TOPOGRAPHIES AND DYNAMICS OF MANY-DIMENSIONAL POTENTIAL SURFACES

R. Stephen Berry
The University of Chicago
5735 South Ellis Avenue
Chicago, Illinois 60637, U. S. A.

Ralph E. Kunz*
Institut für Theoretische Physik
Technische Universität Berlin, Sekr. PN 7-1
Hardenbergstrasse 36
D-10623 Berlin, Germany

Abstract

Multidimensional potential surfaces pose a variety of problems, not least of which is that it is now possible to obtain more information about the minima and other stationary points of such surfaces than we know how to use. This discussion describes a succession of steps to interpreting the topographies of such surfaces and of inferring the nature of the dynamics driven by those topographies. The procedure begins with a statistical search for minima and the saddles that link them. The topography lends itself to an analysis and categorization of local minima into large basins, including the primary basin, secondary and higher-order basins. From a representative sample of minima and saddles, one can construct inter-well rate coefficients and, from them, a master equation governing the flows on the surface. The flows can be categorized into intra-well and inter-well, and comparisons of the rates of these can be made, as the systems change temperature. A preliminary interpretation of the way the features of the topography govern the focusing or glass-forming character of the surface.

1. Introduction: Characterizing the Problem

Interesting properties of clusters fall into two overlapping categories: the properties of the electrons and the properties associated with the nuclei, i.e. with entire atoms or molecules. Fortunately, most clusters in their ground electronic states satisfy the conditions of the Born-Oppenheimer approximation, that the total electronic energy, plus the nuclear potential energy, act as an effective potential energy that governs the motions of the nuclei. This effective potential energy is a function of all the coordinates of all the N nuclei, but since the internal energy and nuclear motions are unaffected by any motion of the center of mass, we can remove three degrees of freedom. Moreover if we can neglect centrifugal distortions, we can remove three more degrees of freedom, corresponding to the orientation of the cluster in the external frame. This leaves us with the traditional 3N−6 independent coordinates, R, and the one independent variable V(R) of internal energy, which we shall here consider a scalar function of those coordinates. The negative gradient of V(R) is the force on the nuclei, and the nuclear Hamiltonian is, for the purposes of this discussion, the kinetic energy $T = -\sum(h^2/8\pi^2m_j)\nabla_R^2$, plus V(R). The transformation

to eliminate the three translations and three overall rotations will not be discussed here.

The structure of a cluster, as we normally use the term, means the geometric configuration of the nuclei with the lowest internal energy, i.e. the global minimum of \( V(\mathbf{R}) \). In practice, this may indeed be the structure we would observe in a moderately cold cluster. However the multidimensional surface defined by \( V(\mathbf{R}) \) typically has many local minima, and at nonzero temperatures, we can expect to find clusters occupying states in the regions around these minima, not only around the lowest minimum on their potential surface. The meaning of "the structure of a cluster" may well have different meanings at different temperatures. At low temperatures, clusters pass very infrequently from one local well on the surface to another; mostly, they vibrate with small amplitudes around local minima, mostly minima at low energies. These are of course the clusters we describe as solid. At higher temperatures, the same clusters may pass among the minima on the potential surface at rates approaching the rates of their oscillations within the wells. Under such conditions, we would say the clusters are liquid-like.

If we remove energy from a cluster, or allow it to evolve from a high-energy configuration to equilibrate with its environment, it may drop into a well around some local minimum. What minimum it finds can depend very much on the way we withdraw that energy. For example the cluster may find its way to the global minimum of the potential in a highly regular structure, or it may, with high probability, find itself in a well whose minimum has an amorphous, irregular geometry. Which of these extremes—or what intermediate situation—the cluster reaches depends partly on the way energy can flow out of the cluster to the environment, but it also depends very much on the topography of the potential surface itself, as we shall see here. The following discussion provides tools to explore, describe and categorize the topographies of potential surfaces of many-particle clusters and other many-particle systems, and then to relate those topographies to the dynamics that occur on those surfaces. For example, we can begin to relate the topography to the tendency of a surface to generate glassy clusters or to focus the system to a well-organized, specific structure.

