

Glassy Crystals

Low-frequency and Low-temperature Properties^a

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GLASSES

Glasses are amorphous like liquids, but are rigid like crystals. To a chemist, this may seem natural: silicon dioxide, when covalently bonded into a well-relaxed random network, should resist deformations as an elastic solid just as it would in a crystalline network. To a theoretical physicist, this is more mysterious. What broken symmetry¹ causes the rigidity?

Of course, the chemist may in the end be right—the observed rigidity may be due purely to short-range order. If so, glasses must flow like a (very viscous) liquid on sufficiently long time scales. Even though it is not favorable for any individual bond to break, rearrangements of sufficiently large clusters of atoms will allow the energy to decrease or remain the same. (If the order is short range with a range R , a cluster of size larger than R will typically allow such an internal rearrangement.) At any finite temperature, these rearrangements will proceed by thermal activation at a slow but nonzero rate. Any external stress applied to the system will produce a bias in these rearrangements, producing in the end the finite shear rate characteristic of a liquid. If the glass is truly solid, it must have some sort of long-range order to produce infinite barriers to rearrangements. The study of the glass transition is the study of the phase boundary between the fluid liquid and the rigid glass. This subject is controversial, and has recently seen several interesting developments.

In this paper we will not discuss the glass transition. We will deal partly with the universal low-temperature² properties of glasses, which are not as controversial; indeed, in many ways they are quite well understood. The tunneling center theory^{3,4} explained why glasses have specific heats proportional to temperature and thermal conductivities proportional to T^2 , in contrast to insulating crystals where both properties are proportional to T^3 for low temperatures T . It predicted correctly that glasses would have a saturable ultrasonic attenuation and a “time-dependent” specific heat; the experimental specific heat varies logarithmically with the measuring time.

We will also deal with the low-frequency response of glassy materials. In the experimental phenomenology, there are two kinds of low-frequency response in glasses, with quite different signatures, which often (or always) coexist. There has been much study of the α -relaxation processes because of their relationship to the glass transition. The α -relaxations typically are observed in the supercooled liquid, and have a

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characteristic time scale that appears to diverge at a temperature somewhat below the temperature at which the liquid falls out of equilibrium (freezes into a glass); their time dependence often is well fit by the Williams–Watts or Kohlrausch form $\chi(t) = e^{-(t/\tau)^\beta}$. The relaxations we will discuss almost certainly correspond to the β -relaxations in glasses, which have not been studied much. The β -relaxations are observed in the glass at lower temperatures; they often span many decades in frequency, and their characteristic time scale diverges only at zero temperature, with an Arrhenius law suggesting thermal activation.

A glass will have a completely different configuration of atoms each time it is formed. Thus very generally, whether or not the glass is truly rigid, there will always be some local rearrangements of the atoms with very small energy costs; since the atoms have no definite positions, they have flexibility in their local configurations. The tunneling center theories use these rearrangements to explain the universality of the low-temperature properties of glasses. All glasses have local rearrangements of atoms with nearly degenerate energies; quantum tunneling of these atoms between their two configurations produces many low-energy excitations with long time scales; these “two-level systems” produce the observed behavior, which is thus naturally common to all glasses. These rearrangements can also proceed by thermal activation, and thus provide a natural explanation for the low-frequency (β) relaxation.

The experimental methods used to understand the structure of crystals are largely useless in studying glasses. Although some average information about the microscopic structure of glasses such as the radial distribution function can be measured, relatively atypical regions like tunneling centers are hard to study. (Tunneling centers that contribute to the specific heat below 1 K involve maybe 1 molecular group in 10^5 .) The development of the tunneling center theory has been hindered both by the lack of a microscopic picture of the centers and by the related lack of experimental or theoretical information about the distribution of tunneling center parameters. The relaxations responsible for the low-frequency properties in glasses are also largely not understood; there is little upon which to base a theory.

Thus the discovery that certain crystalline systems have many properties characteristic of glasses is an exciting opportunity. The mixed crystal $(\text{KBr})_{1-x}(\text{KCN})_x$ shares many properties with glasses; however, unlike glasses, its structure is well understood. In the next section, we will review some of what is known experimentally about the glassy behavior found for intermediate values of x , and give some important parameters describing the dilute ($x \approx 0$) and pure ($x = 1$) limits. In the third section we will discuss our mean-field theory⁵⁻⁷ and describe its predictions for the dielectric loss peak and the time-dependent specific heat at $x = 0.5$. In the final section we will discuss the relationship with true glasses.

EXPERIMENTS ON $(\text{KBr})_{1-x}(\text{KCN})_x$

$(\text{KBr})_{1-x}(\text{KCN})_x$ forms cubic single crystals with a sodium chloride structure. The cyanide ions, CN^- , are shaped roughly like (North American) footballs, and randomly displace bromines in the lattice. Since the molecular size of the cyanide ion is close to that of bromine, mixed crystals of high quality with no apparent chemical clustering can be made over the whole range from the dilute limit $x \approx 0$ to the pure potassium cyanide limit $x = 1$ (FIG. 1). For very low cyanide concentrations ($x \lesssim 0.01$) the

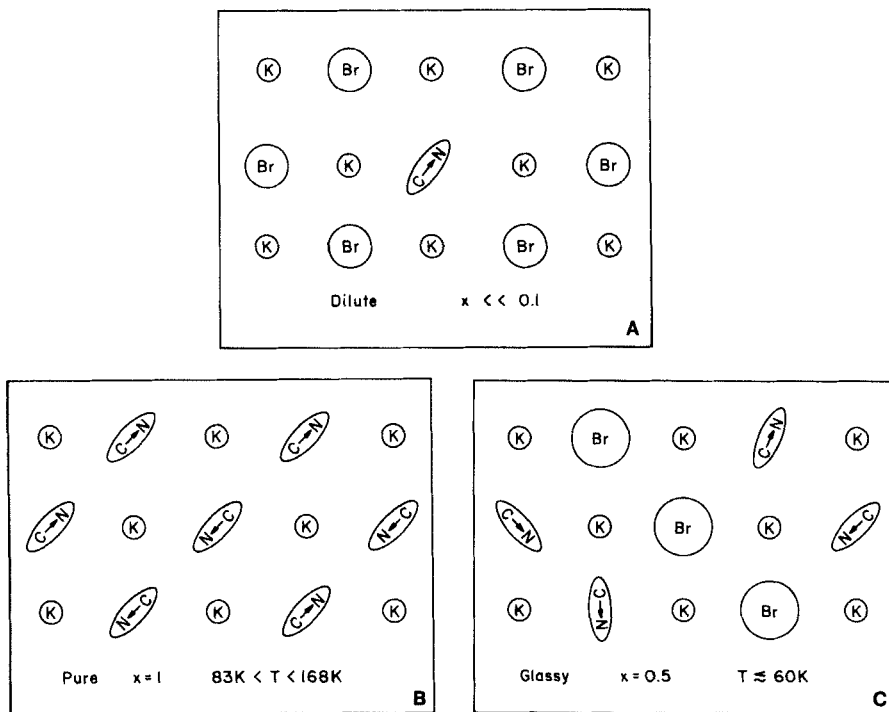


FIGURE 1. A theorist's conception of a typical (1,0,0) plane in (A) dilute, (B) pure, and (C) 50% $(\text{KBr})_{1-x}(\text{KCN})_x$. The arrows on the cyanide molecules indicate the direction of \mathbf{n} . The cyanide molecule in A tilts out of the plane of the paper.

