

Vibrational relaxation of clusters: Relation to potential surface topography

Benjamin Vekhter, Keith D. Ball, John Rose, and R. Stephen Berry

Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, Illinois 60637

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Simulations by isothermal and isoergic molecular dynamics show that vibrationally-cold clusters, initially at some high-energy point on their potential surfaces, relax monotonically down to low-lying minima where they are trapped. The most significant point regarding this relaxation is that species with sawtoothlike and staircaselike potentials show the same qualitative behavior, equilibrating their vibrations after each major saddle crossing. This result justifies the use of transition state kinetics for constructing coarse-grained master equations to describe the well-to-well flow of population distributions on complex potential energy surfaces, even in cases such as $(\text{KCl})_{32}$ and some protein models which have staircase topographies in which large drops in potential energy from one well to the next might suggest nonthermal kinetics could occur. © 1997 American Institute of Physics. [S0021-9606(97)00911-2]

I. INTRODUCTION

Extending molecular dynamics (MD) and quenching methods to systems of many atoms, tens and hundreds to begin, poses problems, both computational and methodological, that do not arise with small systems. First, while it is feasible to explore in detail the topographies of the potential surfaces of small systems, in the sense of locating all the stationary points and the links among them, it is unthinkable to expect (or care) to locate even the local minima on the potential surface of a system of, say, 30 atoms, much less the saddles on such a potential surface. At best, one can hope to characterize potential surfaces for molecules and clusters from about 20 to at least hundreds of atoms through the device of statistical sampling of the potential. One such approach to this problem put forward recently¹⁻⁶ makes the topographies of such surfaces comprehensible in some senses, makes it possible to model the kinetics on the “statistical sample” surface, and provides a microscopic-level rationale for the distinction between those substances that are “glass-formers” and those that are “structure-seekers.”

The master equation approach suggests itself as a natural means to investigate the dynamics of systems in this range of sizes, with the RRK or RRKM method the basis for estimating kinetic coefficients.^{5,7} (These are two related methods to treat unimolecular reactions from the assumption that energy is, on average, equipartitioned among the vibrational degrees of freedom. The RRKM method uses quantum partition functions for the initial and transition state; the RRK method is simpler, whether classical or quantum, using just the statistical distribution of quanta among oscillators, with no contributions from entropic factors in the transition state.) The key to this approach is using as elements in the statistical data base, not simply distributions of stationary points, but of sequences of linked stationary points, monotonic in the energies of the minima. That is, the elements of the database are sequences, minimum-saddle-minimum-..., with the minima rising monotonically in energy from basin bottoms. It is now a practical computational exercise to construct such

databases, if the potential surface is known, particularly if it is in analytic form and the first and second derivatives on the surface can be computed analytically.

With such sequences in hand, we can see immediately why the master equation suggests itself as a way to study dynamics and kinetics of unimolecular processes on even quite complex surfaces. The methods for evaluating the rate coefficients for passage between adjacent minima are well established within the context of transition state theory, and all the tools are available from the data on the potential surface to compute the partition functions necessary to evaluate the well-to-well rate coefficients. However a bit of reflection reveals a potential difficulty. The RRK and RRKM methods for evaluating reaction rate coefficients are valid only if the vibrations of the system are in thermal equilibrium, because only then can one use quasi-equilibrium partition functions and a common value of the temperature for all minima. However such equilibrium is achieved only if the system spends sufficient time in each well for the vibrations to thermalize i.e., for the vibrational energy to equipartition. The principal purpose of this report is establishing, from molecular dynamics simulations, the validity of the assumption that the vibrations of a moderately large cluster equilibrate thermally when the cluster passes over a saddle from one minimum to another. More specifically, the computations support the supposition that the vibrations thermalize even for systems with potential surfaces whose topographies are as staircaselike as that of an alkali halide cluster, $(\text{KCl})_{32}$. Naturally, the potential surfaces of clusters such as the Ar_{55} and $(\text{KCl})_{32}$ clusters used here have some local minima separated by saddles so low that thermal motion carries the system from one of these minima to another in as short a time as single vibrational period; in situations of this kind, all the minima visited in the time for thermal equilibration act as a single, very anharmonic, large minimum.