2. Finding Useful Information: What Is It and What Tools Will Extract It?

We begin this part of our discussion with the assumption that the potential surfaces of interest to us are known and available, and that we can carry out mathematical operations to study them. In practice, it is not necessarily easy to generate such surfaces, particularly for systems with directional, covalent bonds or metallic bonds. However fairly reliable surfaces do exist for many kinds of atomic clusters such as rare gas clusters, which we can describe with Lennard-Jones (LJ) potentials or more sophisticated refinements of this simple form, or alkali halide clusters, which we can describe with Born-Mayer (Coulombic long-range plus exponential, repulsive short-range) potentials, or with more sophisticated refinements including, for example, polarization of the ions. We shall draw our examples from systems for which such simple potentials provide reliable descriptions, but it is important to realize that the tools of our analysis and the inferences we make are as applicable to more complicated potentials as they are to the examples we offer.

The first question to ask about the potential surface is "What information is both accessible and useful?" Fortunately, we can now answer this with reasonably satisfaction; only a few years ago, we would have had to say that the accessible information was too inadequate to be very useful, and the truly useful information was inaccessible.
Some characteristics of topographies are clearly important, whatever the surface may be. The stationary points, and particularly the minima are perhaps the most obvious, not only the global minimum but also the others the system may reach. Next in importance, whether our system be a cluster in its space of 3N-6 independent dimensions or a hiker in mountains, are the saddles, the "minimax" points that are highest points along any lowest-energy pathway from one minimum to another; walking from one valley bottom to an adjacent valley via a saddle is the path of lowest altitude. We should not say "the" way of lowest energy because there may be more than one pass connecting two minima, and each pass has its own saddle. One difference between the hiker and the cluster is that maxima may be important to the hiker, but are of virtually no significance to the cluster. There are other important characteristics which we can also determine, such as the curves on the surface which define the lowest-energy pathways from one minimum over a specific saddle to an adjacent minimum; such a curve is usually called a (or "the") "reaction path."

There are also important characteristics of the topographies which we do not yet know how to obtain, or at least to obtain by any practical algorithm; among these is the analogue of the area of a lake, the "area" of the hypersurface formed by a specified connected region of constant total energy in configuration space or phase space. This is important because it gives us the statistical weight of the accessible region for a system at constant energy; the logarithm of that hyperarea is the microcanonical entropy of the state defined by the energy and the accessibility within the region. We shall discuss reaction paths shortly, but will not go into the issue of microcanonical entropies here.

Now we return to minima and saddles. At its stationary points, the slope of the function is zero; that is, $\nabla R^TV(R) = 0$ at any stationary point. At a minimum, all directions are upward; that is, at a minimum, $\frac{\partial^2 V(R)}{\partial R_i \partial R_j} > 0$ for all components $R_i$ and $R_j$ of $R$. At a saddle, most directions lead upward but at least one axis leads downward whichever way one follows that axis; that is, $\frac{\partial^2 V(R)}{\partial R_i \partial R_j} > 0$ for most $i$ and $j$, but for at least one $k$, $l$, $\frac{\partial^2 V(R)}{\partial R_k \partial R_l} < 0$. The "rank" of the saddle is the number of directions or pairs of variables for which the second derivative of $V(R)$ or curvature is negative. (At a maximum, of course all the components of $\frac{\partial^2 V(R)}{\partial R_i \partial R_j}$ are negative.) The set of $(3N-6)^2$ values of the second derivatives of $V(R)$ form a symmetric, $(3N-6) \times (3N-6)$ matrix, the Hessian matrix. At a minimum of the surface, its eigenvalues are the force constants of the potential, and its eigenvectors are the normal modes, at that minimum.

Most saddles of importance for clusters or molecules are rank-1 saddles but they need not be. If $V(R)$ were continuous and its first and second derivatives existed and were continuous at every point on the potential surface, the lowest-energy path from any minimum to any adjacent minimum would go through only a simple saddle, in accord with the Murrell-Laidler theorem[1]. These conditions need not be fulfilled at isolated points, particularly points of high symmetry, so that it is in fact possible for the lowest-energy path from one minimum to an adjacent minimum, the "reaction path," to pass through a saddle of rank greater than 1[2].