cyanides act as independent tunneling centers; for pure KCN the cyanides align into ordered phases at low temperatures (FIG. 2). For reasonably high cyanide concentrations ($0.6 < x < 1$) the cyanides still develop long-range orientational order, although the phase diagram becomes rather complicated. In the range $0.1 \leq x < 0.6$, the cyanides freeze into a disordered "orientational glass" state. In this section, we will discuss each of these ranges in turn, briefly summarizing the relevant experimental information.

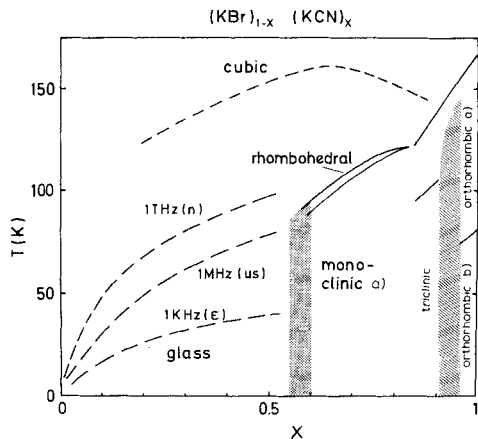
In the dilute limit (FIG. 1A) each cyanide is isolated and has a cubic crystal environment. The cyanide ion has eight $\langle 111 \rangle$ equilibrium orientations,⁹ with a barrier height of 36 K separating them. At low temperatures the cyanide tunnels between these equilibrium orientations, producing, for example, a Schottky anomaly peak in the specific heat and a dip in the thermal conductivity. This behavior is well understood.¹⁰ In particular, we will use the effective moment of inertia of the cyanide ion measured in the dilute limit ($2.65 \times 10^{-39} \text{ g} \cdot \text{cm}^2$);¹¹ this is larger than the corresponding moment of cyanide in vacuum, because of an effective mass contribution from the motion of surrounding ions during the tunneling process.^{12,13} Note the other important fact that we learn from the dilute limit: the crystal field contribution to the local potential is small. In our model, we can safely ignore the 36 K contribution of the

crystal field to the barrier height; the cyanides start as free rotors, and cyanide-cyanide interactions will determine the barrier heights.

Pure potassium cyanide (FIG. 1B) goes through two orientational phase transitions. The higher temperature ferroelastic transition at 168 K aligns the axes of the cyanide ions without introducing dipolar order; the lower temperature antiferroelectric transition at 83 K orders the cyanide dipoles.¹⁴ We can conclude from this (and from measurements in the dilute limit) that the forces that distinguish between the carbon and nitrogen ends of the ion are relatively weak; we shall ignore the dipole-dipole interactions in our model, and concentrate on the stronger elastic forces, which in pure potassium cyanide act to align the quadrupolar axes of the ions. In the ferroelastic phase, each cyanide ion has two equilibrium orientations separated by 180°; thermally activated flips between these orientations produce a dielectric loss peak. From the temperature dependence of this peak estimated from combined dielectric loss, nuclear magnetic resonance, and ionic thermal conductivity measurements, we discover that the barrier height for flipping a cyanide at low temperatures is 1570 K; this gives us a measure of the cyanide-cyanide interaction strength. There is also a softening of one of the phonon modes associated with this transition. (This transition, which is first order, has been studied at length: we will not discuss it here.) The ferroelastic phase transition in a variety of alkali cyanides is well described by quadrupolar mean-field theories;^{7,15-22} our model for the diluted system is a straightforward generalization of these theories. Finally, the asymmetry energy for a cyanide dipole in the low-temperature antiferroelectric phase (the energy difference between the preferred orientation and the metastable flipped orientation) has been measured to be roughly 340 K (L. Wu, Y. H. Jeong, and S. R. Nagel, personal communication); we shall use this as a crude estimate of the spread of asymmetry energies in the glassy cyanides.

For cyanide concentrations above $x = 0.6$, the low-temperature phase has long-range orientational order. The phase diagram in this region is quite complex;^{23,24} the orthorhombic ferroelastic phase of the pure cyanide gives way to triclinic, monoclinic, and rhombohedral regions, which sometimes coexist. (There appears not to be any long-range dipolar order (J. M. Rowe, personal communication) in any phase

FIGURE 2. A phase diagram for $(KBr)_{1-x}(KCN)_x$. Note that the universal glassy properties extend into the region of long-range orientational disorder ($x = 0.7$). Reproduced here with permission, from Loidl and Knorr.⁸



other than the orthorhombic phase). Such complex phase diagrams are common in frustrated systems; the elastic interactions between cyanides depend on their relative positions, and can prefer either parallel or perpendicular relative orientations. We argue below, however, that this complexity is not central to the properties (low-temperature properties and dielectric loss) that we wish to understand; our model will ignore this frustration. The mean-field theory of Kanter and Sompolinsky,²⁵ which we will briefly discuss in the next section, is very frustrated, but ignores the dilution; their results would seem to indicate that the frustration is only partial. Finally, we will note but not discuss a recent announcement²⁶ that the orientational freezing transition

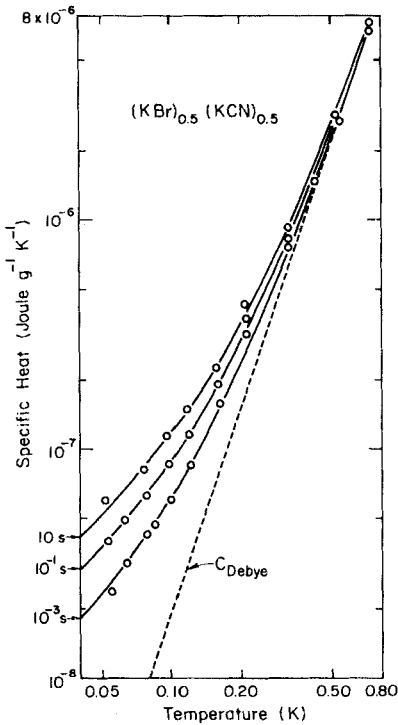


FIGURE 3. Specific heat, determined from the temperature rise of the quasi-adiabatic sample after the times t indicated. The curves are of the form $C = A(t)T + C_D T^3$, where C_D is the Debye value determined from elastic measurements. Adapted from Meissner *et al.*⁶

becomes second order at $x = 0.73$, in the middle of the range 0.6–1 of complex crystalline phases.

