

FINDING SADDLES ON MULTIDIMENSIONAL POTENTIAL SURFACES

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Received 4 March 1988; in final form 4 April 1988

A method is presented which directly locates saddle points on multidimensional potential energy surfaces. The method is simple to implement and can be used whenever steepest descent quenches are applicable. As an example, it is applied to a molecular dynamics study of the low-energy isomerizations of Ar₇.

1. Introduction

While it has become relatively easy to locate the minima on potential surfaces – that is, to find the geometries and energies of local minima – the determination of saddle points has remained relatively intractable, particularly for potential surfaces of more than a very few dimensions. Methods have been introduced [1–5] for locating saddles and more general approaches have been introduced for characterizing the humps and hollows of multidimensional surfaces [6]. However, these techniques become inefficient and therefore expensive when the system contains many atoms. For systems for which molecular dynamics (MD) can be done, steepest descent quenching methods provide a quick, efficient way to find potential energy minima, and this technique has been used by Stillinger and co-workers [7] to study systems with potential surfaces of relatively high dimension. However, their use of this method to determine saddle points invokes a gradient minimization procedure and is rather more cumbersome than necessary for many applications. The approach we introduce here is simple; it can be performed on any system for which one has enough knowledge to perform MD simulations, and it requires the cal-

culaton of no eigenvalues or second derivatives of the potential energy.

We suppose that the local minima of interest have been located and we have chosen the two wells whose connecting saddle we seek. We set up a standard molecular dynamics (MD) simulation with the initial configuration on the potential surface (so as to have no kinetic energy or angular momentum) close to the bottom of the upper of the two wells of interest. We start the simulation and, when we see that the system is trapped within its initial well, we raise the system's energy and restart the simulation, again with no angular momentum. We continue to raise the energy and simulate the molecular dynamics until we find a trajectory along which the potential energy drops below the minimum of the initial well. This indicates that the system has reached another, deeper well. From a point on the trajectory in the new well, we quench the system along a steepest descent path to the minimum of this well, in order to identify it. Assume that this well is the one we want. Then we go back to the trajectory which has succeeded in carrying the system out of its initial well, and examine in detail the region around the point r_m of its maximum potential energy. Note that the point of the maximum potential along the trajectory will in general be in the vicinity of the saddle but will not be

the saddle itself. At several scattered points on the trajectory in the vicinity of this maximum, we quench the system and follow it down the potential surface using steepest descent. Because the rate of descent in this method is proportional to the gradient of the potential energy, the rate of descent becomes slower and slower as the phase point comes toward a stationary point on the potential energy surface. A cutoff value of the gradient of the potential, or alternatively, of the kinetic energy of the system, is used to determine numerically when a suitably small neighborhood of a stationary point has been reached.

It is standard to choose the cutoff value for the kinetic energy, ke_c , small enough so that the steepest descent quenches terminate at local minima exclusively. To find transition states, we choose ke_c large enough to "catch" saddle points as well as minima. If our quench from a point on the MD trajectory near r_m reaches a saddle, and our steepest descent quenches are then carried far enough beyond this point, i.e. if we reduce the value of ke_c sufficiently, the system evolves away from the saddle and relaxes to a local minimum of the potential surface (see fig. 1). Going back to the molecular dynamics simulation and quenching to the saddle from points very close to the original r_m , one can catch the system relaxing back to the other potential well. By following the system down both sides of the saddle, we ap-

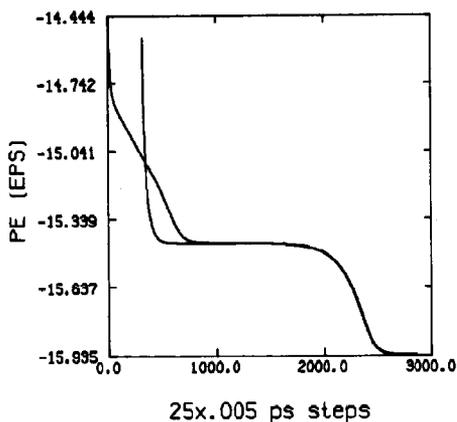


Fig. 1. Potential energy as a function of time during two steepest descent quenches which take a thermally excited Ar_7 cluster (near 20 K) down the potential energy gradient, through the saddle for the 1-2 isomerization to the energy minimum associated with isomer 2. The curves are taken from initial configurations resulting from MD trajectories at energies $-14.06e$ and $-13.00e$, respectively.

proximate the minimum-energy reaction path, which of course defines a suitable reaction coordinate for passage from one well to the other.