Efficient algorithms now enable us to find minima and even saddles quite efficiently. For many years, the most commonly used method to find minima was that of steepest descents[3-5]. One estimates the value and direction of the gradient of the function, and moves a test point down that gradient by an amount proportional to the value of the gradient until the test point moves less than some selected criterion value. The method works but it is one of the slowest. Faster, more recent
methods include conjugate gradient[5, 6], in which moves are made in the "best" direction orthogonal to the previous move, and eigenvector-following[7-15], in which moves are made along a selected, slowly-evolving eigenvector of the Hessian matrix of the potential, the matrix of values of $\frac{\partial^2 V(R)}{\partial R_i \partial R_k}$. Typically, one carries out a search of the potential surface by executing either molecular dynamics or Monte Carlo exploration, i.e. either following the Newtonian equations of motion or a random jumping procedure with a specified criterion for acceptance or rejection of each jump[16-19]. Then, at selected intervals, one stops the search and "quenches" the system[20], removing the kinetic energy, and then follows the potential surface downward from the point at which the search was stopped.

For completeness, we provide references to a number of other methods which have been suggested[21-30]. No critical tests have yet been made to determine in a systematic way which procedure is best for any given situation.

Two methods have proven useful for finding saddles. One is eigenvector-following, turned around to follow eigenvectors uphill instead of downhill[6, 31, 32]; this is the fastest method known now. The other is the method of slowest slides[33, 34], a "skiing-down" method in contrast to the hill-climbing method of eigenvector following, which is useful because eigenvector-following does not always find all the important saddles. The method of slowest slides is based on quenching when a trajectory crosses a ridge, i.e. a local maximum in the potential energy along a molecular dynamics trajectory, followed by an excursion by steepest descent. When the trajectory nears a saddle, its rate of descent goes through a minimum before it veers off toward a minimum. Hence the point of slowest slide is an approximation to the saddle point. Two or three iterations have proved to be enough to locate the saddle, but it is faster to use eigenvector-following when one has made the first approximation[35]. Hence a mixture of the two methods seems suitable for exhaustive searches, and eigenvector-following alone, for statistical surveys.

Finding all the minima and saddles, or at least all the important saddles, is a straightforward task for a cluster of 6, 8 or perhaps 10 atoms. The Ar$_6$ cluster has two geometrically distinct minima, a regular octahedron and a distorted octahedron, of which there are 12 directly accessible from each permutation of the regular octahedron, of which there are 30. There are four geometrically distinct minima for the Ar$_7$ cluster, and the number increases exponentially with N. It is perhaps possible to find all the minima for a cluster of 15 particles, but it may not be possible to demonstrate that the list is exhaustive. For many years, people believed that the Ar$_{13}$ cluster has 988 distinct, locally-stable geometric structures, on the basis of the extensive searches carried out by Hoare and Pal[36-39]. However Tsai and Jordan[40, 41] used the more elaborate jump-step Monte Carlo method[42, 43] to explore the configuration space of this and other clusters, and, thereby, found about 20% more minima for the Ar$_{13}$ surface, bringing the known total to 1328. Table 1 is a compilation of the known numbers g(N) of geometrically distinct minima for Lennard-Jones and Morse clusters. These figures are an indication that we simply have no need for exhaustive catalogues of the minima on the potential surfaces of clusters of 18 or 20 particles, to say nothing of clusters of 50, 100 or 500 particles.

Nevertheless we would like to be able to use information from the powerful search algorithms to give us insights into the topographies of potentials of medium- size and large clusters. This would be particularly valuable if that information allows us to relate topography to dynamics, and to such properties as the tendency of a system to take on amorphous structures and form glassy ensembles, or, at the opposite extreme, to form particular structures or classes of structures. Put this way, the subject looks remarkably like the problem of why a protein folds naturally into a
particularly physiologically active structure. This brings us now to the next Section, in which we shall discuss a way to characterize the topography of a many-dimensional potential surface from statistical information. In the following Section, we shall put that information to use, in a way that allows us to relate topography to dynamics and to glass-forming or focusing character of a surface.