It is useful to define several characteristic times for relaxing, many-atom systems such as clusters and polymers. The first, which we call t_1 , is the effective time for vibrational relaxation; this is normally the shortest. Next is the

mean time t_2 , for passage between neighboring minima. Finally, for isothermal systems, is the time, t_3 , for energy exchange and thermal equilibration between the system and its bath held at temperature T . Only if t_1 is much shorter than t_2 can we give meaning to the vibrational temperature of the system in a basin, and only then can we use a traditional transition state picture, such as the RRK approach, to evaluate well-to-well rate coefficients. (In any case in which t_1 and t_2 are comparable for some set of linked minima, the situation is as described in the previous paragraph: Such a set of linked bowls behave together as a single, anharmonic bowl.) If indeed $t_1 < t_2$, and $t_3 < t_2$ also, then the effective vibrational temperature $T_{\text{vib}} = T$. If, on the other hand, $t_2 \ll t_1, t_3$, the transition occurs between nonequilibrium states; in this case, we cannot use the RRK formalism and, instead, must resort to state-to-state, non-Markovian kinetics. The latter become so much more cumbersome than the former that it is important to establish as wide a range of conditions as possible in which transition-state types of theory (as we shall call all theories based on the assumption of vibrational thermalization after each interwell passage) are valid.

Failure of a cluster or molecule to equilibrate can drastically affect the dynamics of interwell passage. Two situations make natural comparisons with the thermalized case. At one extreme, immediately following an exoergic transition from the j th to $(j+1)$ st minimum, the vibrational modes that contain the excess energy are those that become the reaction coordinate for the next interbasin passage, from basin $(j+1)$ to $(j+2)$. In this case, t_1 would be longer than t_2 , and the next intracuster rearrangement would occur much faster than the same passage in the corresponding thermally-equilibrated system. Conversely, if these momentarily superheated modes were not involved at all in the rearrangements needed for the next transition, then the rate of that next passage would be determined by the rate of energy flow out of the ‘‘hot’’ modes and thus would be lower than if the energy were already equipartitioned among the vibrations. Consequently the value of the ratio t_2/t_1 is crucial for the dynamics of large systems that go through sequences of consecutive transitions as they relax thermally.

The results of the ‘‘topography approach’’ suggest two extremes in the range of types of multidimensional potential surfaces, the sawtooth and staircase topographies shown in Figs. 1(a) and 1(b).⁶ Sawtooth potentials, on which the energy changes from one minimum to the next are typically small compared with the heights of the saddles, are natural candidates for transition state kinetic models. A potential surface would have to have almost pathological special features to prevent thermal equilibration if the typical exothermicity in a downward relaxation step (or well-to-lower-well passage) is small compared with the activation energy of each step. The staircase potentials, with a high proportion of step-to-downward step exothermicities that are large relative to the activation energies, present a situation requiring a more cautious approach. The key issue is whether exothermicity of one step can be significantly more (or significantly less) available for the next step than a thermally equilibrated