At low temperatures and intermediate concentrations, $(\text{KBr})_{1-x}(\text{KCN})_x$ shows all of the universal properties of glasses. The specific heat is proportional to T , and is time dependent (FIG. 3); the thermal conductivity is proportional to T^2 , and crosses over at ~ 2 K into the plateau characteristic of glasses.²⁷ The dielectric constant is glassy.²⁸ Ultrasonic attenuation and phase velocities are characteristic of glasses.²⁹ It has recently been demonstrated that the low-temperature glassy properties persist into the crystalline region⁶ to $x = 0.7$. Thus the glassy behavior is not closely related to the lack

of long-range order in the cyanides; it may well be that the low-temperature properties of glasses are quite independent of the glass freezing transition.

Let us discuss the specific heat at length. Consider the specific heat measurements of Meissner and Knaak⁶ for $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$ shown in FIGURE 3. Note first that the specific heat at a fixed temperature depends on the time scale of measurement (in this experiment, on the time passed since the heat pulse was added to the sample). The specific heat near 0.1 K varies by nearly a factor of two as the measuring time changes from 10^{-3} to 10 sec. This reflects the long internal relaxation times for the cyanide tunneling centers. The tunneling centers in glasses always produce this time dependence: they have a wide range of tunneling rates, and absorb or emit energy as they come to equilibrium. As the time scale becomes longer, the measured specific heat includes more of these slow degrees of freedom, and therefore becomes larger. Note second that the specific heat crosses over from linear in T to cubic in T at a temperature around 0.5 K. The curves fit to the data are of the form $A(t)T + C_D T^3$. The linear term $A(t)$ is universally found in glasses; its magnitude and time dependence are within the normal range. The cubic term is not fit to the data; it is the Debye specific heat due to phonons calculated from the elastic constants. It gives a good fit to the data around 1 K (although beyond 1 K there are deviations). Usually in glasses the Debye contribution does not exhaust the cubic term, and there is an anomalous T^3 contribution to the specific heat. For $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$ this anomalous term is absent within experimental accuracy.

The low-frequency behavior of $(\text{KBr})_{1-x}(\text{KCN})_x$ has caused some confusion in the past. There are several experimental probes of the dynamics that have been used. Ultrasonic, Brillouin, and inelastic neutron-scattering experiments were used to measure the temperature at which the sound velocity softened at high frequencies; dielectric loss measurements were used to measure characteristic relaxation rates at low frequencies. Two groups interpreted the results in terms of a single Arrhenius law—suggesting that the relaxation slows down continuously with a single activation energy and that there was no glass transition.^{30,31} Not everyone accepted this view; Rowe, Rush, and Michel (personal communication) claimed that continuous slowing down was incompatible with their neutron-scattering measurements, that dielectric loss was probing a different susceptibility (in particular, was observing 180° cyanide reorientations), and that the sound velocity measurements when taken alone showed a much steeper temperature dependence (compatible with a freezing of the cyanide quadrupolar order). These ideas have now been confirmed by torsional oscillator experiments that overlap the frequency range of the dielectric loss measurements.^{8,32} These measurements show that the frequency of the sound velocity anomaly does decrease very quickly with temperature, and is decoupled from the frequency of the dielectric loss peak. (It is tempting to identify the former with the α -relaxations in real glasses, but the analogy will probably not hold; the disorder here is fixed whereas in glasses the disorder is freezing in while the glass is forming.) Thus the elastic interactions between the cyanide quadrupoles freeze their long axes into a disordered configuration, but the cyanide ions remain able to flip over, just as in pure potassium cyanide.

The dielectric loss measurements gave more information than just a characteristic frequency. FIGURE 4 shows the frequency-dependent dielectric loss for $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$, at three fixed temperatures, measured by Birge *et al.*³³ Notice three

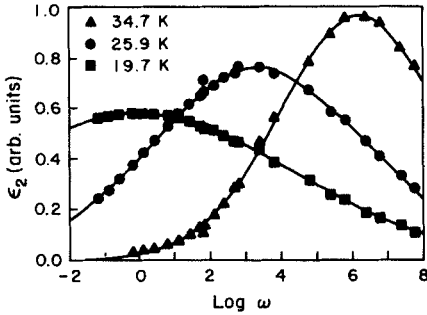


FIGURE 4. Dielectric loss as a function of frequency for $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$. The horizontal scale is measured in decades. Note that ϵ_2 versus $\log_{10}\omega$ is shown for several temperatures with least-squares Gaussian fits (solid lines). Adapted from Birge *et al.*³³

things about these data. First, the peaks span up to eight decades in frequency, indicating the very broad range of relaxation times characteristic also of glasses. (In contrast, the dielectric loss peak in KCN forms a good Debye peak with a width of 1.1 decades.) Second, the peak shifts to lower frequencies and broadens as the temperature is lowered. Indeed, the peak frequency follows an Arrhenius law over their experimental range; also, if the relaxation is due to a distribution of barrier heights, the peak should broaden like $1/T$ (differences in activation energies producing larger differences in rates at lower temperatures). Third, the loss peak is described beautifully by a log-normal distribution (the solid Gaussians in FIGURE 4).

Birge *et al.*³³ proposed that their log-normal loss peak was due to a Gaussian distribution of barrier heights hindering cyanide reorientations

$$P(V) = (\sqrt{\pi}\sigma_v)^{-1} \exp [-(V-V_0)^2/\sigma_v^2] \tag{1}$$

Theories involving distributions of relaxation times have become unpopular in the study of glasses. Independent centers relaxing with a distribution of barrier heights suffer from the same criticism; almost any relaxation, whether due to independent or collective effects, can be described by a suitable distribution. It is crucial for credibility that the distribution be temperature independent. If the barrier crossing rate is Arrhenius

$$\omega(V) = \omega_0 e^{-V/k_B T} \tag{2}$$

the dielectric loss is well described by the distribution shown in equation 1 with a weak temperature dependence

$$\begin{aligned} V_0 &= 659 \text{ K} \\ \sigma_v &= 300 \text{ K} - 1.5 T \end{aligned} \tag{3}$$

That is, the peak position of the loss and most of the width variation are characteristic of a distribution of barrier heights. The experimental data at different temperatures test different regions of the barrier height distribution; FIGURE 5 shows the range over which the dielectric loss measurements have checked the Gaussian form of the distribution.