<table>
<thead>
<tr>
<th>N</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>g(N)_{LJ}</td>
<td>2</td>
<td>4</td>
<td>8</td>
<td>21</td>
<td>64</td>
<td>152</td>
<td>464</td>
<td>1328</td>
</tr>
<tr>
<td>g(N)_{M}</td>
<td>2</td>
<td>4</td>
<td>9</td>
<td>&gt;8</td>
<td>&gt;16</td>
<td>&gt;24</td>
<td>&gt;22</td>
<td>&gt;36</td>
</tr>
</tbody>
</table>

Table 1. Numbers of geometrically distinct minima for Lennard-Jones and Morse clusters. These are of course lower bounds for the Morse clusters of 9 or more atoms, probably the actual numbers for the Lennard-Jones and small Morse clusters. The Lennard-Jones results are from Refs. [40, 41], and the Morse results, from [39, 44]. This Morse potential has the same dissociation energy, equilibrium distance and curvature at the minimum as the Lennard-Jones.

3. Topographies: Wells, Basins and Saddles

The foregoing discussion makes it clear that in order to consider potential surfaces of medium-size or large clusters, we must work with a statistical data base, not with complete information. Moreover the kind of information we can expect to have, at least for some time, concerns the minima and saddles of the potential surface. We can expect to know the energies, geometries and Hessian matrices for a modest sample of the minima on a potential surface, and to be able to find saddles that connect minima in the data base to each other or to other minima which we can then add to the data base. We can also expect to know energies, geometries and Hessian matrices associated with these saddle points. It may be possible to find anharmonicities of the vibrational modes at some small selection of these stationary points. We have one other important piece of information regarding these data: the stationary points are, in general, not geometrically degenerate; each energy corresponds to a unique geometry, and the only structures that have a particular energy are permutational isomers with the same geometry.

Our procedure for mapping a multidimensional potential surface is this[45-47]: we first construct a statistical data base of minima and saddles. In our first example, we used the Ar_{19} cluster, modeled with pairwise Lennard-Jones potentials, to generate 299 minima and a larger number of saddles, most of which linked the minima in the data set. These minima and saddles were the products of molecular dynamics simulations and quenching. This set is in fact quite a small sample; we expect the potential surface for Ar_{19} to have about 500,000 geometrically distinct minima. The minima were sorted according to increasing energy; the saddles were sorted according to three energies, those of the two minima they linked and the height of the saddle above the upper minimum. Then the minima and saddles were linked into triples of points corresponding to connected minimum-saddle-minimum sets. These in turn were ordered according to the energy of the lower minimum. Figure 1 shows the set of all such triples from the statistical data base.

The next step comes from recognizing that the energies are associated with unique geometries. Hence a point at energy E' on the right side of Fig. 1, which is therefore the upper minimum of one min-sad-min triple, may also appear on the left side of the figure as the lower energy of another triple. Consequently we can unfold
the chevrons of Fig. 1 into extended sequences. More specifically, we can construct the sequences whose minima go monotonically upward in energy from the global minimum. We shall call any such sequence a "primary monotonic sequence" or, for convenience, a PMS. Figure 2 shows the primary monotonic sequences of our data base for Ar_{19}.

![Graph showing primary monotonic sequences](image)

Figure 1. A set of linked, minimum-saddle-minimum three-point sets in the database of Refs.[45-47] for the Ar_{19} cluster. The lower minima are on the left. The triples shown here include all minima in the data base. The horizontal scale and the straight-line links between the points are arbitrary.

Not all the minima, not even all the minima in the statistical data base, fall on these monotonic sequences. Some are separated from the primary monotonic sequences by a single maximum; these fall on other monotonic sequences that lead to regional minima different from that of a primary minimum. We call these "secondary monotonic sequences," or SMS's. Monotonic sequences separated from a primary monotonic sequence by two divides are of course "tertiary monotonic sequences," and so forth.

The primary monotonic sequences together define a large region of the potential surface which we shall call a "primary basin." Likewise, the secondary monotonic sequences define "secondary basins" and so on. For clusters of moderate size, for which a single global minimum is significant, it is useful to refer to a primary basin, but for large clusters, for which the structural type—crystal lattice,
polyhedral or amorphous, for example—is far more important, it is useful to consider all basin bottoms of the same structural type as being primary, secondary or tertiary basins, depending on which type is lowest in energy. In situations in which the equilibrium structure type changes with temperature, it is probably going to be sufficient just to distinguish basins of different structure types, without any particular emphasis on which is primary and which is secondary[48]. For example it is useful, with large clusters based on Lennard-Jones, Morse and Gupta potentials, to distinguish basins that have icosahedral structures, fcc (face-centered cubic) structures and any other crystalline structures.