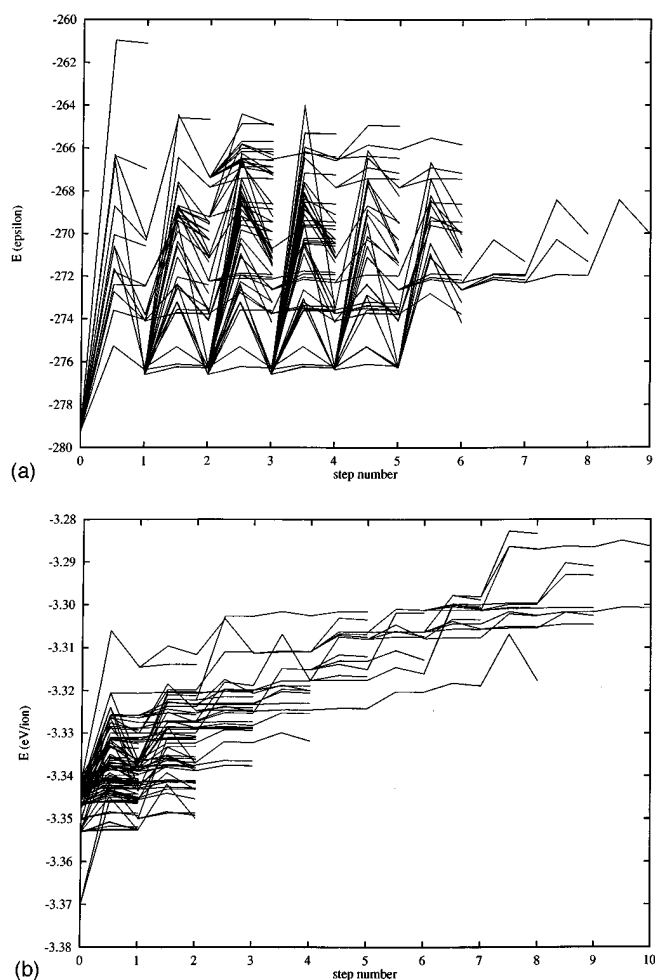


FIG. 1. Examples of sawtooth and staircase topographies on potential surfaces. (a) a sawtooth, Ar_{55} ; (b) a staircase, $(\text{KCl})_{32}$ (adapted from Ref. 6). Since the Ar_{55} is based on pairwise Lennard-Jones potentials, the vertical scale for (a) is in units of the well depth parameter ϵ , whose value for argon is 1.67×10^{-21} joule. The low-lying steps for the argon cluster which have low barriers correspond to the movements of promoted ‘‘floaters’’ from one face to another; the cluster cannot reach the global minimum from the next ‘‘plateau’’ without passing over at least one barrier of some size.

model would predict. Simplistic projections of downward reaction paths onto a single dimension make such nonequilibrium phenomena quite plausible, but such an impression must be tempered by the realization that the space of molecular vibrations of such systems has a very high dimensionality, and what may occur in one or two dimensions can be very different from what happens in many dimensions. For example, while an increase in *regularity* occurs with a softening transition in a very simple system,^{8–10} even slightly larger systems show no such regularizing,^{9,10} and still larger systems become more chaotic with melting transitions.¹¹

The main questions we address now are:

(1) Under what circumstances is relaxation of a cluster from a randomly-selected high-energy configuration a one-step process of ‘‘rolling down’’ directly to the global minimum (or a basin minimum), under what circumstances does it pass through a succession of well-marked downward steps, under what circumstances does it wander up and down through

recognizable steps, and under what circumstances does it just wander randomly, with no “resting places”?

(2) How do the relaxation times depend on the vibrational and external temperatures?

(3) How does the cluster relax when its temperature is in the range of solid-liquid coexistence?

II. OBJECTS AND METHODS

We have investigated clusters $(\text{KCl})_{32}$ and Ar_{55} . The first provides an example of a staircase potential.⁶ The potential for the Ar_{19} cluster is an example of a sawtooth topography.^{1,5} While no full analysis of monotonic sequences and topography has yet been done for Ar_{55} , evidence based on some short sequences [D. J. Wales, private communication] supported the assumption that the Ar_{55} cluster is also a member of the sawtooth family. The study reported here continues to support that interpretation. The reason we have chosen Ar_{55} , and not Ar_{19} , is that it is closer to $(\text{KCl})_{32}$ in the number of atoms, and thus in the number of vibrational degrees of freedom and time scale, which becomes important when we begin to compare relaxation processes in the two systems.

The procedure we have used to study the isothermal evolution of the system is to carry out classical molecular dynamics simulations of the evolution of clusters initially in highly improbable, high-potential-energy configurations. The initial configurations are random, but are required to correspond to very high internal energies. We have carried out both constant-temperature and constant-energy simulations. For the constant-temperature cases, we have used both Nosé-Hoover (extended-system)^{12–17} and stochastic^{18,19} isothermal algorithms. We have averaged the results over a variety of initial configurations and initial small distortions around these configurations. (Note that for such problems as protein folding, isothermal relaxation, possibly from a moderately well-specified initial configuration, is likely to be more relevant than controlled-temperature annealing.) In the calculations of the KCl clusters, we have used the same pairwise potential and parameters as Rose;^{20–22} the initial high-energy configurations have been chosen to be amorphous configurations at high minima, corresponding typically to steps 8–10 in the notation of Ref. 6, with energy ~ -3.28 eV/ion. For the Ar_{55} cluster, the potential and its parameters are those used frequently for argon,²³ and all runs have started from ‘liquidlike’ configurations with energy ~ -0.047 eV/atom, as used previously,²⁴ as well as other configurations in the same energy range that we have generated. The vibrational temperature has been varied between 0 and 800 K for $(\text{KCl})_{32}$ and between 0 and 40 K for Ar_{55} ; the upper values are close to the upper limits of the regions of solid-liquid coexistence, T_m .

