

Randomness and Complexity in Chemical Physics

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In a seemingly abrupt change in the conversation, Professor Feynman turns to the theoretical chemist and says, "Some guy comes up to you and says, 'What odds will you give me that the 10 billionth digit of π is 7?' What do you say to him?" Innocently the chemist replies, "Let's see, π is a transcendental number, right? I think somebody proved that transcendental numbers have random digits in their decimal representation. There must be 9 to 1 odds, or is it 10 to 1? I'm never good at these things." "Not so fast, young man!" ...Feynman cautions, arching his eyebrows. "That *bas-* - - might have calculated it! ...By the way, I once had a statistical argument to prove Fermat's last theorem...."

The yearnings for complexity and for simplicity are important psychological factors in science. Chemistry is no exception! There is great pleasure in understanding the intricate ways in which many different elementary phenomena come together in the complex world of chemical transformations. There is also pleasure in appreciating how simple systems can be exactly analyzed and controlled. Snatching simplicity from complexity is perhaps the most satisfying activity. This is best illustrated in chemical physics by such developments as chemical thermodynamics itself, transition state theory, nonequilibrium linear response theory, and the universal descriptions of phase transition phenomena. Statistical ideas are at the heart of all these areas and are thus not strange to chemists. Nevertheless, as the encounter with Feynman illustrated, the true meaning of "randomness" can be tricky. In this account, I venture to describe some of those riskier applications of randomness to complex situations in chemical physics. The main notion is that some phenomena occurring in a specific complex system are typical of those that occur in most systems chosen randomly out of an ensemble of possible systems. If this is so, the study of systems with *random* Hamiltonians can tell us what to expect for particular systems just as probabilistic arguments may help in number theory.¹

Enormous advances have been made in the last decades in the theory of random systems arising in condensed matter physics. These studies have taught us how generic random systems differ in behavior from the simple homogeneous systems first studied by physicists. Entirely new phenomena occur in these systems, and very different ways of thinking must be applied to the typical random system than to simple

homogeneous systems. The most striking phenomena in random media are Anderson localization^{2a} and the spin glass transition.^{2b} In Anderson localization, a particle moving quantum mechanically in a random system, for example, an electron hopping between impurities in a doped semiconductor, may remain trapped solely due to destructive phase interference effects, even though escape is classically allowed. In spin glass phase transitions, which occur in dilute magnetic alloys, such as $\text{Cu}_{1-x}\text{Mn}_x$, magnetic spins on the impurity atoms may become frozen into complex patterns which cannot be described by a single-order parameter like the average magnetization. Instead the behavior of the impurity spins depends on the time course of the thermal treatment of the system, proving that there is a wide diversity of possible states into which the system can freeze. Spin glasses thus represent a radical departure from ordinary phase transitions and even require modifications to the usual approach of thermodynamics where a few parameters specify the state of a system. Since these phenomena occurring in a random system are typical of many complex systems, it immediately becomes attractive to see how these ideas can be applied to some of the outstanding problems of physical chemistry.

The problem of energy flow in isolated molecules resembles the Anderson localization problem. Even though many states of a molecule may be nearly isoenergetic, transitions freely occur between the states in some circumstances while, in others, the molecule remains largely in whatever quantum state it starts in, despite the availability of other states.³ The behavior of liquids in their high viscosity regime resembles the problem of spin glass phase transitions. Very long time scale relaxations occur in viscous liquids, and at the highest viscosities, the properties of the system depend on its precise history of preparation, admitting no simple thermodynamic description.⁴ In these problems, the Hamiltonian for the chemical system is something definite. Benzene presumably has a unique vibrational Hamiltonian, even if spectroscopists argue over it. Liquid glycerol has a unique potential energy function, even if different ones are provided by molecular software vendors. But in both cases, the relevant parts of phase space or configuration space are richly complex. Thus we might seek guidance from studying the behavior of random systems where quantum states have statistically defined connections to each other or where the configurational energy landscape is described statistically.

(1) Erdős, P.; Ulam, S. *Rocky Mt. J. Math.* 1971, 1, 613.

(2) (a) Anderson, P. W. *Phys. Rev.* 1958, 109, 1492. (b) Mezard, M.; Parisi, G.; Virasoro, M. In *Spin Glass Theory and Beyond*; World Scientific Press: New York, 1987.

(3) McDonald, J. D. *Annu. Rev. Phys. Chem.* 1979, 30, 29. Felker, S.; Zewail, S. *Adv. Chem. Phys.* 1988, 70, 265.

(4) Angell, C. A. *J. Phys. Chem. Solids* 1988, 49, 863.

