

EXPLORING POTENTIAL SURFACE LANDSCAPES AND HOW THEY GOVERN DYNAMICS

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THE MULTIDIMENSIONAL POTENTIAL SURFACE

The subject of multidimensional potential surfaces and the dynamics on those surfaces was just reviewed by this writer¹, and the closely related topic of the analytic representation of potential surfaces, largely of small systems, had been reviewed shortly before by Schatz². Consequently we will here very tersely review some of the fundamentals, briefly survey aspects of the subject treated in those reviews and discuss some aspects not covered in those reviews.

The description of any system of two or more atoms usually begins with consideration of how to deal with the combination of relatively fast electronic motions and the relatively slow nuclear motions. Traditionally this involves invoking the approximate separability of electronic and nuclear motions, which justifies the concept of an effective potential energy for the nuclear motion, and that is the starting point for this discussion. However, in light of the concern about cases in which this separation is inapplicable, we begin with the caveat that here we shall not concern ourselves with situations in which energy flows between electronic

and nuclear degrees of freedom so as to change any quantum numbers. (This is the condition for the validity of the *adiabatic* approximation, which was long ago justified by Ehrenfest's Theorem.) Rather, we will assume that the electronic degrees of freedom always equilibrate so fast, with respect to nuclear motion that the energy of the electrons--kinetic and potential--plus the instantaneous, configuration-dependent potential energy of the nuclei, constitute an effective potential energy. The limitations of this assumption were recently discussed by Sutcliffe³. The effective potential energy is a function of the nuclear coordinates only; it, together with initial conditions, governs the motion of the nuclei, whether classical or quantum-mechanical. We can think of this potential as defining a surface.

We suppose that the polyatomic system we are describing, be it molecule or cluster, consists of N atoms, and that these are assigned positions relative to the center of mass or to some other convenient choice such as that of Radau coordinates. Thus three coordinates fix the position of the system in the laboratory frame. We also assume that the system is not rotating (or that the coordinate system rotates with the molecule or cluster) so that three (angular) coordinates are also fixed. This leaves $3N-6$ independent coordinates on which the effective potential depends. Hence we can think of the effective potential as a dependent variable which defines a surface in a space of $3N-5$ dimensions, $3N-6$ of which are those of the independent variables. For a three-atom system, $3N-6=3$ so the surface is the dependent variable in a 4-dimensional space. We shall be concerned here with clusters not only of three but of 6, 7 and even many more atoms, as many as 55 and 64, so we shall be dealing with spaces of roughly 12 to about 185 dimensions, and the surfaces in these spaces.

All problems concerning potential surfaces, even within the limited context we have chosen, begin with the issue of constructing the potential surface itself. This is an industry of moderate size and considerable sophistication which does not need further review here⁴⁻⁶. This subject is far from closed. Most approaches to it are based either of two approaches. One involves the construction of effective interaction potentials such as sums of pair interactions, or such pair potentials supplemented with three-body potentials or even four-body contributions and sometimes with mean-field effects such as one-body, density-dependent terms. The other approach requires finding the eigenvalues of the electronic Schrödinger equation at a sufficient number of configurations, that is, at a sufficient number of points on the surface, to permit us to construct an adequate approximation to the surface from those points.

Some of the difficult, open issues regarding construction of multidimensional potential surfaces are these: What is the minimum number of points for which the potential surface can be constructed to yield results of a given desired accuracy? How should these points be

distributed? Presumably they should be taken rather densely in the vicinity of stationary points; how can we locate the regions of stationary points from some very economical procedure, just to get the procedure started? If we can fit each region of the surface near a stationary point to an analytical representation, how do we join the representations from regions of different stationary points?

If one pursues the line of finding relatively simple, effective potentials, one is on firm ground with the rare gas atoms and with simple alkali halides, possibly even with other ionic solids such as alkaline earth oxides. For the rare gases, the Lennard-Jones distance-dependent pair potential⁷ has been an excellent approximation to the accurate potential surfaces for these systems⁸⁻¹¹. Likewise, the Born-Mayer potential, consisting of long-range Coulombic interactions and exponential short-range repulsions¹², is a good approximation to more accurate, more complex forms of potential energies of interacting polarizable ions¹³⁻¹⁵. However the use of such potentials to describe covalently bound insulators and semiconductors is hazardous, and metals are even less amenable to such descriptions--despite the use of such methods for modeling metals, even by this writer. "Effective medium" and "embedded atom" potentials, two popular, closely related approximate potentials that combine explicit pair interactions with mean-field many-body effects, can be used with caution to carry out indicative calculations to help guide intuition, but should only be used in that spirit.