III. RESULTS

Results of MD runs show that at low vibrational temperatures, the relaxation is not a one-step process: A cluster goes down the potential surface by clearly-defined jumps [Figs. 2(a) and 2(b)]. The first step, corresponding to relax-

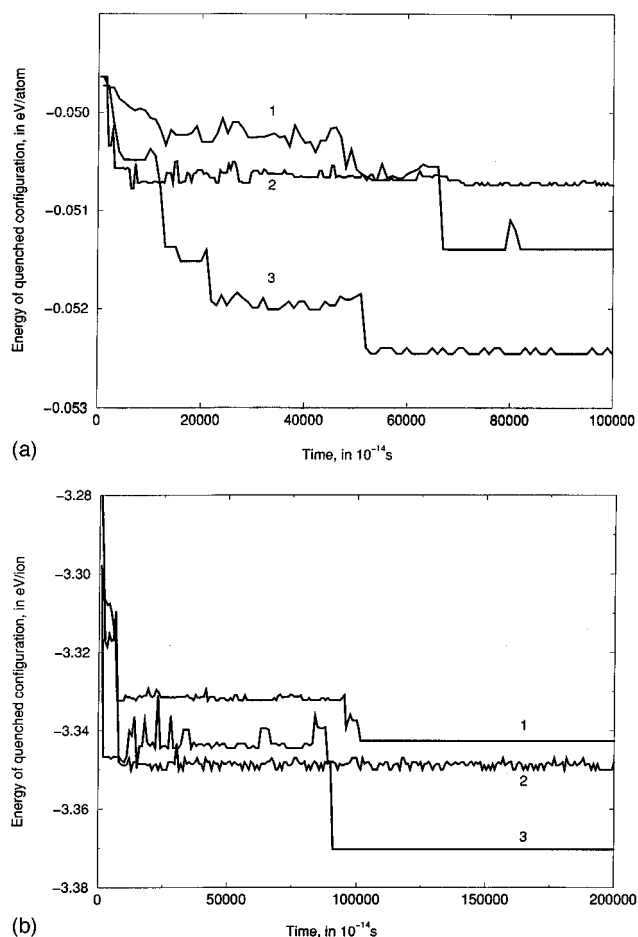
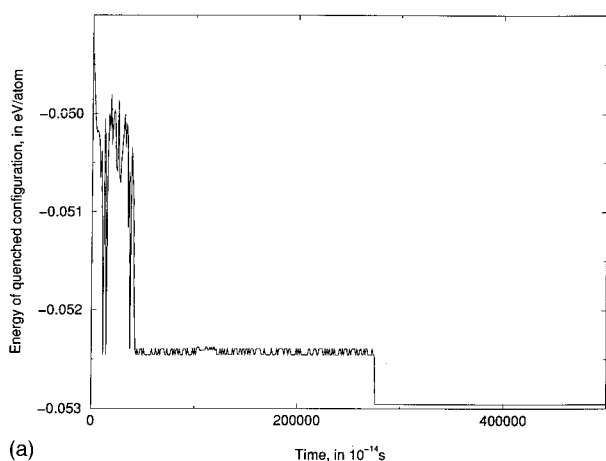
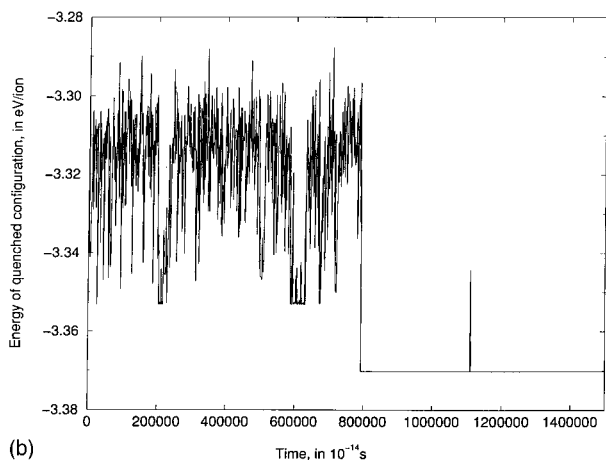