Figure 2. The primary monotonic sequences of minima in the statistical data base for Ar19. The global minimum is at the left. There is no particular significance to the horizontal scale or to the straight lines used to connect the minima and saddles.

This categorization of the monotonic sequences gives us a way to structure our conception of the multidimensional potential surface. Such a structuring is the schema of Fig. 3. We can conceive of the surface as having very large basins with smaller, subsidiary minima making up the "sides" of these basins. The idea has been put forth in the context of protein folding that those systems might show a kind of scaling, in which there is a hierarchy of sizes of minima[49, 50], with small wells within larger wells, which are within still larger wells. To bring the idea to our context, we simply recognize that the wells at the large end of the hierarchy define what we have called the basins of the potential, the largest-scale regions of the potential surface which can be associated with a regional minimum. In our terms, basins at each scale might be defined by the monotonic sequences at the next smaller scale. For the clusters we have examined thus far, notably Lennard-Jones clusters of 19 atoms and the 32-molecule ionic-salt clusters exemplified by (KCl)32, there has been neither need for nor indication of a hierarchy of more than two scales; local minima and large basins seem to suffice for such systems. In fact, a useful question to ask may well be, "At what size of cluster do the minima begin to fall into a hierarchy of scales?" Furthermore it is now important to examine the potential surfaces of model protein systems in terms of the monotonic sequences and basin structures.
The monotonic sequences of the \((\text{KCl})_3\) cluster have an appearance rather different from those of \(\text{Ar}_{19}\). They differ in that the sequences are considerably steeper over much of the range of at least the deep basins. This, as we shall see, reflects itself in the comparison of the dynamics of relaxation and annealing of the two systems.

It is useful to look at the distributions of saddles as well as those of the minima. The saddles require classification according not only to their own energies but also to the energies of the minima that they link. Alternatively, as we mentioned previously, it may be more useful to use the height of the saddle above the upper minimum as an explicit index, rather than the energy at the top of the saddle, as a classification variable. Fig. 4 shows the distribution of saddle heights in the primary basin of \(\text{Ar}_{19}\), as a function of the energy of the upper minimum. The saddle heights grow slightly as the wells drop further into the basin. In other words it becomes energetically more difficult for clusters to find their way to the global minimum of this system as the energy drops.

![Diagram](image)

Figure 3. A schematic representation of the primary, secondary and tertiary basins and monotonic sequences of a multidimensional potential surface.

The \(\text{Ar}_{19}\) system shows a more specific and telling characteristic: the saddle heights increase in energy at roughly the same rate as the energies of the minima drop. Consider a cluster, initially at thermal equilibrium in a specific well, that passes one saddle into a new well with a minimum deeper than that of its previous well; initially, this cluster has an effective temperature higher than it had in the previous well. If the saddle to the next well is about as high as the saddle the system has just crossed, then it must be roughly as difficult (or as improbable) for the cluster to cross the next saddle as it was to cross the previous one. If the cluster comes to thermal equilibrium in the well soon after it enters, then it may well be more difficult or less probable for the cluster to cross that next saddle than it was to surmount the last one. This is reflected in the difficulty one has in annealing the \(\text{Ar}_{19}\) cluster to its global minimum. Cooled (in isothermal simulation) at a rate as slow as \(10^9\) K/s, which is a very slow rate indeed for such a small system, the single most populous state or energy band is that of the global minimum, but the aggregate number of clusters that end their annealing adventure trapped in high-energy minima is considerably larger than the number in the global minimum. If the cooling rate is five times faster, then the global minimum need not be the most populous state.
By contrast, the saddles of the (KCl)$_{32}$ cluster do not particularly increase in energy or in height above their upper minima as the energies of the minima drop. Moreover the successive drops in energy of the minima, along primary monotonic sequences, tend to be large relative to the heights of the next saddles the clusters encounter as they move down along monotonic sequences. This cluster, unlike Ar$_{19}$, finds its way to its global minimum or to another of the hundred or so rocksalt structures on its potential surface, even if cooled as fast as $5 \times 10^{12}$ K/s! This happens even though the surface has roughly $10^{12}$ amorphous minima for every rocksalt minimum[51, 52]. Statistically, this is even more remarkable than protein folding!