Through the determination of the first r_m , our method is that of Stillinger and co-workers [7]. Instead of beginning a steepest descent quench at this stage, they minimize

$$\Psi = (\nabla U)^2 \quad (1)$$

to locate stationary points. Such a calculation, even via the efficient method of Powell (see ref. [6] and references therein), is costly because it requires the calculation and inversion of an approximate Hessian, or force constant, matrix. Also, because Ψ will, in general, have many more stationary points than will the potential energy, it is necessary to characterize the stationary point once it has been reached to ensure that it is the desired saddle [6]. A Hessian matrix is constructed and the sign of its eigenvalues used to determine whether or not a saddle has been located. Negative eigenvalues at a stationary point signify a region of negative curvature in the potential surface; a transition state in the reaction is associated with the presence of a single negative eigenvalue, and the local reaction path is given by the eigenvector associated with this eigenvalue.

Starting from a given r_m , our method is more likely to produce the "right" stationary state than is the gradient minimization treatment because it can distinguish saddle points from potential minima and from some other points on the potential surface where Ψ is a minimum. However, it cannot distinguish a transition state from a stationary point of index higher than one, i.e. one at which the Hessian matrix has more than one negative eigenvalue. In all but pathological cases we can expect that the potential has a negative second derivative along only one direction at the transition state, so our procedure is unambiguous [8]. Where a check on the integrity of the saddle is desired or a very accurate estimate of the reaction path is needed, the Hessian formalism should be used in conjunction with our method.

For Ar_{13} , whose potential has 33 dimensions, finding the saddle separating the lowest (icosahedral) minimum from the next higher minimum required 5 min of computation with a VAX 11/750. It would not be surprising if finding saddles by either our method or gradient minimization were slow in some

instances because of narrow channels or nearly blind entries into their saddle regions; nevertheless we have not encountered any needle-threading cases of this kind.

We now present the results of our trial calculations, first for Ar_7 and then for Ar_{13} . The results given here for Ar_7 will be followed by a more complete discussion of the form of its potential surface and the relation between the form of the surface and the way the cluster explores its phase space, a subject discussed previously by Amar and Berry [9].

2. Ar_7

There are four important types of low-energy minima of the potential surface for Ar_7 with Lennard-Jones potentials. They correspond to the pentagonal bipyramidal, octahedron+1 (also called the 3+3+1), incomplete stellated tetrahedron and skew structures; throughout the paper, we refer to these as isomers 1–4, the numbers increasing with potential energy of the isomer [10] (see fig. 2 and table 1). Amar and Berry [9] have used steepest descent quenches to determine the relative reaction rates for isomerization processes between the structures at

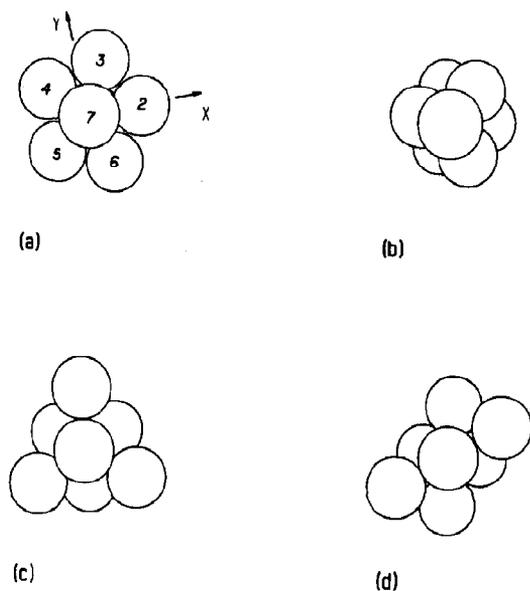


Fig. 2. The four most stable isomers of Ar_7 . (See text and table 1 for relative energies.) The figure is taken from ref. [10].