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There are many features of biomolecular dynamics that have been described via analogies with systems involving statistically defined potential energy surfaces.⁵ It is no surprise that biomolecular problems can be approached in this statistical way, since proteins with very different sequences (such as the class of lysozymes which thus constitute a statistical ensemble) can have very nearly the same physicochemical behavior. The use of statistical ideas in biomolecular reactions and protein folding has already been reviewed; thus this Account will focus on the applications of the random system physics to nonbiological problems.

Random Models of Energy Flow in Molecules

Some of the longest standing questions in physical chemistry are, to what extent and at what rate does energy flow within a molecule?⁶ The validity of transition state theory and its microcanonical analog, RRKM theory, depends on having sufficiently rapid energy flow so that statistical estimates of the probability of escape are valid.⁷ In recent years, the problem has gained renewed importance because lasers can excite specific parts of a molecule directly. Within the classical approximation, a great deal of progress has been made. This is both because classical mechanics allows detailed computer calculations of the motions of a molecule and because of insights from the mathematical theory of chaos in low-dimensional systems.⁸ Nevertheless, molecules are described by quantum mechanics and not classical mechanics. It has been a challenge to translate the study of classically chaotic systems into the quantum regime. Indeed, the phrase "quantum chaos" can elicit extraordinarily strong, complex and negative reactions in people.⁹ While direct quantum mechanical calculations on dynamics in very small systems are now becoming possible, only the most heroic numerical efforts have yielded results on quantum energy flow in molecules as simple as benzene.¹⁰ The difficulty is that the concept of irreversibility is only sensible in the limit of a high total density of states. A few-state quantum system reversibly oscillates back and forth. A high density of states, making effective irreversibility possible, can be achieved in two ways: in the classical limit (Planck's constant, h , small or, equivalently, large quantum numbers) or for large molecules at modest excitation with the actual value of h . This is why the strict computational approach is strained for describing this problem. When there is a high density of states, a statistical approach might be helpful. Wigner was the first to appreciate this.¹¹ In describing the states of highly excited nuclei, he realized that ab initio approaches would not bear fruit for a long time to come. For nuclei, the underlying interactions were also uncertain. Even if they were known, it would be daunting to calculate exactly the 10 000th energy level

of a heavy nucleus. Thus Wigner suggested that the properties of the spectrum of highly excited nuclei might be imitated by a *random* Hamiltonian in which all states were roughly equally coupled to each other. It is surprising that such an unstructured model has interesting consequences, but it does. For example, the avoidance of degeneracy due to level repulsion leads to a characteristic hole in the distribution of level spacings. Also the statistics of nuclear transition rates are well described by these models.¹² We have come to understand that Wigner's insight was still deeper. A variety of routes suggest that the random matrix behavior for many quantities is generic for systems that are chaotic in the classical limit. These studies indicate that the randomness has its origins in deep properties of number theory.¹³

How can one use random matrix models to describe energy flow? The global models of Wigner are inadequate because all states are equally coupled together, but detailed studies of small molecules, experimentally, and classical calculations suggest that there are specific couplings that are most important for energy flow. Chirikov pointed out that a major mechanism of energy flow classically is the overlap of Fermi resonance regions in the phase space.¹⁴

A single Fermi resonance occurs when a few oscillators have their frequencies tuned such that their nonlinear coupling reinforces itself through many periods. The most familiar example is that of a child swinging. Only when she pumps her legs (first oscillator) in harmony with the period of the swing (second oscillator) is there a significant transfer of energy. In principle, strong enough children could entirely invert themselves on a playground swing! To get chaotic motion, one needs several combinations of oscillations in Fermi resonance. (Imagine a classroom of children on swings holding hands. Or better, take into account other modes of motion of the single-child system!) This corresponds with Chirikov's overlap criterion. Simple Fermi resonances are familiar in molecular systems. The infrared spectrum of CO₂ provides a classic example. Several workers have recognized, therefore, the importance of overlapping quantum Fermi resonances for getting energy flow in bigger molecules.¹⁵ Both the classical resonance condition and the energy conservation criterion limit the ways energy can flow. Only a few quanta can be exchanged between different modes at a time. See Figure 1.

To reach an understanding of the general issues of intramolecular vibrational relaxation (IVR), David Logan and I analyzed the problem of energy flow in a many-dimensional system of quantum nonlinear oscillators with *random* frequencies involved in Fermi resonance.¹⁶ This system should be representative of a whole class of models in which there is a "local" character to energy transport, that is, in which only regions of phase space that are close to each other directly communicate.

(5) Frauenfelder, H.; Sligar, S.; Wolynes, P. G. *Science* 1991, 254, 1598. Wolynes, P. G. In *Spin Glasses and Biology*; Stein, D., Ed.; World Scientific Press: New York, 1992.