Figure 4. The distribution of saddle heights in the primary basin of Ar$_{19}$, as a function of the energy of the upper minimum. The data have been collected into histogram bins.

If the (KCl)$_{32}$ cluster begins as an amorphous liquid and ends its descent of a monotonic sequence at a crystalline structure, that process must somehow involve the formation of one or more crystalline bits, which presumably accrete more ions to themselves. This is of course immediately suggestive of a process of nucleation and growth. In fact, if one examines the structures taken on by this cluster as it descends a typical monotonic sequence, one quickly recognizes that this is precisely what is going on in the descent. It is not simply a matter of one ion after another accreting to the growing nucleus; rather, sometimes an entire group of particles can slip from an amorphous configuration into an ordered form attached to the nucleus. These seem to be the kinds of steps that are associated with particularly large drops in the potential energy of the cluster.

So far as we know now, the reason for the great difference between Ar$_{19}$ and (KCl)$_{32}$ is that the saddles in the latter become no more difficult to cross, and may even become easier to cross, as the system drops deeper and deeper into its basins. If the salt cluster is quenched at a rate above $10^{13}$ K/s, it seems likely that it may trap itself in a locally stable amorphous structure, so that an ensemble of such clusters, quenched at such a rate, could perhaps form a glass[52, 53].
At this point, we can introduce such questions as "How can we establish the validity of the statistical data base? How do we know whether it is large enough or is representative enough of the entire potential surface?" Two criteria serve as tests; there may be others as well. The two in hand depend on comparison of two independent samples, in effect two (or perhaps more) independently-drawn statistical samples. It is important to construct these by quenching from a high enough initial temperature—and an isothermal simulation is better for these purposes than an isoergic simulation because the former can reach regions closed to the latter—to assure that the system is ergodic. It is also important to carry out the simulations long enough to assure that the systems achieve a reasonable degree of ergodic exploration of the surface. Determining how long a system requires to achieve ergodicity is itself a subject in its infancy\cite{54, 55}, but the principle is clear. In any case, if two or more such statistical samples have been drawn, one can compare them in two ways. The easier is simply to ask whether they show essentially the same distributions of minima and saddles over the energy scale. The second is to ask whether they also show essentially the same distributions of monotonic sequences among the basins. We have applied the former to one system, the (KCl)$_{32}$ cluster, represented by Born-Mayer pairwise potentials. Simulations carried out from an initial temperature of 1000 K with several hundred quenches over intervals of 100 ps to 1 ns yield reproducible distributions of the energies of minima. Simulations of the same length, started with different initial conditions and run at 800 K, do not necessarily yield very similar distributions. As yet no one has made comparisons of distributions of monotonic sequences from different statistical samples. Furthermore we know little or nothing about how the minimum size of a satisfactory data base depends on the number of particles in the cluster or on topographical characteristics of the surface.

The next question is "What can we do with our knowledge of the potential surface?" This brings us to examine the connection between topographies and dynamics, which we shall outline briefly in the next section.

4. Dynamics: A Master Equation

One finding from traditional chemistry that we can draw on now is the rather high reliability with which it is possible to compute rate coefficients and rates of passage from one well on a potential surface across a given saddle and into an adjacent well. This can be done at several levels of sophistication and detail, ranging from the Rice-Ramsperger-Kassel-Marcus (RRKM) theory which separates fast, intrawell motions and averages over them while treating one coordinate as a slow reaction coordinate, to more sophisticated approaches which can reveal state-specific properties, such as the phase space theory of Light, and its later refinements\cite{56-58}. With any of these methods, we can construct, from a knowledge of the minima, the saddles and properties of the surface in the vicinity of these points, rate coefficients for unimolecular reactions which are just the elementary processes of passage from a well to an adjacent well. These may be done classically or quantum-mechanically, and at constant energy or at constant temperature. Thus far, only the latter has been used\cite{45, 47}. In fact we can construct an entire matrix of such rate coefficients for all the linked wells of our data base.