EXPLORING THE SURFACE

The topography of a multidimensional potential surface is complex, so complex that for any system of more than eight or ten particles we are unlikely to know all the information we might obtain, even if we had a reliable analytic representation of the surface. However there are useful things to know, even for quite complex surfaces: the most important minima, the saddles that link these minima with other, higher minima, the density of locally stable states as a function of energy, and the microcanonical entropies of the important basins of the surface--in effect, the logarithms of the areas of many-dimensional lakes at all levels of their surfaces. Contemporary techniques enable us to find all but the last of these. Finding minima is routinized to the level of a textbook subject¹⁶; finding saddles is not as thoroughly explored but satisfactory methods are available now¹⁷⁻³⁴. The development of this subject is included in the review mentioned previously. One of the most interesting open problems in this field now is how to find reliable estimates of the microcanonical entropy.

Another kind of exploration of potential surfaces is that carried out by the clusters

themselves. This can be traced by comparing isomerization rates from simulations with those predicted by RRKM theory, for example³⁵, and the results imply that RRKM theory is a good predictor of such isomerizations. A more subtle kind of investigation explores the extent of chaotic and ergodic behavior of the cluster, as a function of energy and of time. This is a relatively new topic which has been reviewed very recently³⁶ so we will give only a brief summary of the findings. Small clusters are only slightly chaotic and ergodic but become more so as their energy increases. However when very small clusters, of 3, 4 or 5 particles, become energized enough to pass over saddles on their potentials, they lose some chaotic and ergodic character because they spend long intervals in saddle regions where their kinetic energies are low and their trajectories seem rather regular. Larger clusters do not show such drops because of two reasons: their many other degrees of freedom hide the characteristics of the "soft" modes, and the saddles become sharper, offering less phase and configuration space than do the saddles of small clusters. Ergodicity seems to develop with definite separations of time scales for different degrees of ergodicity. It is possible to associate the curvature of the potential surface with a local contribution to the extent of chaotic behavior, as measured by the Kolmogorov entropy.

COMPLEX SURFACES, GLASSES AND "PROTEIN FOLDING"

One fairly complex system that has been studied in some detail is the $(KCl)_{32}$ cluster. It was used as a vehicle to develop methods of estimating densities of locally stable configurational states from statistical samples of minima, and of categorizing those locally stable states^{37, 38}. This system has as its lowest-energy structure a 4x4x4 rocksalt crystal. It has other low-energy structures, all essentially rocksalt-like, some in slabs or sticks, some with a defect or two or three. There are many more locally stable structures that are rocksalt-like on one side and amorphous on the other, structures that emerge from quenching hot clusters that are solid on one side and liquid on the other, a situation possible because alkali halide melts do not uniformly wet their corresponding solids. At still higher energies are many, many more entirely amorphous structures. If a simulated molten $(KCl)_{32}$ cluster is quenched "instantaneously" in the sense of computer time steps, then the number of available amorphous structures is greater than the number of rocksalt structures by a factor of roughly 10^{12} to 10^{14} to 1, depending on the precise energy from which the cluster is quenched. On this basis one might expect the $(KCl)_{32}$ cluster to be a good glass former.

To the contrary, if one simulates a quench at a very fast but finite rate, say 10^{12} K/s (about 50 vibrational periods) or even 5×10^{12} K/s, the cluster finds its way to a rocksalt-like

structure--perhaps one of the defective structures but rocksalt nonetheless. In other words the potassium chloride cluster wins against odds of order 10^{12} :1 to find a special, low-energy structure. This is even more amazing, statistically, than the folding of a protein or other polymer of the same number of atoms. If one carries out the cooling at a rate of 10^{13} K/s or higher, or if the long-range Coulomb forces are replaced by shielded Coulomb forces, the cluster can be trapped in an amorphous structure. This leaves us with a final challenge: what makes a potential surface "focusing"? Is it perhaps better to answer this question before we try to find out why proteins fold into physiologically active shapes as they move on their potential surfaces? Might we learn more about protein folding and other systems with many complicating constraints such as maintenance of primary skeletal structure by first examining simple systems which have no such constraints? Perhaps we should begin by learning how the topography of a potential surface "guides" a system down to a particular structure, and then go on to apply what we learn to more complex molecules.

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