FIG. 2. Typical time histories of the ‘quenched’ energies (a ‘quenched’ energy is the energy of the local minimum around which the system is vibrating at the instant of quenching) for the two model systems, from constant-temperature runs at various low to moderate temperatures. The higher is the vibrational temperature, the shorter is the time to reach lower minima, and, on average, the lower is the energy of the minimum in which the system is finally trapped. (a) Ar_{55} , with curves 1, 2, and 3 at vibrational temperatures of 15, 20, and 25 K, respectively; (b) $(\text{KCl})_{32}$, with curves 1, 2, and 3 at vibrational temperatures of 350, 550, and 600 K, respectively.

ation to some intermediate configuration, is the fastest and does not depend sensitively on the vibrational temperature. (See the left sides of the figures.). The most probable reason for this is that the typical height of barriers near high-lying initial configurations is small, so the system can easily overcome them and does not need to wait for assistance from thermal fluctuations. We might suppose then that the deeper the system rolls down into the potential surface, the higher are barriers that it meets. The analysis of the surface for Ar_{19} , however, shows that this need not be the case, and that the barriers in the middle and in the depths of the surface may be comparable. The relaxation process does slow somewhat after the first few steps—and here the role of the vibrational temperature becomes important. At low temperatures, the system is very rapidly trapped at one of intermediate or high-energy configurations; increasing T gives the system better opportunity to continue its wanderings down the surface (see the right sides of the figures). The higher is T , the



(a)

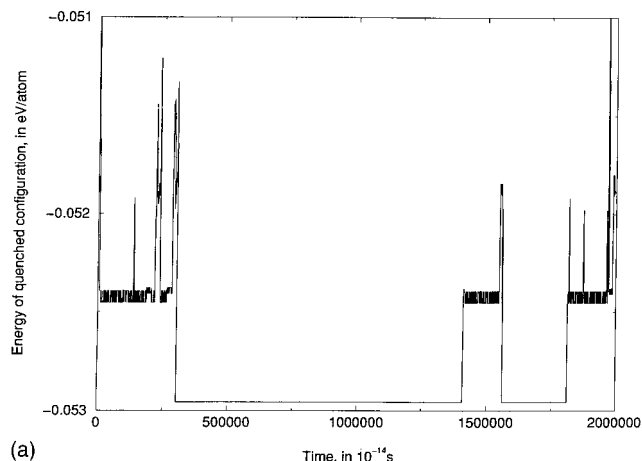


(b)

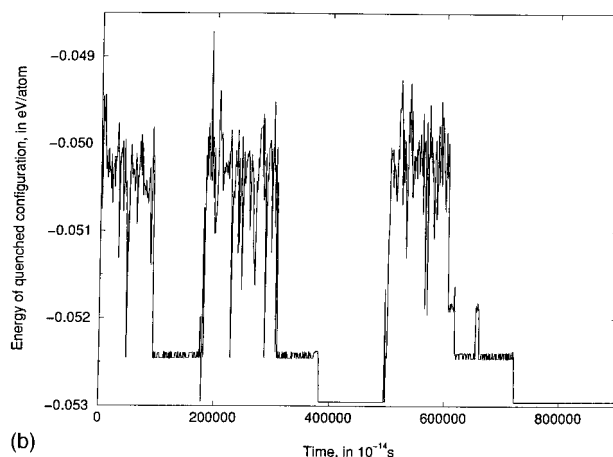
FIG. 3. Time histories of the quenched energies from constant-temperature molecular dynamics simulations for the two model systems at *high* vibrational temperatures, showing that a cluster remains for long periods at energies near that of its initial, high-energy configuration. (a) Ar_{55} at 33.4 K; (b) $(\text{KCl})_{32}$ at 700 K.

shorter is the time between jumps and the lower down the system can eventually go, without being trapped.