(6) Tolman, R. C. *J. Am. Chem. Soc.* 1920, 42, 2506.

(7) Marcus, R. A. *Philos. Trans. R. Soc. London, A* 1990, 332, 283.

(8) Noid, D. W.; Kozykowski, M.; Marcus, R. A. *Annu. Rev. Phys. Chem.* 1981, 32, 267.

(9) Gutzwiller, M. C. *Chaos in Classical and Quantum Mechanics*; Springer: New York, 1990.

(10) Chang, J.; Wyatt, R. *J. Chem. Phys.* 1986, 85, 1826. Wyatt, R. E. *Comments At. Mol. Phys.* 1989, 22, 185. Lederman, S. M.; Marcus, R. A. *J. Chem. Phys.* 1988, 88, 6312.

(11) Wigner, E. P. *Proc. Cambridge Philos. Soc.* 1951, 47, 790.

(12) Brody, T. A.; et al. *Rev. Mod. Phys.* 1981, 53, 385.

(13) Berry, M. V. *Proc. R. Soc. London, A* 1987, 413, 183. Pechukas, P. *Phys. Rev. Lett.* 1983, 51, 943.

(14) Chirikov, B. V. *Phys. Rep.* 1979, 52, 263. Oxtoby, D. W.; Rice, S. A. *J. Chem. Phys.* 1976, 65, 1676.

(15) Uzer, T.; Noid, D. W.; Marcus, R. A. *J. Chem. Phys.* 1979, 71, 2864. Voth, G. A. *J. Phys. Chem.* 1986, 90, 3624. Voth, G. A.; Marcus, R. A.; Zewail, A. H. *J. Chem. Phys.* 1984, 81, 5494. Sibert, E. L.; Hynes, J. T.; Reinhardt, W. J. *Phys. Chem.* 1983, 87, 2032.

(16) Logan, D. E.; Wolynes, P. G. *J. Chem. Phys.* 1990, 93, 4994.

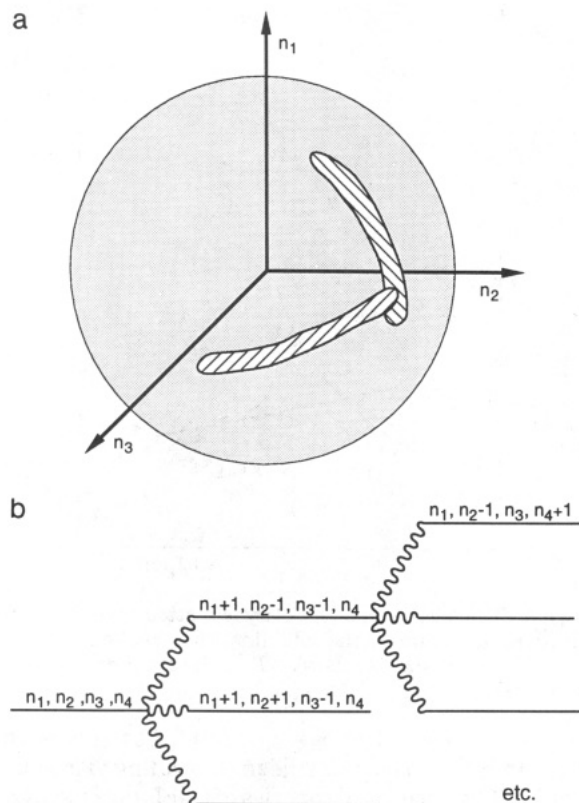


Figure 1. (a) This figure shows a cut through quantum number space. The axes are labeled by the number of quantum excitations in modes 1, 2, and 3. Motion occurs easily on the energy shell, shown as a sphere. In the two cross-hatched regions a resonance between modes 1 and 2 occurs (i.e., their frequencies match approximately $2\omega_1 \approx \omega_2$) or a resonance between 2 and 3 occurs. Through the overlap the system can wander from one resonance region to the other. By a continuing chain of resonance overlaps, excitation can be transferred to other modes not illustrated in this figure. Classically the path would resemble a random walk. (b) Another representation of the multidimensional set of resonances is the familiar tier diagram of radiationless transition theory, shown here for a four-oscillator system. Only some of the possible flow paths are illustrated by the squiggly lines.

The Logan/Wolynes (LW) model is characterized by a distribution of Fermi resonant coupling parameters with a typical value, V , and a local density of states, ρ_{loc} , which gives the probability of finding Fermi resonance within a certain energy range. In a high-dimensional system the local density of states can be very different from the total density of states, which must be large for irreversibility. A local random matrix model of energy flow like the LW model resembles models of quantum transport in disordered solids. The Fermi resonant coupling is analogous to the tunneling matrix element for an electron between sites, and the local density of states in the molecule is analogous to the probability of finding a neighboring resonant site in the solid. The main distinction between the models is that the energy states in the LW model will be correlated, while in electron transport in disordered systems, this correlation can be ignored. The analogy allows mathematical techniques from Anderson localization theory to be used. Even more important, that theory has been experimentally confirmed, leading to confidence in many of the qualitative results.