The next step is arraying these coefficients into a matrix $W(T)$ \begin{equation*} W_{jj'}(T) \end{equation*} or $W_{jj'}(E)$ where each element is the transition probability or rate coefficient for passage from well $j$ to well $j'$. In RRKM theory, the elements have the form
\[ W_{j'} = \sum \frac{k_B T \Omega_{j'}^{I_g}}{h} \exp(-\Delta \phi_{j'}^{I_g}/k_B T) \]

where \( k_B \) and \( h \) are of course Boltzmann's and Planck's constants, \( \Delta \phi_{j'}^{I_g} \) is the saddle height above well \( j' \) to reach the saddle \( l_{j'} \) leading to well \( j \), and the \( Q \)'s are the partition functions of the system at the saddle and in well \( j' \). This method assumes that the system spends long enough intervals in the well and in the saddle region to establish local thermal equilibrium and thereby justify the use of partition functions. It is now useful to define a transformation of the \( W \)'s because it simplifies the next step. We write

\[ w_{j'} = W_{j'} - \delta_{j'} \sum_{j''} w_{j''} j' \]

so that the term for which \( j' = j \) corresponds to transitions out of state \( j \), and all the others, to transitions into state \( j \). If we now let \( P(t) \equiv \{ P_{i}(t) \}^T \) be the (column) vector of probabilities that the system be in well \( J \), or the distribution among the \( j's \) of an ensemble, then we can immediately write the coupled set of equations for the time evolution of \( P(t) \), the master equation of this system:

\[ \frac{dP_{i}}{dt} = \sum_{j'=1}^{n} w_{j',i} P_{j'} \]

This set of equations conserves probability, and, so long as \( w_{j'} \) cannot be put into block form, has only one solution corresponding to the equilibrium state, which is of course the Boltzmann distribution of \( P_{j} \)'s. We can write a symmetric form for the master equation by renormalizing the \( P_{j} \)'s as

\[ u_{j} = P_{j}/\sqrt{P_{j}} \] which requires that we also renormalize the \( w \)'s as

\[ w_{j'} = \sqrt{P_{j'}}/P_{j} w_{j'} \]

The solutions to the master equation are then a set of eigenvectors \( u^{k} \) and corresponding eigenvalues \( \lambda_{k} \), of which the largest is the equilibrium value of zero. All the others are negative and correspond to the characteristic rates of flow of the eigenvector distributions.

Thus far, only one set of model calculations has been carried out to illustrate the approach. The system to which it was applied was a highly simplified idealization of the \( \text{Ar}_{19} \) cluster, in which the vibrational frequencies were taken to be the same for all modes (Einstein model) and all modes were assumed harmonic. Because the eigenvector basis functions correspond to populations of individual wells, and the wells are all categorized according to the basins where they are, the eigenvectors could be classified as intrabasin or interbasin flows, and the latter, in turn are either flows into or flows out of the primary basin, in this example. The eigenvalues were found for several temperatures. Fig. 5 shows the distributions of these spectra for four temperatures, with the interbasin flows into the primary basin (light areas) and out of the primary basin (heavy lines) distinguished from all the nonzero flows (dark areas). At the lowest temperature, the interbasin flows are roughly two orders of magnitude slower than the intrabasin flows, but at the highest
temperature, the rates of inter- and intra-basin flows are virtually indistinguishable. This is a first step to understanding the molecular basis of thermal relaxation.

Figure 5. Distributions, at several temperatures, of the eigenvalues of the master equation for the model 19-particle cluster with an Einstein model for the vibrational frequencies—all harmonic, with the same frequency. The dark areas show the distributions of all nonzero eigenvalues; the light shaded areas correspond to eigenvalues of intrabasin flows into the primary basin, and the heavy lines, to eigenvalues of flows out of the primary basin.