However the higher the temperature, the more high-energy configurations the system can explore. Because the number of attainable configurations increases exponentially with the mean kinetic energy (temperature), as the temperature increases, the system spends more and more time in these configurations [Figs. 3(a) and 3(b)]. Thus quite hot systems take longer times to find their way to the low-energy minima than systems of intermediate energy or temperature. Consequently the relaxation time shows a minimum as a function of temperature. This had been seen for $(\text{KCl})_{32}$,^{21,22} and was found later to occur with protein models. The closer to the solidliquid transition, the slower becomes the relaxation—the well-known result for the fluctuation damping near phase transitions.²⁵ At temperatures ~ 730 K for $(\text{KCl})_{32}$ and ~ 36 K for Ar_{55} , a band of solid–liquid phase coexistence occurs, above which the MD simulations show that clusters stay mainly in high-energy regions of the potential surface, and that the time a cluster spends in the vicinity of an individual minimum is very short. The transition width



(a)



(b)

FIG. 4. Time history of quenched energies, illustrating the phase coexistence phenomenon in the Ar_{55} cluster, from a constant-temperature, molecular dynamics simulation; the histories show both (a) two-phase behavior at 35 K (solid and surface-melted, in this example) and (b) three-phase behavior at 35.9 K.

is about 60 Kelvin degrees in $(\text{KCl})_{32}$ and 3 Kelvin degrees in Ar_{55} , i.e., it is approximately 8% of the absolute temperature T_{eq} at which the free energies of the two forms of $(\text{KCl})_{32}$ and of Ar_{55} are equal.

The relaxation process near T_{eq} is influenced greatly by the phase coexistence. The MD simulation results clearly illustrate that in some temperature range the cluster passes between different phaselike forms, spending a time in each of them much longer than its vibrational periods. In Ar_{55} , MD simulations reveal at least three phases near T_{eq} , consistent with earlier results,^{26–28} as the plateaus of Fig. 4 show. However in $(\text{KCl})_{32}$ we have observed coexistence of only two phases, the rocksalt crystal and the liquid, as Fig. 5 illustrates.

The results shown in Figs. 2–5 are typical examples chosen from many MD simulations; however one should keep in mind that by slightly changing the initial configuration or velocity distribution, or even by running the supposedly-identical simulations on different computers, one can get results that look rather different, at least at the first glance; see, for example, Fig. 6. These differences reflect the chaotic na-

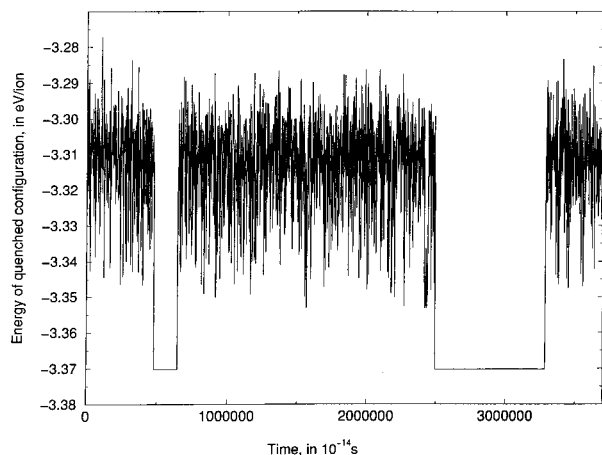


FIG. 5. Time histories of quenched energies showing phase coexistence in $(\text{KCl})_{32}$, from a constant-temperature molecular dynamics simulation; in contrast to Fig. 4, this system shows only two phases. However liquid alkali halides are known not to wet the corresponding solids, so that surface melting does not occur with these systems.

ture of the system and the limitations of finite round-off in any real computer. (Testing trajectories for mechanical reversibility is one way to demonstrate these limitations, especially if the same initial conditions are used on different computers.) Thus individual MD runs can be sources of reliable information only (1) after averaging, or (2) in a case in which they illustrate regular common features. The equilibrium populations of the different phaselike forms have been discussed elsewhere.²⁹ Figures 7(a) and 7(b) show the temperature dependence of the average relaxation times for $(\text{KCl})_{32}$ (see also Refs. 21 and 22) and for Ar_{55} .

Returning to Fig. 6, we see individual instances indicating that, at least for moderately hot, solid clusters, the transition to the global minimum, with energy -3.37 eV/ion, is preceded by a brief preliminary elevation to a rather high-