The first thing we see from the analogy is that there should be a reasonably well defined transition from weak energy flow involving only nearby states to a global

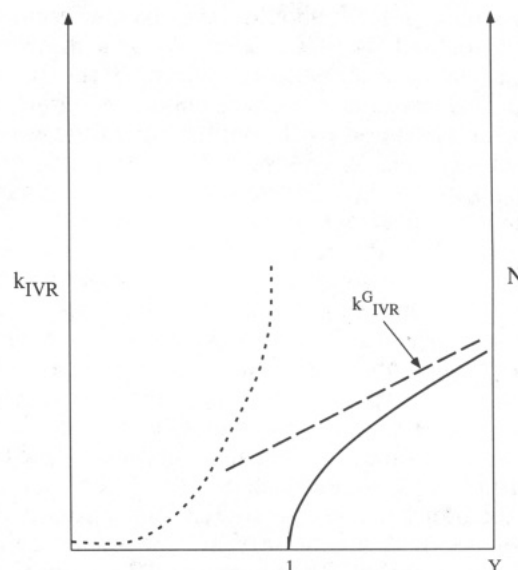


Figure 2. The IVR rate, k_{IVR} , is plotted against the coupling $Y(2\pi/3) = (V\rho_{loc})^2$ as the solid line. The dashed line is the golden rule result for k_{IVR} , both according to scale on the left. The number of states accessible from a given one is indicated as a dotted line, with scale on the right.

energy flow in which most states of the molecule eventually communicate. This is the analog of the localization transition first found by Anderson. The criterion for this transition is that $Y = (2\pi/3)(V\rho_{loc})^2 \approx 1$. (The factor $2\pi/3$ depends on the detailed distribution of the matrix elements.) If $Y < 1$, quantum dynamics will cause transitions only to nearby quantum levels, but if $Y > 1$, all the states can eventually be reached from others. Criteria for energy flow like this have been derived many times in chemical physics.¹⁷ This criterion is in harmony with Marcus's notion of multiple avoided crossings leading to quantum chaos.¹⁸ While there are low-dimensional exceptions to that view, our analogy suggests that it is typically correct for high-dimensional systems.

The analogy makes clear that there is stereotypical behavior near the transition which should be rather sharp. Much above the transition, the golden rule expression for the intramolecular energy flow will be reasonably adequate; near the transition the rate will be strongly suppressed. One expects a power law behavior for the intramolecular vibrational relaxation (IVR) rate near the transition. The LW analysis gives the result $k_{IVR} \sim (Y - 1)^{1/2}$ near the transition as illustrated in Figure 2.

On the localized side of the transition, the number of states, N , that can be accessed, starting from a given one, shows a critical behavior, $N \sim (Y - 1)^{-1}$, also in Figure 2. These scaling laws suggest simple ways of analyzing detailed experimental and computational studies of specific systems.

The analogy with Anderson localization anticipates some interesting effects on intramolecular vibrational energy flow in a molecule in contact with a fluctuating environment. Anderson localization is a phase coher-

(17) Kay, K. G. *J. Chem. Phys.* **1980**, *72*, 5955. Nordholm, K. S. J.; Rice, S. A. *J. Chem. Phys.* **1974**, *61*, 203. Stuchebrukhov, A.; et al. *Chem. Phys.* **1986**, *107*, 429. Freed, K. *Top. Appl. Phys.* **1976**, *15*, 24. Carmeli, B.; Nitzan, A. *J. Chem. Phys.* **1980**, *72*, 2070.

(18) Lee, P. A.; Stone, A. D. *Phys. Rev. Lett.* **1985**, *55*, 1622. Altshuler, B. L.; Khmel'nitskii, D. *JETP Lett.* **1985**, *42*, 359.

ence phenomenon. It should never be confused with trapping caused by rearrangements of a disordered medium such as occurs with the polaron or the solvated electron. Because it is a phase coherence effect, the transition is smeared by the dephasing influence of an external environment. A very interesting nonmonotonic behavior of the IVR rate with external dephasing can occur. If the isolated molecule is in the localized regime, the IVR rate increases with dephasing, whereas if it is strongly delocalized, IVR decreases for small amounts of dephasing. Near the transition a non-monotonic behavior in which the rate first increases with dephasing and then decreases should be seen.