Our model for $(\text{KBr})_{1-x}(\text{KCN})_x$ is based on the mean-field theory of ferroelastic freezing in pure potassium cyanide.⁷ One could argue that it is overambitious to extrapolate from a theory of long-range crystalline order to a glassy state that is

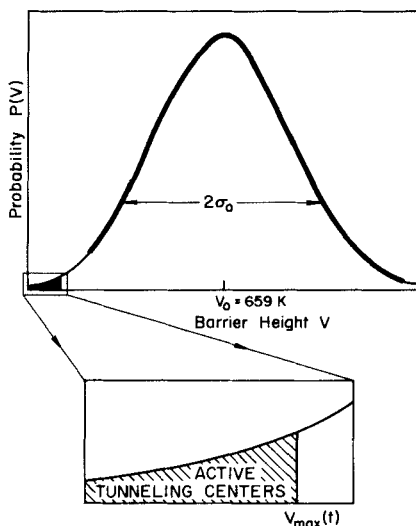
separated from it by several other crystalline phases. I claim that this is not so; the properties we are interested in are local, and do not depend strongly on frustration or nonexistence of long-range order. Despite the complexity of the phase diagram, the dielectric loss peak corresponding to the 180° cyanide reorientations in the pure cyanide broadens smoothly and continuously into the loss peak observed in the glassy material.¹¹ The glassy low-temperature properties, on the other hand, extend into the region with long-range crystalline order, as noted above. Thus there are good experimental reasons to believe that the low-frequency and low-temperature behavior can be described by a diluted ferroelastic mean-field theory.

MEAN-FIELD THEORY

In this section we will develop a mean-field theory for $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$ in terms of a diluted lattice of interacting quadrupoles. There have been other theories applicable to this material;³⁴⁻³⁷ indeed, Fischer and Klein³⁴ stimulated interest in it by predicting that it would have glassy low-temperature properties. The approach of Michel *et al.*³⁵ is probably closest to ours, although they concentrate on the glass transition and mostly do not explore lower temperature behavior.

First, we will discuss the dielectric loss. The Gaussian form for the peak will follow from the central limit theorem; its width will be explained as fluctuations in the number of nearest neighbors. The (weak) temperature dependence of the barrier height distribution will be explained from the temperature dependence of the order parameter. Briefly, the barrier height to reorienting a cyanide will be due to cyanide-cyanide interactions, and will become smaller as the surrounding cyanides become thermally disordered. Second, we will discuss the time-dependent specific heat. Extrapolating the Gaussian distribution to very low barrier heights, we can (largely independently of the mean-field theory) predict the number of active

FIGURE 5. Main graph: Proposed Gaussian distribution of barrier heights for $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$ at zero temperature. The darkened regions of the curve represent the range over which the dielectric loss measurements have tested the distribution. Expanded section: Low-barrier tail showing those tunneling centers that contribute to the specific heat below 1 K. Note that $V_{\text{max}}(t)$ is the largest barrier to reorientation that a cyanide molecule can tunnel through in a time t ; $V_{\text{max}} = 96$ K for $t = 1$ sec.



tunneling centers as a function of the time scale. From this extrapolation, we are able to get a good description of the time dependence of the specific heat, and its absolute magnitude.

We could describe the orientation of a cyanide molecule by a vector \mathbf{n} pointing from the carbon to the nitrogen. Since the cyanides remain free to flip by 180° , however, we should ignore the difference between the carbon and nitrogen ends of the molecule by writing Hamiltonians that are even in \mathbf{n} . Thus, we shall use the quadrupole $Q_{\alpha\beta}^i = (n_\alpha^i n_\beta^i - \frac{1}{3}\delta_{\alpha\beta})$ to describe the orientation of ion i . Our Hamiltonian will give the elastic energy of the crystal in terms of the $Q_{\alpha\beta}$. It will describe the elastic forces on a cyanide due to its cyanide neighbors; these forces are mediated by lattice deformations.

There are two model Hamiltonians that have been used to study this problem. The one we will discuss at length incorporates only the effects of dilution. If we let $\chi_i = 1$ if a CN^- occupies site i , and $\chi_i = 0$ if a Br^- occupies site i , our Hamiltonian is given by

$$\mathcal{H}_D = -\frac{1}{2} J \sum_{\langle ij \rangle} Q_{\alpha\beta}^i Q_{\alpha\beta}^j \chi_i \chi_j \quad (4)$$

This Hamiltonian will generally have a ferroelastic ground state; some cyanides have more neighbors than others, but all cyanides prefer to be aligned. The mean-field theory for this Hamiltonian can easily be solved explicitly,⁵ as we shall see.

The other model, studied by Kanter and Sompolinsky,²⁵ ignores dilution but incorporates frustration in a fashion paralleling spin glasses. Their Hamiltonian is

$$\mathcal{H}_F = \sum_{\langle ij \rangle} J_{ij}^{\alpha\beta\gamma\delta} Q_{\alpha\beta}^i Q_{\gamma\delta}^j \quad (5)$$

where the coefficients $J_{ij}^{\alpha\beta\gamma\delta}$ are, apart from obvious symmetries, independent random variables. They solve this approximately in mean field, using replica symmetry breaking. It is clearly true that their model contains more of the glassy physics; they have a multiplicity of disordered ground states. The trivial, unfrustrated way we have included the disorder produces many ground states only insofar as each cyanide has two orientations. In the microscopic energetics of the tunneling centers, however, surely the dilution is important (cyanides with few neighbors will have lower barriers), and surely the frustration is only partial (the cyanides are not dilute; all the near-neighbor cyanides will presumably have the same J_{ij}). Indeed, the width of the barrier height distribution predicted from Kanter and Sompolinsky's model is far too large, and the predicted distribution is not Gaussian.

For the diluted Hamiltonian of equation 4, the force experienced by a quadrupole at site i is given by the derivative

$$\frac{\partial \mathcal{H}_D}{\partial Q_{\alpha\beta}^i} = -J \sum_{j \text{ nbr of } i} \chi_j Q_{\alpha\beta}^j \quad (6)$$

We now make a mean-field approximation that all neighbors are equivalent to an average neighbor with field strength $Q_{\alpha\beta}^b$. Thus, if the number of neighbors is

^bThis is exact on a Bethe lattice with a random number of neighbors, if the average coordination number Z_0 is taken to infinity keeping the probability distribution $P(Z/Z_0)$ of having Z neighbors fixed.

$$\sum_{j \text{ nbr of } i} \chi_j = N_i$$

$$\left[\frac{\partial \mathcal{H}_D}{\partial Q_{\alpha\beta}^i} \right]_T^{MF} = -JN_i Q_{\alpha\beta} \quad (7)$$

With the assignment $J_i = JN_i$, this gives the effective mean-field Hamiltonian

$$\mathcal{H}_{\text{eff}} = -JN_i Q_{\alpha\beta} Q_{\alpha\beta}^i = -J_i Q_{\alpha\beta} Q_{\alpha\beta}^i \quad (8)$$