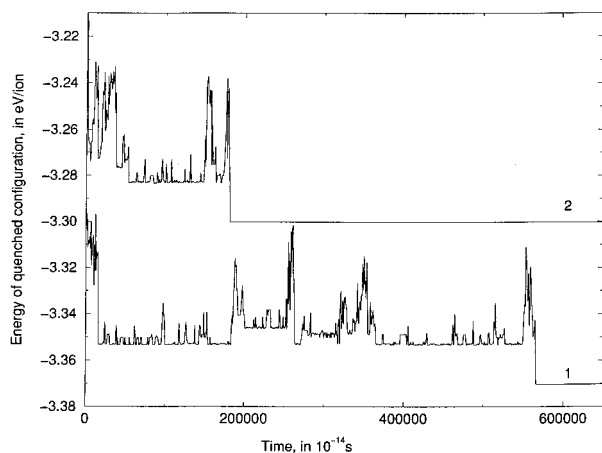
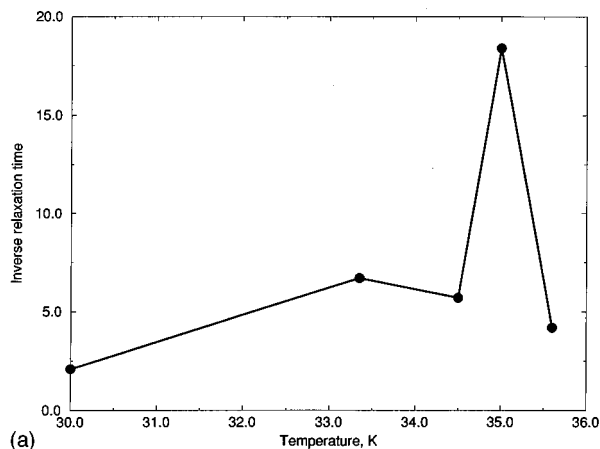
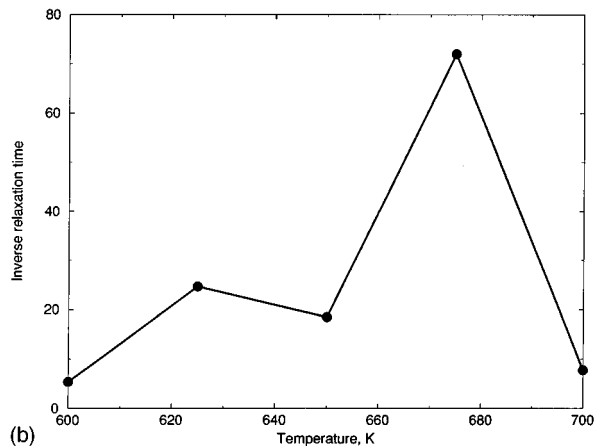


FIG. 6. Two typical isothermal molecular dynamics histories of quenched energies for a $(\text{KCl})_{32}$ cluster, at the same temperature (650 K) but with different initial conditions; these illustrate the phenomenon of ‘heating-up’ before the cluster enters the well of the global minimum, for this system. Curve 2 has been displaced upward by 0.07 eV to make the two histories easily distinguishable; both go to the global minimum at -3.37 eV/ion.



(a)



(b)

FIG. 7. Temperature dependencies of the relaxation times to the global minima in (a) Ar_{55} ; (b) $(\text{KCl})_{32}$. The units on the ordinates are 10^8 s^{-1} .

energy state. The energy spectra of local minima of clusters, particularly of the most stable which correspond to the magic numbers, generally have wide gaps separating their ground levels, corresponding to the regular configurations of the global minima, from a relatively dense set of higher-energy minima. For some systems, such as the rare gas clusters, all but the lowest of these higher minima correspond to the variety of amorphous structures associated with liquidlike,^{23,30} or surface-melted behavior.^{26–28} Below the amorphous configurations, there are typically states with structures related to that of the global minimum, e.g., ‘defective’ solidlike configurations, or, in the case of $(\text{KCl})_{32}$, slabs and other rock-salt arrangements other than the $4 \times 4 \times 4$ cube. Clusters typically reach these relatively low-lying excited configurations as a result of fast ‘first-step’ or ‘few-step’ relaxation from initial nonequilibrium liquidlike configurations. For $(\text{KCl})_{32}$, these most-frequently-visited intermediate states are concentrated around the energy -3.35 eV/ion; in Ar_{55} , there are just two kinds, at -0.0517 and -0.0525 eV/atom, corresponding to one- and two-particle-hole excitations from the surface layer.