The analogy with Anderson localization is rich, and much remains to be explored. One feature is the observation in quantum transport of mesoscopic fluctuations.¹⁸ The nonlocal character of the quantum phase coherence causes the conductivity of a disordered material to fluctuate more than one might naively expect. Analogously, IVR rates should fluctuate a great deal around their typical value. This suggests a new route to mode specificity in reactions analogous to the fluctuations in rate constants studied by Miller and Moore for small molecules.¹⁹ If one is lucky, a few of the many states that might exist in a large molecule will have precisely the mode structure needed to accelerate a particular reaction.

Random Models of the Energy Landscape of Liquids

The dynamics of liquids remains a central problem of chemical physics. It is remarkable, but true, that the pictures of liquid dynamics most used really don't speak to the fundamental issue of the origin of the fluidity of liquids. The most successful pictures view a liquid as merely an extremely dense gas and use the collision picture so prevalent in gas-phase problems.²⁰ Phenomenological pictures extending continuum theories such as hydrodynamics to the molecular realm have also been useful.²¹ There are theories that are weak perturbations to the collisional or hydrodynamic ones such as the mode-coupling theories of simple fluids²² and the theory of dielectric friction for polar fluids.²³ Given the successes of these pictures, why should one say the origin of fluidity is still mysterious? This is because of the universal phenomenon of the glass transition.

Because of their ubiquity, we take glassy materials for granted. Materials with all kinds of bonding, for example, ionic, covalent, van der Waals, or even metallic, form glasses. The viscosity of fluids ranges from a few centipoise to more than 10^{14} P in the glass transition regime. When the viscosity is as large as 10^{14} P, relaxation times are so long that the material is, for practical purposes, a solid. Understanding the fluidity of a liquid requires explaining this transition to a glass. The gas-like pictures of fluidity cannot account for the large variation of time scales. As chemists, we are open to the notion that large variations are easily obtained

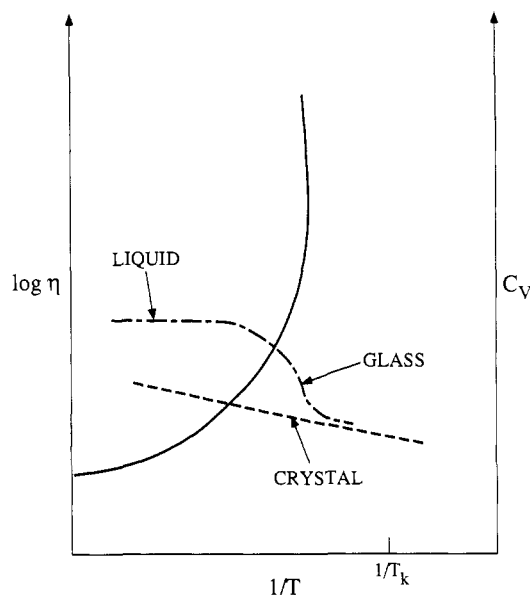


Figure 3. The logarithm of viscosity is plotted against $1/T$ for a glass-forming liquid, as the solid line. The heat capacities of liquid and crystal are also shown. T_k is the temperature of the entropy crisis.

from an Arrhenius law, $\eta = \eta_0 e^{\Delta E/k_B T}$, but this is the exception rather than the rule in describing viscosities of fluids. The successful theories of fluids don't explain the existence of barriers at all. Simple fluids above their melting point show almost no activation energy for molecular motion when the volume is kept constant. As the fluids become supercooled, their viscosity dramatically increases, as in Figure 3. The apparent activation energy near the glass transition regime can be 1 eV, even for fluids with weak van der Waals forces. This dramatic change is observed also at constant volume. The data for many fluids can be fit empirically with the Vogel-Fulcher law, $\eta = A \exp(B/(T - T_0))$. This law exhibits divergence of the activation energy at a temperature T_0 . If this law continues to hold down to T_0 , it would be impossible to have fluidity below this temperature. The law cannot be tested very near T_0 because the relaxation times of the fluid exceed the investigator's patience.

There are thermodynamic puzzles associated with viscous liquids, too. The heat capacities of a glass and the corresponding crystal also are sketched in Figure 3. Because the liquid's heat capacity exceeds the crystal's, upon cooling, the liquid loses entropy much faster than the crystal. If the glass transition did not intervene, at a temperature T_k , the liquid's entropy would be smaller than the crystal's. Something has to give.²⁴ T_k is within 10 deg the same as the T_0 in the Vogel-Fulcher law expression!