Table 1
Energies of the four lowest-energy isomers of Ar_7 ^{a)}

| Isomer | Energy (ϵ) |
|-----------|-----------------------|
| 1 (PBP) | -16.505 |
| 2 (oct+1) | -15.935 |
| 3 (IST) | -15.593 |
| 4 (SKEW) | -15.533 |

^{a)} Energy given in units of ϵ , the Lennard-Jones well depth.

various temperatures, but they did not calculate saddle point energies.

Our Newtonian MD simulations have used the second-order Verlet method of propagation [11] and a Lennard-Jones potential energy function ($\sigma=3.4$ Å; $\epsilon=1.67 \times 10^{-14}$ erg); the intrinsic step size (τ) was 10^{-14} s. The steepest descent quench technique is described in ref. [8]. With this method, the system evolves according to

$$d\mathbf{q}/dt = -\nabla U(\mathbf{q}), \quad (2)$$

where \mathbf{q} is the coordinate vector for the system.

A combination of Runge-Kutta and Adams-Moulton propagators [12] was used to perform the quenches. The intrinsic step size was 0.5τ . It had been determined empirically that for an Ar_{13} cluster, a value of $10^{-6}\epsilon$ for the cutoff kinetic energy "held" the system at both saddle points and minima, but when the cutoff energy was decreased to $10^{-8}\epsilon$ the quenches appeared to terminate exclusively at potential minima. A cutoff of 10^{-6} was also used successfully in this work to distinguish the types of stationary points for the Ar_7 system.

Because we had previous knowledge of the Ar_7 cluster, we were able to shortcut the full method described in section 1. It had been observed previously [9] that at temperatures above 20 K, isomerizations occur rapidly in Ar_7 . A short Monte Carlo simulation at 21 K was used to obtain an initial configuration for our MD simulation. When this configuration was entered into the MD program and the initial velocities of all particles set to zero, the total energy of the system was -22.2×10^{-14} erg, or -13.3ϵ . From earlier MD simulations of Ar_N (N ranging from 3 to 33), a time interval of 500τ was known to be sufficient to span a few of the natural breathing periods of the cluster. This gave us an interval for short-time averaging of $U(t)$ from the MD,

Table 2
Saddle energies for the X-Y-type isomerizations of Ar₇^{a)}

| Isomerization | Energy (ε) |
|---------------|------------|
| 1-2 | -15.44 |
| 1-3 | -15.03 |
| 1-4 | -15.02 |
| 2-3 | -15.32 |
| 2-4 | -15.28 |

^{a)} The uncertainties in the energies of the saddles are $\pm 0.003\epsilon$ based on a single trajectory. For the 1-2 saddle, the same uncertainty has been obtained on the basis of three trajectories. The kinetic energy cutoff used to locate the saddle was $10^{-6}\epsilon$ (see text). "Homogeneous" saddles, of the type i to i' , have not been found in preliminary studies.

i.e. to obtain a plot of $\langle U \rangle(t)$. The differences between the energies of the four isomers are large enough that isomerizations can be recognized directly from the behavior of $\langle U \rangle(t)$. The saddle for the 1-2 reaction was determined using less than 2 min of computer time on a VAX 11/750. We found the saddle energies for four other isomerizations (1-3, 1-4, 2-3 and 2-4) in less than 30 min total computer time. Table 2 contains the potential energy values of the five saddles we determined. Note that the relative magnitude of these agrees with the order implied by the study of Amar and Berry. Hessians were constructed at all saddles. At each, there was indeed exactly one negative eigenvalue, confirming that we have located simple saddles. The "reaction path", the trajectory from one minimum to another, is determined by finding gradients from their intervening saddle to the two minima. This is illustrated in fig. 3 for isomers 1 and 2 of Ar₇, with the potential shown for equal time steps.