Now the average neighbor is not an average cyanide. Those cyanides that have more cyanide neighbors affect proportionately more cyanides, and thus contribute more to the mean field. Let there be M cyanides in the sample. Then the probability of a cyanide having N neighbors is

$$P(N) = \left(\sum_{i=1}^M \delta_{NN_i} \right) / M \quad (9)$$

On the other hand, the probability that a neighbor j of a cyanide has N neighbors is

$$\begin{aligned} P'(N) &= \left(\sum_{i=1}^M \sum_{j=1}^{N_i} \delta_{NN_j} \right) / \left(\sum_{i=1}^M N_i \right) \\ &= \left(\sum_{j=1}^M N_j \delta_{NN_j} \right) / (MN_0) \\ &= \frac{N}{N_0} \left(\frac{\sum_{j=1}^M \delta_{NN_j}}{M} \right) \\ &= \frac{N}{N_0} P(N) \end{aligned} \quad (10)$$

where N_0 is the average number of neighbors. That is, each cyanide is counted once in $P(N)$, but counted N_i times as a neighbor in $P'(N)$. The average quadrupole moment of a cyanide depends on the number of its neighbors.

$$Q(N) = \frac{\text{Tr}(Q e^{-\beta N J Q Q})}{\text{Tr}(e^{-\beta N J Q Q})} \quad (11)$$

Thus the average neighbor moment Q will then be an average over N , weighted by

$$\begin{aligned} Q_{\alpha\beta} &= \sum_N P'(N) Q_{\alpha\beta}(N) \\ &= \sum_N \frac{N}{N_0} P(N) Q_{\alpha\beta}(N) \\ &= \int dJ \frac{J}{J_0} P(J) [Q_{\alpha\beta}^J]_T \end{aligned} \quad (12)$$

where J_0 is the mean of the distribution $P(J)$.

By a change of coordinates, \mathbf{Q}_{ij} can be diagonalized. We assume \mathbf{Q} is uniaxial, with major axis in the z direction. We can then write the traceless symmetric tensor \mathbf{Q} in terms of a single function $\alpha(T)$

$$\mathbf{Q}_{ij} = \begin{pmatrix} -\alpha(T) & 0 & 0 \\ 0 & -\alpha(T) & 0 \\ 0 & 0 & 2\alpha(T) \end{pmatrix} \quad (13)$$

In terms of α , \mathcal{H}_{eff} is then

$$\mathcal{H}_{\text{eff}} = J\alpha(T)(1 - 3n_z^2) \quad (14)$$

and the barrier height for a 180° flip of a cyanide orientation is

$$V = 3J\alpha(T) \quad (15)$$

Thus within our model, the distribution of coupling constants J is directly scaled into a distribution of barrier heights V by a temperature-dependent order parameter $\alpha(T)$. We must now discuss the form of $P(J)$. The coupling of an ion to the mean field, and therefore the barrier hindering the dipolar reorientation, will be a sum of contributions from the (randomly distributed) neighboring cyanides. Our model assumes that these contributions are uncorrelated; since each cyanide has 12 near neighbors, the distribution is given by the binomial distribution

$$P(N) = 2^{-12} \binom{N}{12} \quad (16)$$

This distribution is very nearly Gaussian; if we assume^c that next-nearest-neighbor interactions are large enough to smear out the discreteness in the tails, the central limit theorem implies a Gaussian form for $P(J)$

$$P(J) = (\sqrt{\pi}\sigma_J)^{-1} \exp[-(J - J_0)^2/\sigma_J^2] \quad (17)$$

where the mean coupling J_0 will scale linearly with the cyanide concentration x . (This also implies that the transition temperature scales roughly with x ,^{7,35} which is pretty accurate (FIG. 2).) Using equation 9, this leads to a barrier height distribution of precisely the form seen in equation 1 with V_0 for $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$ half that of the 1570 K Arrhenius barrier height for the dielectric loss peak in pure KCN. Thus the mean-field prediction for the mean coupling strength in $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$ is 20% higher than the experimental value $V_0 = 659$ K. The ratio of the width to the peak of

^cThis is a crucial assumption, as the entire contribution to the specific heat comes from cyanides with "between zero and one neighbors." On the one hand, we can see in FIGURE 5 that the dielectric loss peak remains Gaussian and smooth to quite high barriers; if it is symmetric and represents the barrier height distribution our extrapolation is justified. On the other hand, $P(J)$ is convolved with a Debye peak to produce the dielectric loss, which may smooth out effects of discreteness. There is a recent report of evidence for some kind of discreteness in Brillouin scattering off $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$.³⁸

the (nearly Gaussian) binomial distribution is $1/\sqrt{6}$; this prediction is 12% smaller than the experimental ratio $\sigma/V_0 = 300 \text{ K}/659 \text{ K}$.

In the rest of the paper, we will use the experimental values for the zero temperature barrier height distribution (equation 3) to determine the distribution of coupling constants (rather than using our extrapolations from the pure KCN). Thus since $\alpha(0) = 1/3$

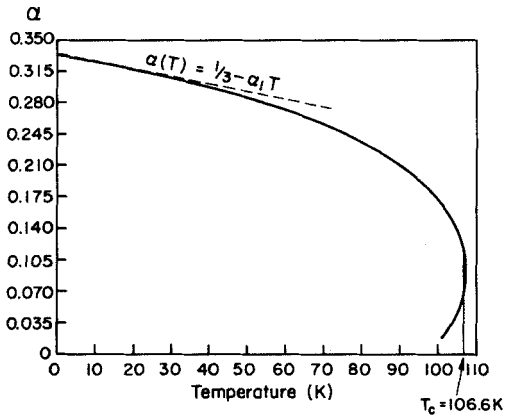
$$J_0 = V_0 = 659 \text{ K}$$

$$\sigma_J = \sigma_V(T = 0) = 300 \text{ K} \tag{18}$$

(See FIGS. 4 & 5.)