The thermodynamic and the kinetic puzzles combine to suggest that there would be an equilibrium transition near T_0 to a solid. What might the nature of the underlying transition be? We know from model-building studies and from computer simulations that collections of atoms can form aperiodic structures that are mechanically stable. Bernal patiently built models of such rigid aperiodic solids;²⁵ and Stillinger and Weber have studied such aperiodic structures extensively on

(19) Miller, W. H.; et al. *J. Chem. Phys.* 1990, 93, 5657. Polik, W. F.; Guyer, D. R.; Moore, C. B. *J. Chem. Phys.* 1990, 92, 3453.

(20) Jonas, J. *Acc. Chem. Res.* 1984, 17, 74.

(21) Hynes, J. T. *Annu. Rev. Phys. Chem.* 1977, 28, 301.

(22) Kirkpatrick, T. R. *Phys. Rev. A* 1985, 31, 939; *J. Non-Cryst. Solids* 1985, 75, 437.

(23) Bagchi, B. *Annu. Rev. Phys. Chem.* 1989, 40, 115.

(24) Kauzmann, W. *Chem. Rev.* 1948, 43, 219. Simon, F. Z. *Anorg. Allg. Chem.* 1931, 203, 217.

(25) Bernal, J. D. *Proc. R. Soc. London, A* 1964, 280, 299.

computers.²⁶ Rigid aperiodic structures should be good models of an ideal glassy state. These structures are, by construction, stable to infinitesimal displacements. What can be said about their stability to larger amplitude motions? It has long been recognized that the stability of a solid to finite amplitude thermal fluctuations is a prerequisite for its thermodynamic stability. Lindemann showed that when the width mean square thermal displacements of molecules ($\langle r^2 \rangle$) becomes roughly one-tenth of an interparticle spacing, melting occurs.²⁷ Equivalently, for stability, the Debye-Waller factor for the solid must exceed a critical value. Theories based on a self-consistent phonon picture and on density functional approaches provide quantitative-
semiquantitative estimates of maximum thermal displacements from microscopic considerations. When these theories are applied to aperiodic lattices, they give a critical Lindemann ratio for the stability of a glass.²⁸ There is some evidence for this ratio in glasses. The ratio never much exceeds 0.1, when a glass is sensibly solid on simulation time scales.²⁹ In the laboratory the Mossbauer effect³⁰ and neutron scattering³¹ show that there is a dramatic change in the mobility of a glassy material when the thermal displacements reach such a critical value.

The Lindemann criterion for devitrification ($\langle r^2 \rangle_{\max} \approx 0.1$) and the theories giving rise to it are themselves puzzling. Since the mean square displacement reaches a maximum, there should be a discontinuity at the transition point. The transition should be first order: This is true for periodic crystals. The actual thermodynamic transition occurs before the limit of stability because the fluid phase becomes lower in free energy than the solid before the vanishing of the solid's local stability occurs, with rising temperature.

An underlying transition resembling a first-order one comes from a different route. Moderately viscous fluids are well described by mode-coupling theories.^{22,32} These theories ascribe some part of the fluctuating forces and, therefore, the friction on a moving molecule to long-lived fluctuations in the structure of the fluid around it. These structural fluctuations themselves decay by means of diffusion. When the coupling goes up, the friction increases, leading to slower diffusive fluctuations. This further enhances the effect of the coupling. Thus, a self-consistent mode-coupling theory carries the seeds of a catastrophe within itself. Self-consistent mode-coupling theories of the glass transition have been elaborated in great detail. They fit many of the properties of viscous fluids while not describing well the very large viscosity behavior. These theories, when they are used below the transition, also give a discontinuous jump in the Debye-Waller factor.

Both the stability analyses of the aperiodic structures and mode-coupling theory lead to the same kind of

transition. Kirkpatrick and Wolynes have shown that the two approaches are fundamentally equivalent and only differ in some details of approximation.³³ These approximate microscopic theories lead to an underlying first-order transition of some kind.

If the underlying first-order transition were conventional, it would not explain the viscosity. A crucial difference between aperiodic structures and periodic ones is that there are many aperiodic structures but relatively few periodic ones. Consideration of a single periodic structure suffices to give us an idea of its stability. For aperiodic crystal structures, one must understand their statistics and the transitions between them. Calorimetry tells us one feature about the aperiodic structures: their number. Since the vibrational entropies of a given aperiodic structure and the crystal are close, the entropy difference of the liquid and the crystal shows that the number of aperiodic structures grows exponentially with the system size above T_k . Below the transition temperature, T_k , the number of such structures should be smaller, perhaps growing in only a polynomial way with the size of the system. We should seek analogies for the glass transition then in systems in which many different structures can become frozen. This is where systems with random Hamiltonians come in.

Systems of spins with random interactions can freeze into many different states. The most studied system of this type is the Ising spin glass.²⁶ It is a model of amorphous magnets such as copper manganese alloys. A set of spins with two states (up or down) interact with each other through an exchange interaction, J_{ij} , giving the Hamiltonian $H = -\sum J_{ij} S_i S_j$. The J_{ij} in this expression are randomly positive and negative.

