Such an effect would explain the development of a lupus-like disease in transgenic mice that overexpress BAFF (*12–14*). BAFF attenuates apoptosis of mature B cells, heightens humoral responses, and costimulates the response of mature B cells to CD40L (*15*). Thus, BAFF and BAFF-R may be important for the survival of antigen-activated B cells as well as resting mature B cells. Further work is also required to resolve how BCMA and TACI are involved in B cell activities. That TACI may be a positive regulator of T cell–independent responses or a negative regulator of B cell activity awaits clarification. Given the B cell–selective expression of this subfamily of TNFRs, future studies should provide insights into how these receptors guide transition of emergent B cells into the mature pool, sustain antigen-specific immune responses, and support the longevity of post–germinal center B cells.

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PERSPECTIVES: ENERGY LANDSCAPES

Flirting with Catastrophe

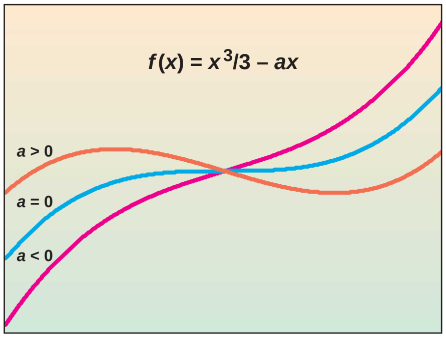
Robert H. Leary

The behavior of atomic and molecular assemblies is governed by potential energy surfaces, which describe the complex interactions between the components and determine how chemical reactions progress or whether a material forms a glass or a crystal. On page 2067 of this issue, Wales (*1*) brings a new analytical tool—catastrophe theory—to the study of potential energy surfaces. He shows that neighboring stable states and the reaction paths that connect them can often be described by universal functional forms dictated by catastrophe theory.

A potential energy surface is commonly described as a landscape. Mountain peaks (local maxima), valley bottoms (local minima), and passes (saddle points representing a minimum in one direction and a maximum in a second, independent direction) are critical points where the gradient vanishes. Except for certain degenerate cases (called non-Morse points), these are the only possible types of critical point for smooth functions of two variables. Smooth functions of one variable typically have only minima and maxima. But in higher dimensions, we must distinguish between different types of saddles.

In 1931, Morse developed a general characterization of nondegenerate critical points (*2*, *3*) in what is regarded as one of the most important contributions to 20th century mathematics (*4*). Morse showed that in the vicinity of any nondegenerate critical point, the potential can be decomposed by a smooth coordinate transformation into a sum of simple, one-dimensional quadratic terms in the individual coordinates. The critical point represents a local maximum along coordinates associated with negative coefficients and a local minimum along coordinates with positive coefficients. In higher dimensions, saddle points are thus distinguished by an index d that represents the number of independent directions for which the potential is at a maximum. Local minima ($d = 0$) are of special interest because they represent stable bound states.

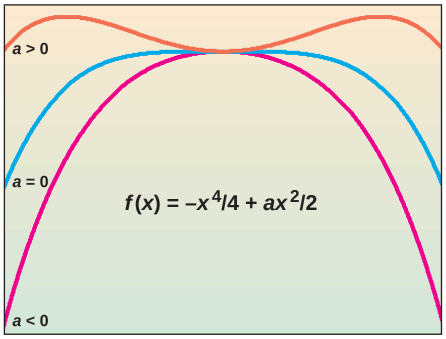
The simplest degenerate case resisting such a decomposition is the one-dimensional cubic polynomial $f(x) = x^3/3$, for which $x = 0$ is a non-Morse critical point that is neither a minimum nor a maximum. This function is a special member of the family of cubic polynomials $f(x) = x^3/3 - ax$ (see the first figure). For $a > 0$, there are two Morse critical points, a minimum at $a^{1/2}$ and a maximum at $-a^{1/2}$. For $a < 0$, there are no critical points. The non-Morse $a = 0$ case separates these two regions where Morse theory applies.



The simplest fold catastrophe.

In higher dimensions, the potential around a non-Morse point may be split into a Morse part (which itself may be decomposed into quadratic pieces) and a non-Morse part. For singly degenerate critical points, an M-dimensional potential splits into an $(M - 1)$-dimensional Morse part and a one-dimensional non-Morse part. The analysis of the non-Morse parts at singly and doubly degenerate critical points and their classification into universal forms is the stuff of Thom's celebrated [and, with respect to models of prison riots and stock market crashes (*5*), controversial] elementary catastrophe theory (*5*–*8*).

For families of potentials with up to five parameters, there are only 11 structurally stable non-Morse universal functional forms or catastrophe functions. For one-parameter families, the situation is even simpler. In the absence of special symmetry conditions, the cubic example (see the first figure)—the fold catastrophe—is the only possible such function. Occasionally, nature restricts the class of applicable functions to those with even symmetry, for example, to describe a reaction path between geometrically equivalent local minima that is symmetrical about the intermediate transition point. The quartic cusp catastrophe function $f(x) = -x^4/4 + ax^2/2$ (see the second figure) and its negative then form the universal family of one-parameter catastrophe functions.



The simplest cusp catastrophe.

Wales (*1*) uses catastrophe theory to analyze the reaction path followed by atomic and molecular clusters that are undergoing a conformational change from one local minimum to another. Such a path passes through a transition point (a saddle of index $d = 1$). If the local minima are geometrically and energetically distinct, the path is asymmetrical and the transition point generally more closely resembles the energetically higher of the two minima.