We can find the temperature-dependent order parameter $\alpha(T)$ by solving the mean-field theory using the standard self-consistent calculation. The mean alignment

FIGURE 6. Mean-field order parameter α as a function of temperature, for the Gaussian distribution of coupling strengths given by the experimental parameters of equation 18. The ferroelastic transition temperature T_c obtained from minimizing the free energy is 106.6 K. (This temperature need not correspond to the glass transition temperature; our model does not describe the glass transition.)



of a given cyanide

$$\langle (n_z^J)^2 \rangle = \frac{\int dn_z n_z^2 e^{\beta J 3\alpha(T) n_z^2}}{\int dn_z e^{\beta J 3\alpha(T) n_z^2}} \tag{19}$$

depends on the strength $\alpha(T)$ of the mean field. The mean-field strength

$$\alpha(T) = \frac{1}{2} \int dJ P(J) \frac{J}{J_0} \left\langle (n_z^J)^2 - \frac{1}{3} \right\rangle_T \tag{20}$$

depends in turn on the alignment of the cyanides. In FIGURE 6, we may see the results of our self-consistent calculation for $\alpha(T)$. (Details can be found in Sethna and Chow.⁵)

At low temperatures, $\alpha(T)$ is approximately linear in T . As for pure KCN,^{7,33} we can see that the peak frequency of the dielectric loss will continue to have an Arrhenius form. The peak J_0 of the coupling constant distribution corresponds to a temperature-dependent peak $V_0(T) = 3J_0\alpha(T)$ of the barrier height distribution. If $\alpha(T) = (1/3) -$

$\alpha_1 T$, then barrier crossing over the temperature-dependent barrier $V_0(T)$ is indistinguishable from crossing the zero temperature barrier $V_0(0) = J_0$ with a different prefactor

$$\omega_0 e^{-V_0(T)/k_B T} = \omega_0 e^{-3J_0 \alpha(T)/k_B T} = (\omega_0 e^{3J_0 \alpha_1/k_B}) e^{-J_0/k_B T} \tag{21}$$

Thus the measured Arrhenius slope should be temperature independent, as is observed experimentally. The width of the barrier height distribution (and thus of the dielectric loss peak), however, scales directly with $\alpha(T)$

$$\sigma_V = 3\alpha(T)\sigma_J \tag{22}$$

The value of α_1 leads to a prediction $\sigma_V(T) = \sigma_V(0) - 0.708T$; our mean-field theory predicts roughly half of the experimental temperature dependence (equation 3).

Thus fluctuations in the number of nearest neighbors plausibly explains the Gaussian form, width, and peak position of the dielectric loss in $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$. The temperature dependence of the width is explained within a factor of two by describing the thermal disorder in the neighboring cyanides using a mean-field theory with a

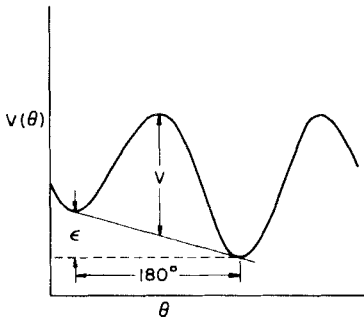


FIGURE 7. A typical double-well potential plotted against θ , the orientation angle of the cyanide molecule. The barrier height V and asymmetry ϵ are functions of the local environment of the cyanide.

distribution of coupling constants. The low-frequency dielectric loss is due to cyanides independently crossing over a distribution of barriers; because the barriers are due to cyanide-cyanide interactions, they become smaller as the neighboring cyanides become thermally disordered.

We have explained dielectric loss in terms of 180° cyanide reorientations that were thermally activated; the specific heat will be explained by 180° cyanide reorientations mediated by quantum tunneling. We will get the magnitude of this time-dependent specific heat within a factor of two. To give some context for this result, we can compare it to a naive extrapolation from low concentrations: if the cyanides did not interact, and each contributed the Schottky anomaly characteristic of dilute impurities, the specific heat at 0.1 K would be 10^5 times larger than that observed on a 10-sec time scale.²⁸ The factor of 10^5 reduction of the specific heat comes out of the calculation in two ways. First, interactions between cyanides raise the barrier to reorientation. Unlike dilute cyanides, most cyanides in the glassy regime will not relax by quantum tunneling on a human time scale, and will not contribute to the specific heat. Second, interactions between cyanides produce an asymmetry between the two preferred orientations. Only those cyanides whose two orientations are degenerate

within $k_B T$ will contribute to the specific heat; most cyanides are frozen into their lower state.

As mentioned in the introduction, the low-temperature properties of glasses have traditionally been explained using tunneling centers.^{3,4} These centers are formed by atoms or groups of atoms of unknown microscopic structure, with two metastable configurations. Just as for the cyanide impurities, these centers are characterized by a barrier height V and an asymmetry ϵ (FIG. 7). Because the microscopic structure of the centers is unknown in glasses, little can be said about the distribution of tunneling center parameters $P(\epsilon, V)$. Significant conclusions, however, can be drawn on very general grounds. For example, the distribution must be even in the energy asymmetry $P(\epsilon, V) = P(-\epsilon, V)$ (each center has two wells, one higher in energy, one lower), and smooth on scales of tenths of eV. Thus, assuming $P(0, V) \neq 0$, the density of tunneling states is roughly constant in the energy range of interest. Roughly speaking (see below), because only those centers with $\epsilon \lesssim kT$ contribute, this leads to a specific heat linear in temperature.

By using our microscopic model of the tunneling centers in $(\text{KBr})_{1-x}(\text{KCN})_x$, we will be able to make more detailed predictions about the low-temperature properties. In particular, we have definite information about the distribution of tunneling centers, gleaned from our understanding of the isolated cyanide impurity and the pure alkali cyanides. The traditional model *assumes* a flat distribution in the tunneling parameter, which corresponds to a distribution $P(V, \epsilon) \propto V^{-1/2}$. From the dielectric loss experiments, we know the distribution of barrier heights is the Gaussian of equation 1. We do not have a direct experimental probe of the distribution of asymmetries ϵ ; however, the inverse density of centers near zero asymmetry should be roughly given by the asymmetry energy ~ 340 K between the two orientations in the pure cyanide antiferroelectric phase.

The rate Γ of tunneling by an angle θ through a barrier of height V is given by a simple WKB calculation

$$\Gamma(V) = \Gamma_0 \exp(-A\theta \sqrt{2IV}/\hbar) \quad (23)$$

where A is a numerical constant; for a sinusoidal $V(\theta)$, $A = 4/\pi$. Because our cyanides are reorienting by 180° , $\theta = \pi$. The magnitude of the attempt frequency Γ_0 has been estimated in the pure cyanide to be 8.3×10^{13} Hz;⁷ our results are quite insensitive to the value chosen for this prefactor. We use $I = 2.65 \times 10^{-39}$ g \cdot cm² \approx 16 amu \cdot Å². The probability that a cyanide molecule with barrier height V will flip over within t seconds is thus $1 - \exp(-\Gamma(V)t)$. In calculating the specific heat, we will weight the contribution of each cyanide by this factor. To get a rough idea of the number of active cyanides at a measuring time t , let us define a maximum crossable barrier $V_{\max}(t)$, for which $\Gamma(V_{\max}(t)) = t^{-1}$. For $t = 1$ sec, $V_{\max}(t) = 96$ K (FIG. 5).^d This implies (evaluating

^dAt temperatures above about 2 K, the dominant relaxation process on a 1-sec time scale will be thermal barrier crossing. This will lead to a temperature dependence of the number of active tunneling centers, which gives a small contribution to the specific heat that goes roughly as T^3 . In addition, there should be modes within the individual wells (librational modes) that give a similar contribution. Perhaps the anomalous T^3 specific heat in real glasses will be explained eventually by these effects. The experimental value for this term in $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$ is compatible with zero, however, and the theoretical value for the effects of thermal activation and libration are swamped by the Debye phonon contribution. There appears to be a substantial anomalous T^3 term for $x = 0.25$; we await measurements of the dielectric loss.

an error function) that 0.35% of the cyanide molecules have a flip rate higher than 1 Hz. Thus roughly one cyanide in 300 can tunnel in 1 sec, and one in 340 has asymmetry small enough to contribute to the specific heat below 1 K; crudely, these together explain why the specific heat is down by 10^5 .