The Ising spin glass may seem like an esoteric system, but it is typical of many problems in which conflicting interactions are present. A well-known social analogy is exactly isomorphic. Consider the problem of a group of people deciding to divide itself into two parties. Imagine, however, that half of all possible pairs of people at random hate each other and that the other half of all pairs would be bosom buddies, individually. How can you find the best way of dividing the group? In the case of a small initial group the division is easy to find, but for a large one there are many divisions that are nearly optimal.

A rather elaborate mean field theory of this spin glass shows that it can freeze into many states. The transition is continuous and in that way differs from the results of the simple microscopic approaches to structural glasses. Even though analogies between spin glasses and structural glasses have long been expected, it is widely agreed that the Ising spin glass is not an appropriate analogy.

Kirkpatrick and Wolynes proposed that the analogy to a random system can be made, not to the Ising spin glass, but to the Potts spin glass with long-range interactions.³³ The underlying objects, Potts spins, rather than having two states, can point in multiple directions. In the social analogy, the Potts spin glass corresponds to the problem of dividing the group into three (or more) parties. Variables with Potts-like symmetry arise naturally in the study of orientationally disordered plastic crystals, where they represent dif-

(26) Stillinger, F. H.; Weber, T. *Science* 1984, 225, 983.

(27) Sutherland, W. *Philos. Mag.* 1890, 30, 318. Lindemann, F. A. Z. *Phys.* 1910, 11, 609.

(28) Stoessel, J. P.; Wolynes, P. G. *J. Chem. Phys.* 1984, 80, 4502. Singh, Y.; Stoessel, J. P.; Wolynes, P. G. *Phys. Rev. Lett.* 1985, 54, 1059.

(29) Woodcock, L. V.; Angell, C. A. *Phys. Rev. Lett.* 1981, 47, 1129.

(30) Champeney, D. C.; Sedgwick, D. F. *J. Phys. C* 1972, 5, 1903. Nienhaus, G. I.; Frauenfelder, H.; Parak, F. *Phys. Rev. B* 1991, 43, 3345.

(31) Mezei, F. In *Liquids, Freezing and the Glass Transition*; Hansma, J. P., Levesque, D., Zinn-Justin, J., Eds.; North-Holland: Amsterdam, 1991; pp 629-688.

(32) Götze, W. In *Liquids, Freezing and the Glass Transition*; Hansma, J. P., Levesque, D., Zinn-Justin, J., Eds.; North-Holland: Amsterdam, 1991; pp 287-504.

(33) Kirkpatrick, T. R.; Wolynes, P. G. *Phys. Rev. A* 1987, 35, 3072.

ferent ways the molecules can be oriented. In a liquid undergoing a glass transition, the Potts variables could correspond with the amplitudes of conflicting density waves characteristic of different polymorphic crystal forms. Individual atoms must decide to which of these density waves they most want to contribute. Potts spins lack the fundamental up/down symmetry of Ising spins, and Potts ferromagnets undergo a first-order transition rather than a continuous one. The Potts spin glass with random interactions was solved in the mean field limit by Gross, Kanter, and Sompolinsky.³⁴ They showed that the long-time spin correlations $q = \lim_{t \rightarrow \infty} \langle S(0) S(t) \rangle$ undergo a discontinuous change at the transition. The parameter q is the analogue of the Debye–Waller factor. On the other hand, as in the case of the Ising spin glass, there are many different states into which the Potts system could freeze, and because of this, the transition is thermodynamically continuous. Unlike an ordinary first-order transition, there is no latent heat but rather a discontinuity in the heat capacity and other susceptibilities. At a structural glass transition, the heat capacity shows a near discontinuity that would presumably become sharper as the time scale of measurement becomes longer. The behavior of a Potts spin glass is universal. Random spin systems with long-range interactions violating the up/down symmetry of the Ising model have transitions which have discontinuous susceptibilities. Another example is the random three-spin-interaction glass³⁵ for Ising spins, $H = \sum J_{ijk} S_i S_j S_k$. Here the triplet interactions J_{ijk} are randomly positive and negative.

