK theory with some of the rates from MD. RRK gave rates that were consistently higher, but predicted the correct order and qualitative energy dependence. The actual values were almost always within a factor of 2 of those obtained from MD.

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17. K. Takatsuka and C. Seko (personal communication).