The author is at the San Diego Supercomputer Center, La Jolla, CA 92037, USA. E-mail: leary@sdsc.edu

This empirical rule is known as Hammond's postulate.

Wales shows (*1*) that the transition point and one of the local minima often emerge from a single non-Morse critical point at a fold catastrophe. If the two points are sufficiently close that the cubic fold catastrophe function remains a reasonable approximation to the energy along the reaction path, the basis of Hammond's postulate becomes clear: The higher energy minimum and the transition point correspond to the relatively closely spaced minimum and maximum of the cubic catastrophe function and share a common parent structure at the non-Morse critical point. The lower energy minimum lies at a considerable distance down the descending left-hand tail of the catastrophe function and is not related by shared parentage to the transition point.

Wales also shows that for fold catastrophes, a quantitative relation holds between the seemingly independent quantities of energy difference, vibration frequency, and path length for the linked minimum and transition point. The results are validated with large databases of paths for various potentials, with excellent agreement where the minimum lies in close vicinity of the transition point.

A similar relation is also derived from the cusp catastrophe function for symmetrical paths. Here the non-Morse critical point gives birth to two geometrically equivalent transition points linked to a central minimum or to a central local transition point linked to equivalent peripheral local minima. Such symmetrical critical point triples arise, for example, in simple rearrangements between permutational isomers in clusters of identical atoms.

Wales' application of catastrophe theory, an analytical tool not widely familiar to the scientific community, to energy landscapes is an exciting new development. It is too soon to tell how useful the theory will prove in explaining the complex behavior of such diverse systems as glasses, clusters, and proteins, but an intriguing beginning has been made.

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PERSPECTIVES: CHEMISTRY

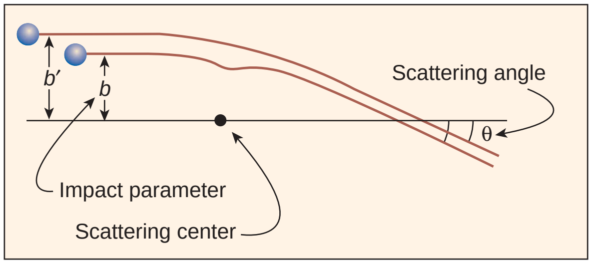
Close Encounters

F. Fleming Crim

For a chemical reaction to occur, molecular collisions must deposit energy in a reactant or bring reactants together such that they can rearrange bonds. Powerful experimental and theoretical techniques are unraveling the details of these encounters, as the report by Lorenz *et al.* (*1*) on page 2063 of this issue illustrates. The authors combine several experimental and computational techniques to measure and analyze the sense of rotation of a molecule after a collision. The study reveals the role of subtle quantum mechanical effects in such encounters.

Today's arsenal of experimental techniques for studying atomic and molecular collisions comprises scattering probes, which observe the direction and speed of molecules after a collision, and spectroscopic probes, which detect the quantum state of the molecules—that is, their particular configuration of energy, spin, momentum, charge, and other quantum properties. In combination, the two techniques yield detailed information about molecular motion during a collision.

In such a combined experiment, a beam of molecules prepared in one or a few quantum states crosses another beam of similarly prepared atoms or molecules. The pressure is low to ensure that each molecule collides at most once, at the point where the beams cross. Collision may result in energy transfer (inelastic scattering) or a reaction (reactive scattering). Some experiments determine the recoil speed and angle of the scattered molecules and infer their total internal energy. Others use spectroscopy to observe the population of individual quantum states, determine the internal energy of a single product state, and identify the molecular motion (such as vibration or rotation) in which this energy resides.



Different paths—same outcome. Two trajectories with different initial conditions (shown here in the center of mass) give the same scattering angle. Attractive forces draw the trajectory with the smaller impact parameter *b* toward the scattering center until repulsive forces direct it outward, resulting in the scattering angle θ. The trajectory with *b*′ experiences mainly attractive forces, which carry it to the same scattering angle θ. A quantum mechanical particle may sample both paths, producing interferences.

One of the most informative observations in a scattering experiment is the range of angles in which the products appear. This angular distribution reveals a great deal about the interaction of the molecules. For example, a broad, symmetric distribution often signals that the interaction is "sticky"; that is, it proceeds through a complex that rotates many times before it decomposes. In contrast, a narrow, asymmetric distribution indicates an interaction that is much shorter than the rotation time.

One may measure the angular distribution by moving a detector about the intersection region and measuring the intensity of scattered molecules at each angle. Alternatively, laser spectroscopy can provide similar information about the recoil direction and speed of the scattered molecules by viewing the entire distribution (for a single quantum state) at once (*2*, *3*). The first imaging experiments of this kind observed photolysis products (*4*). One of the earliest applications to scattering measured the energy transfer in collisions of Ar atoms with NO molecules (*5*, *6*). This system is the same one that Lorenz *et al.* studied to determine the sense of rotation of scattered NO.

These experimental tools are only part of the machinery required to understand collision dynamics. Modern ab initio electronic structure techniques allow the interaction energy of a system to be calculated in various geometries. These discrete calculations can be knit together into a smooth function that gives the interaction potential for different orientations and separations, often visualized as a potential energy surface. One of the first triumphs of molecular reaction dynamics was the use of the qualitative topology of such a surface to predict energy requirements and disposal in chemical reactions (*7*).

The author is in the Department of Chemistry, University of Wisconsin, Madison, WI 53706, USA. E-mail: fcrim@chem.wisc.edu