3. Ar₁₃

The icosahedral ground state of Ar₁₃ has an energy of -73.65ϵ . The first minimum above that is a structure with one of the 12 atoms of the icosahedron raised to the surface and a vacancy generated 180° opposite the promoted particle. The energy of this structure is -68.91ϵ . The energy of the saddle between them is -67.61ϵ . The structure and this and other saddles of Ar₇ will be discussed in a future publication.

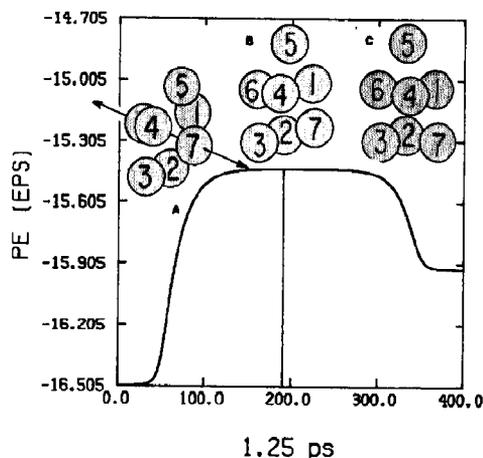


Fig. 3. Reaction profile of the 1-2 isomerization of Ar₇, obtained from piecing together data in equal-time steps as in fig. 1, for two quenches leading to the same saddle from adjacent wells. Configurations (a) and (b) correspond to isomers 1 and 2; (c) is the structure at the saddle, and differs from (b) by the tilt of the 2-3-7 triangle. The axis of the pentagonal bipyramid (a) is the double-headed arrow.

4. Conclusion

We have outlined an efficient method for determining saddle energies and geometries on multidimensional potential surfaces, and for finding the corresponding least-energy reaction paths. The method works by locating the region of "slowest slide" along a set of trajectories passing very close to the desired saddle points. Using this method, it has been possible to uncover the reaction mechanisms for various isomerizations of the Ar₇ and Ar₁₃ cluster.

The method makes use of classical molecular dynamics, quenching and steepest descents on classical potential surfaces. One might ask why, if one is carrying out molecular dynamics simulations, is it worthwhile to extract the saddle point energies and geometries of a multidimensional potential surface. There are several justifications, one of which has been illustrated here. That first reason harks back to the traditional dual aspect of what is considered an "understanding" of a chemical reaction: one wants to know both kinetics and mechanism. Molecular dynamics alone can reveal the kinetics, but some additional manipulation, such as what we described here, is required to tell us the mechanism. The energy at a saddle, relative to that of the potential minimum of the initial state, should of course be

essentially the same as the activation energy of an Arrhenius expression for the reaction rate, but it is much easier to compute the energy of a saddle as we have described here than to compute reliable rates of reaction at several temperatures. Hence finding a saddle efficiently provides one of the phenomenological parameters determining kinetics. But finding the geometry at the saddle is new information, the most important single glimpse we can get of the *mechanism* of the reaction.

By applying the steepest descents method to generate the minimum-energy paths from a saddle to the potential minima on either side, we find the "mechanism" of the reaction in the traditional sense of the word. The rearrangements of Ar₇ and Ar₁₃ described here have been examined in just this way, thereby enabling us to gauge the relative motion of the atoms and to determine which motions are most important at each stage of an isomerization. Finding classical mechanisms in this manner is surely a second justification for locating and using saddle points.

A third reason for finding energies and geometries of saddle points on multidimensional potential surfaces is that such information is precisely what is required to tell us which rearrangements may occur and how much of a potential surface is accessible to a molecule with a fixed internal energy. Knowledge of the saddles tells us the connectivity of the surface at any specific energy [13].

Lastly, the reaction path determined by classical steepest descent paths from a saddle is precisely the curvilinear reaction coordinate one would use for a quantum mechanical analysis of the same reaction. The procedure outlined here is likely to be a particularly efficient way to generate such reaction coordinates [14].

Acknowledgement

This research was supported by the Materials Research Laboratory of The University of Chicago and

by a Grant from the National Science Foundation. HLD wishes to thank Paul A. Braier for helping elucidating the Ar₇ saddle structures and isomerization mechanisms.

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