The isothermal MD many-step relaxation runs for $(\text{KCl})_{32}$ illustrate, as Fig. 6 shows in two examples, that this cluster may nucleate and grow to any of many rock-salt

forms, each of which is the bottom of some basin on the potential, and all but one of which is, in a sense, a trap keeping the cluster from the global minimum. To reach the global minimum from any of these higher basin bottoms, the cluster must go up to some high-energy region and only from there, find its way down to the global minimum. This reveals itself in histories of quench energies as a rise in the quenched energy just before the system moves to the global minimum, reflecting its climb out of a secondary basin. In a structure-seeker such as $(\text{KCl})_{32}$ these higher-energy crystalline (or defective crystalline) configurations are themselves the results of growth of crystal nuclei in the solidification process. There are staircases leading down to each of the basins, and passage from one basin to another requires some serious climbing. In Ar_{55} , the situation is quite different; in the vast majority of runs the cluster rolls down nearly monotonically, from $E = -0.0525$ to the global minimum (see Fig. 1) and even though a few runs show a preliminary jump-up, this jump is very low and brief. Thus this cluster seems not to have a great multiplicity of basins comparable to the hundreds of rocksalt structures of the KCl cluster, so almost all the intermediate states are on some relaxation path to the icosahedral global minimum structure.

Constant-energy simulations (available, but not displayed here) show essentially the same kind of behavior as the constant-temperature simulations. If the total energy is comparable to the initial potential energy, then the cluster may remain near the initial configuration or at a comparable energy for a long interval, partly because the kinetic energy is necessarily low. The higher is the total energy, the faster the system leaves the initial high-energy region and the deeper it rolls down the potential surface before it is trapped.

The constant-energy simulations necessarily differ from constant-temperature simulations insofar as, in the former, the mean temperature or vibrational kinetic energy increases as the cluster wanders downhill on the potential surface. Hence the further down the cluster travels, the more readily it passes over saddles of any given height. As a result, the relaxation times for these simulations depend more sensitively on energy than do the isothermal relaxation times on temperature, if mean temperatures in the former are compared with fixed temperatures in the latter, or if the fixed energies of the former are compared with mean energies in the latter.

The constant-energy relaxation processes for Ar_{55} and $(\text{KCl})_{32}$ follow the same pattern as the isothermal simulations. The argon cluster shows only a single, dominant basin with its global minimum at the bottom, while the potassium chloride cluster may fall into any of a large number of basins corresponding to rocksalt structures with energies that may be above that of the global minimum.

One significant difference between the isothermal and isoergic simulations that is particularly important for multi-basin systems is this: While passage over the interbasin divides involves both mode–mode and mode–bath coupling under isothermal conditions, only mode–mode coupling can contribute to enabling such processes under isoergic conditions. Hence systematic comparison of the two may reveal

the relative contributions of these two sources of the fluctuations that carry clusters from one basin to another.

The simulations reported here are all based on classical mechanical equations of motion. The question might arise regarding quantum effects. Throughout the temperature range considered here for the KCl cluster, the system is well into the region of validity of the correspondence principle, so the classical model is appropriate. In the range of the transition temperature and above for the argon cluster, the same is true. However for clusters of neon, one may expect quantitative differences between classical and quantum models.^{31–33} In the very lowest reaches of the potentials of the rare gases, the rates of passage between wells may be somewhat higher than the classical model indicates, because of tunneling. For example, tunneling may be detectable in very cold argon clusters whose numbers of constituent atoms do not correspond to closed shells. Calculations of the quantum-mechanical diffusion of a 56th atom of argon on the surface of the $(\text{Ar})_{55}$ cluster would answer this question.

IV. SUMMARY AND CONCLUSIONS

Molecular dynamics simulations, both isothermal and isoergic, indicate that clusters relax configurationally, from high-energy regions on their potential surfaces, by sequences of well-to-well passages followed quickly by vibrational thermalization. This behavior occurs not only for Ar_{55} , a system whose potential has a sawtooth topography, where such thermalization is expected. It also occurs for $(\text{KCl})_{32}$, a system whose potential is an archetype of a staircase topography, for which thermalization was not necessarily obvious. Such relaxation processes exhibit well-defined steps as the system moves downhill on its potential, so long as the internal vibrational energy or temperature of the system corresponds to that of a solid cluster or to a cluster not very high in the band of coexistence of solid and liquid forms. If the cluster is hot or energetic enough to be liquidlike most or all of the time, then instead of dropping to a low-energy region on the potential surface, it travels freely over large regions or all of the potential, as one expects of a liquid.

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