Because of the randomness in the Hamiltonian, the energy landscape of a Potts spin glass can be analyzed much more thoroughly than that of a structural glass. Individual minima of the mean field Potts spin glass become unstable to small finite size thermodynamic fluctuations at a temperature, T_A , which exceeds the thermodynamic transition temperature. This stability limit coincides with the result of mode-coupling theory for the Potts spin glass.³⁶ The mode-coupling equation for the three-spin-interaction spin glass coincides³⁷ precisely with the simplified equations used in structural glasses by Leutheusser. For this random model the mode-coupling theories delineate the emergence of stable minima. If the stability limit T_A exceeds the thermodynamic transition temperature, what is the mechanism of the thermodynamic transition? Kirkpatrick and Wolynes showed that Potts glass minima can be counted below T_A , and their configurational entropy makes up the difference between the free energy of each state and the free energy of the disordered state.³⁸ The transition occurs when the configurational entropy vanishes. The mean field Potts spin glass is a model whose phase transition occurs precisely through an entropy crisis. As the system is cooled, one samples lower and lower energy minima which are uncorrelated in their structure until finally there are no more states.

The infinite range Potts glass would exhibit the dynamics of the mode-coupling theory, leading to a freezing at the temperature T_A . The entropy catastrophe

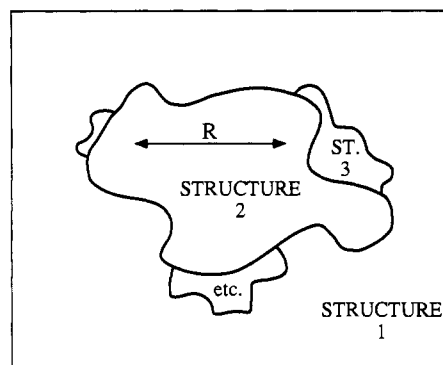


Figure 4. A snapshot of a new minimum nucleating in an aperiodic structure. Its surface will be "wetted" by still other structures.

trope occurs at the lower temperature, T_k . Between T_k and T_A one must account for the finite range of interactions. The finite range Potts spin glass is not exactly solved, but using the infinite range results as a starting point, one sees a new mechanism of instability for individual minima.³⁸ Since there are exponentially many minima of the infinite range system below T_A , one can imagine the nucleation of droplets of one phase (one of the minima within the other) as shown in Figure 4. Such droplet states would no longer be minima but transition states for converting one structure of another. There should be a free energy cost dependent on the mismatches in the structures at the borders of a droplet. This will increase with the size of the droplet. On the other hand, the extensive configurational entropy means that there is a driving force for creating such droplets: there are many more possible kinds of droplets for large regions than for small ones. Thus the free energy for nucleating a new structure has the form $F(R) = -k_B T S_c R^d + \sigma R^{\nu}$. The maximum of this free energy gives the barrier for converting one minimum to another. The activation energy increases with decreasing configurational entropy $F^* \sim S_c^{-\alpha}$. Kirkpatrick, Thirumalai, and Wolynes have developed a scaling theory for the exponents.³⁹ This theory presupposes that the finite range Potts glass exhibits an entropy crisis just as for the mean field model, and that the susceptibilities are discontinuous at this transition as in the mean field model and the extrapolated laboratory structural glass transition. This scaling hypothesis uniquely fixes the exponents and leads precisely to the Vogel–Fulcher expression for the activation free energy!

In summary, a system with a random Hamiltonian, the Potts spin glass, has many close analogies with the structural glass. The simplest theoretical levels of mode-coupling and stability analyses reveal the many similarities. A new kind of phase transition occurs in the Potts spin glass by means of an entropy catastrophe, just as impends for structural glasses. Scaling analyses of this random Hamiltonian show how the Vogel–Fulcher law arises. These results suggest that the energy landscape of a structural glass which has some specific Hamiltonian, in the temperatures studied in viscous liquids, has a configurational space topographically similar to that of finite range Potts spin glasses.

(34) Gross, D. J.; Kanter, I.; Sompolinsky, H. *Phys. Rev. Lett.* 1985, 55, 304.

(35) Gardner, E. *Nucl. Phys. B* 1985, FS14, 747.

(36) Kirkpatrick, T. R.; Thirumalai, D. *Phys. Rev. Lett.* 1987, 58, 2091.

(37) Leutheusser, E. *Phys. Rev. A* 1984, 24, 2765; *Z. Phys. B* 1984, 55, 235.

(38) Kirkpatrick, T. R.; Wolynes, P. G. *Phys. Rev. B* 1987, 36, 8552.

(39) Kirkpatrick, T. R.; Thirumalai, D.; Wolynes, P. G. *Phys. Rev. A* 1989, 40, 1045.

Final Remarks

Just as in number theory, randomness is a useful tool for orienting oneself to problems of complexity in chemical physics. At the very minimum, random Hamiltonian models make us aware of new phenomena and new mechanisms. This is illustrated in the random Fermi resonance model of IVR and the random Potts spin glass model for liquid glass transitions. Because of their universality, the various scaling laws found for random systems should be roughly valid for specific systems.

Random models can be a guide for detailed studies, but be sure to place your bets *before* the computations are done.

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