More explicitly, at low temperatures, the cyanide double-well center can for most purposes be considered a two-level system. The lowest two states of the double well can be nearly degenerate, and higher states are not accessible at low temperatures.^e We can truncate, keeping only these states; we write the Hamiltonian \mathcal{H}_{2L} in a "position" eigenstate basis (where (1, 0) and (0, 1) correspond to the two stable orientations of the cyanide). The two-level system is then defined by the asymmetry ϵ and a tunneling matrix element Δ

$$\mathcal{H}_{2L} = \begin{pmatrix} -\epsilon/2 & -\Delta \\ -\Delta & \epsilon/2 \end{pmatrix} \quad (24)$$

The energy splitting between the two levels is $2[(\epsilon^2/4)^2 + \Delta^2]^{1/2}$. Because $\Delta \ll \epsilon$ for most centers contributing to the specific heat, we approximate the energy splitting by ϵ .^f As in the traditional models, we make the approximation that $P(\epsilon, V) = n_0 P(V)$ (that is, is independent of the asymmetry ϵ) for $\epsilon \lesssim kT$. With these approximations, the specific heat of the distribution of two-level systems is^{3,4}

$$A(t) = \frac{\pi^2}{6} k_B^2 n_0 \int_0^\infty dVP(V) [1 - \exp(-\Gamma(V)t)] \quad (25)$$

Fitting the experimental specific heat at $t = 1$ sec gives the value $n_0 = 1/(k_B \times 292 \text{ K})$. This agrees well with the inverse of the asymmetry (340 K) found for the pure cyanide (L. Wu, Y. H. Jeong, and S. R. Nagel, personal communication).⁸ We then use equation 25 to predict the time dependence of the linear term in the specific heat (FIG. 8). This one parameter fit is in good agreement with the experimental data, and is almost as good as the two-parameter fit given by the traditional models (straight line in FIG. 8).

CONCLUSIONS ABOUT GLASSES

We have explained that the time-dependent specific heat and the dielectric loss peak in $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$ are due to 180° cyanide reorientations. These properties are universal in glasses; all glasses show a broad distribution of relaxation times, and all show the same time-dependent linear term in the specific heat. We have deliberately chosen to study these universal properties in a single well-characterized material. Many rather general and abstract theories of glassy behavior have been motivated by

^eThey can be accessed virtually, however, and are important in mediating tunneling in the presence of interactions.^{12,13}

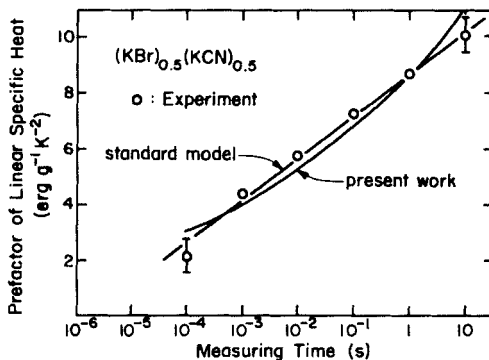
^fWe have estimated the importance of Δ in the specific heat of $(\text{KBr})_{1-x}(\text{KCN})_x$; it produces slight deviations from the linear form at low temperatures.

⁸This agreement is probably accidental; the two numbers should agree maybe to within a factor of two.

the idea that universal properties cannot depend on details of the particular glass. The converse, however, is also true—an explanation for a universal property must apply to each individual glass, and in particular to $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$.

Although the microscopic structure of $(\text{KBr})_{1-x}(\text{KCN})_x$ is well understood, we emphasize that our model is not microscopically derived: we ignore the frustration completely. The elastic interactions that freeze the quadrupoles do not typically favor parallel relative orientations; they compete, and this competition is responsible both for the variety of phases between $x = 0.6$ and $x = 1$ and for the orientational glass state for $x < 0.6$. Although the results of Kanter and Sompolinsky²⁵ suggest that completely random interactions do not form a sensible model for this material, they do demonstrate that new physical effects—particularly level repulsion causing a reduced density of low barriers—should very generally follow from incorporating frustration. We may suggest that the dilution substantially reduces the effects of frustration and “level repulsion,” but we should certainly agree that a model calculation with more realistic interactions ought to be done.

FIGURE 8. The open circles are the prefactors $A(t)$ of the measured linear specific-heat anomaly (FIG. 2). The curve is the result of our calculation; it has one free parameter n_0 that we can independently estimate within a factor of two. The straight line is the prediction of the standard model; both the slope and the intercept are free parameters.



What have we learned about glasses? First, we have a microscopic picture of the tunneling centers in at least one glassy material. The original tunneling center papers^{3,4} did not attempt to provide a microscopic model for the centers. There has been much speculation since these papers appeared about the nature of these two-level systems; proposals run from rearrangements of large clusters of atoms to topological inversions of defect lines.³⁹ Although these exotic centers may occur in some materials, in this case ordinary tunneling defects of the form well known in alkali halides¹⁰ determine the glassy behavior.

Second, we have started with roughly one tunneling center per molecular unit, and explained the magnitudes of the universal properties. The form of the specific heat is naturally explained by the traditional tunneling center models, but the small variation found in the magnitude is surprising: why should all glasses have the same density of active tunneling centers (within a factor of 10)? At least in this case, the density arises naturally from the statistical origin of the distribution of barrier heights.

Third, we have connected the low-temperature and low-frequency properties, explaining both in terms of the same centers. Our discussion cannot be directly

transferred to glasses in general. Dielectric loss peaks are not usually of the log-normal form found in $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$. Apart from another glassy crystal,⁴⁰ most low-frequency β -relaxation peaks found in glasses are asymmetric, often fit by the Williams–Watts function mentioned in the introduction. It is possible that the glassy crystals are in fact atypical. On the other hand, it is intriguing to speculate that they may be ideal, clean systems, where the low-frequency physics is not obscured by dirt effects so far unavoidable in normal glasses. What we can surely conclude from the cyanide system is that the low-frequency and low-temperature properties are at times linked; we should look for a common origin in glasses as well.