5. Future Directions and Applications

Clearly it is very desirable now to apply these ideas to more realistic systems. For example, even introducing real vibrational frequencies into the master equation, particularly introducing anharmonicities, is an important next step. A more precise concept of classification of basins is important. Application of this approach to the transition between polyhedral and close-packed structures of Lennard-Jones and Morse clusters is an obvious immediate task.
Another refinement that should come soon is a more specific, detailed analysis of the distinction between the two extremes illustrated by Ar$_{19}$ and (KCl)$_{32}$. The former has a potential surface in which the well-to-well drops in energy along the monotonic sequences are small and the saddle heights remain high, so that thermalization is likely to occur after a system crosses one saddle and before it can reach the region of a next saddle along the sequence. The argon clusters never get very "hot" as a result of crossing a saddle as they descend a sequence. The latter has a potential surface with some drops in energy along monotonic sequences that are large compared with the heights of the next saddles to be encountered, so that the system may well pass over one or more saddles, perhaps even many saddles, before reaching local thermal equilibrium. The KCl clusters can become quite hot, at least for a very brief interval, as a result of crossing a saddle along a downward course. Do many systems fall naturally into such extreme classes, or are most clusters somewhere between these? What thermal equilibration is relevant here? How large a system can act as its own environment and heat sink to provide the means of equilibration? Presumably a necessary criterion must be that the heat capacity of all the combined modes not participating in the reaction coordinate is large enough that the excess energy released into mean kinetic energy by a system crossing a saddle on its downward path hardly changes the effective vibrational temperature of all those modes. Another necessary criterion for local thermal equilibration must be that enough modes are coupled strongly to make the effective heat capacity large enough to satisfy the first criterion, in a time interval brief compared with the time required for the "hot" system to find the next saddle in the downward sequence. A large system has a lower probability of finding a specific saddle than does a small system, so we might expect the larger clusters to thermalize more readily than small clusters. However large clusters can have more than one saddle leading down a sequence, and the number of such saddles probably increases very rapidly with $N$. How these balance and govern the dynamics of relaxation is a fascinating question that combines the problems of energy flow with those of topographies and dynamics.

Still one more direction that needs to be pursued is the question of how the effective complexity of a system behaves as it descends a monotonic sequence. Do more and more degrees of freedom become unimportant as the system approaches a basin bottom? Is there a systematic way to reduce the number of effective degrees of freedom of a system as it descends a sequence? Can we define an effective dimensionality of the relevant part of the multidimensional potential on the basis of how far, for example in terms of the number of minima separating the one of interest from the basin bottom? When descent along a sequence corresponds to nucleation and growth of a crystalline structure, this must be so, because the degrees of freedom of the particles already incorporated into the growing crystalline nucleus do not participate in further growth of that nucleus. If such a reduction is possible, how can we incorporate that information into an analysis that relates topography to dynamics?

One direction that we have already pursued, which will be reported soon, has almost immediate applicability to materials technology. This the use of the solutions of the master equation at different temperatures to carry out an optimization procedure, to find the time-temperature profile that will bring the system closest to some preselected distribution of energies, meaning to some preselected morphology. At the extremes are the simple questions, "How slowly can I cool the system and still get a glass," and "How fast can I cool the system and still have it find its way to its global minimum?" Between these extremes, one might seek a specific mix of amorphous and regular structures, to obtain particular electronic and mechanical properties.
In summary, we have outlined the tools available for finding the most important characteristic details of potential surfaces, and then, with illustrative examples, shown how one can go from these details of minima, saddles and reaction paths to a global characterization of the topographies of multidimensional potentials. Then we sketched the basis of the relation of topography to dynamics, starting with the evaluation of individual well-to-well transition rates and going on to incorporate these into a master equation. That section closed with an application of the master equation to compare rates of inter- and intra-basin flows at different temperatures. Finally, we described some of the most important and most obvious problems immediately ahead in this new approach to studying multidimensional potential surfaces.

6. Acknowledgments

The authors would like to express their gratitude to their colleagues Heidi Davis, Thomas Beck, Tanya Astakhova, John Rose, Keith Ball, Feng-Yin Li, Ana Proykova and David Wales. R.E.K. would like to thank E. Schöll for the opportunity to pursue this work. R.S.B. would also like to acknowledge the support of the National Science Foundation and the Alexander von Humboldt-Stiftung, which made possible our contributions to this research.

* R.E.K. has also published under the surname "Breitengraser-Kunz".

References

40. Tsai, C.J. and Jordan, K.D. (1993) Use of the justogram and jump-walking methods for overcoming slow barrier crossing behavior in Monte Carlo simulations:
Applications to the phase transitions in (Ar)$_{13}$ and (H$_2$O)$_8$ clusters, *J. Chem. Phys.* 99, 6957-6970.