Finally, the $(\text{KBr})_{1-x}(\text{KCN})_x$ system may provide answers to many of the remaining puzzles about glasses. We have already mentioned a possible role for thermal reorientations and librational modes of the cyanides in explaining the anomalous T^3 specific heat; this would presumably carry over directly to normal glasses. The plateau in the thermal conductivity between 1 K and 10 K has also provoked much theoretical speculation over the years, without a satisfactory resolution. A rough calculation of the low-temperature T^2 thermal conductivity (due to resonant scattering from the cyanide centers) has been presented;⁶ we are currently working to understand the thermal conductivity in more detail.⁴¹

We believe that more insight is yet to come from the glassy crystals, as new experiments are done and more sophisticated theoretical methods are used.

SUMMARY

Glasses are amorphous like liquids, but are rigid like crystals. Unlike a crystal, in which each atom has a set position, a glass will have a completely different configuration of atoms each time it is formed. Sometimes atoms or local groups of atoms will have two low-energy configurations and will be able to shift between them. Some of these atoms shift much faster than others, leading to a broad distribution of relaxation times. These two-level systems are also responsible for the universal low-temperature properties shared by all configurational glasses. The microscopic configurations of the two-level systems, however, have remained a mystery.

The mixed crystal $(\text{KBr})_{1-x}(\text{KCN})_x$ shares many properties with glasses; however, unlike glasses its structure is well understood. The two-level systems in this material are cyanide ions which can reorient by 180° . Because each cyanide has a different set of cyanide neighbors, some can flip over more easily than others: there is a distribution of barrier heights hindering the 180° rotations. The broad distribution of relaxation times exhibited by the dielectric loss measurements comes from random thermal rotations of cyanide ions over these barriers. The time-dependent specific heat (one of the universal low-temperature properties of glasses) comes from quantum tunneling of these ions through the same barriers.

ACKNOWLEDGMENTS

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DISCUSSION OF THE PAPER

A. NAVROTSKY (*Princeton University, Princeton, NJ*): The model for a range of activation energies rests on the binomial distribution of next-nearest neighbor occupancies, that is, a random CN-Br distribution. Do experiments detect either clustering (positive ΔH_{mix}) or ordering (negative ΔH_{mix})? If there is local order, how seriously are the theoretical predictions affected? What would be the stable low-temperature structure, as opposed to glass? [NOTE: This same question is answered in the discussion of the paper by A. Loidl and K. Knorr in this volume—*Ed.*]

SETHNA: The mixed crystal $(\text{KBr})_{1-x}(\text{KCN})_x$ forms good single crystals, which cleave nicely and are optically transparent, throughout the concentration range. This indicates that there is no large-scale inhomogeneity. I naturally will defer to my experimental colleagues for further details, but I know of no measurements that rule out clustering or ordering on a local level. I can say that, although the qualitative features of the theory would survive some clustering, the Gaussian form for the barrier height distribution assumes independent contributions to the barrier height—clustering even on a very local level would distort the distribution. (In some ways this may be evidence against clustering because the Gaussian is observed experimentally.)

Let me also emphasize here that our model is not an explanation from first principles. In order to produce the observed behavior, we assumed that the interactions were ferroelastic, tending to align the cyanides. Although it is true that the high-temperature phase in the pure cyanide is ferroelastic, the microscopic interactions are surely more complex, and frustrated. I have hopes that dilution may reduce the frustration, but certainly a numerical simulation with honest pair interactions is necessary before the Gaussian distribution of barrier heights can be considered understood.

J. T. BENDLER (*General Electric Research and Development Center, Schenectady, NY*): I wish to agree with Dr. Sethna's comment that any nonexponential time-decay law may be represented in terms of a superposition of exponential decay processes, and in the case of the Kohlrausch function, this leads directly to the L'evy stable probability densities

$$e^{-(t/\tau)^\alpha} = \int_0^\infty \rho(\mu, \alpha) e^{-(t/\tau)^\mu} d\mu$$

with $\mu = C/T$ a dimensionless relaxation rate. The inverse transform is an asymmetric stable density of characteristic exponent α (Montroll, E. W. & J. T. Bendler, *J. Stat. Phys.* **34**: 129, 1984). These solutions to the Chapman-Kolmogorov equation were studied by L'evy as generalizations of (or exceptions to) the central limit theorem, and were termed stable because, like the Gaussian, distributions of sums of stable random variables are invariant to addition of further variables. Asymptotically they behave as power laws, and hence have interesting scaling properties, which Mandelbrot has exploited in modeling phenomena with self-similarity (Mandelbrot, B. B., *The Fractal Geometry of Nature*, W. H. Freeman, San Francisco, CA, 1982).

If one interprets the Kohlrausch law as resulting directly from jumps over barrier distributions, it is hard to see why a stable density appears as a natural choice. On the other hand, if the dipole relaxation is dependent on another process, such as defect

diffusion, the defects may hop over a Poisson barrier distribution (Bendler, J. T. & M. F. Schlesinger, *Macromolecules* **18**: 591, 1985), and this, folded into the first-passage time distribution to reach the dipole, generates the Kohlrausch law (Schlesinger, M. F. & E. W. Montroll, *Proc. Natl. Acad. Sci. USA* **81**: 1280, 1984). In polymers, bond isomerizations display activation barriers even in dilute solution so that a Gaussian barrier distribution did not seem appropriate.

Let me emphasize that I agree that the Kohlrausch function does not fit the KBr-KCN dispersion, although the Wagner function does. In this case of low-temperature relaxation, the direct model described by Dr. Sethna is reasonable. It is for the high-temperature (Kohlrausch) behavior that something else is needed.

SETHNA: The fact that the binomial distribution converges to a Gaussian is no accident. It is a special case of the central limit theorem; the sum of many uncorrelated random quantities, if they are "well behaved," will have a Gaussian distribution. In particular, the sum of any number of uncorrelated quantities, each of which has a Gaussian distribution, automatically is Gaussian: the Gaussian distribution is stable. Dr. Bendler points out that there are other stable distributions with longer tails, which have been discussed in the context of $1/f$ noise and the Kohlrausch form for the α -relaxation in glasses. There are two relevant issues I should mention, however, to avoid confusion.

First, as I understand it, these other distributions are sums of random times, whereas the log-normal frequency distribution in $(\text{KBr})_{1-x}(\text{KCN})_x$ comes from sums of random contributions to the barrier height.

Second, at least within our model, there is no question that the contributions to the barrier height are well behaved. The contributions may or may not be correlated (that is, clustering might be important, as Dr. Navrotsky points out), and they may or may not sum to form the total barrier height (that is, the quadrupolar fields add but the barrier, as an eigenvalue difference, may not, as Kanter and Sompolinsky point out). But surely each contribution has a finite range of possible values (no long tail), and the contributions have roughly equal magnitudes; they are well-enough behaved.