Low-Temperature Properties of a Model Glass

Eric R. Grannan, Mohit Randeria,[(a)] and James P. Sethna
Laboratory of Atomic and Solid State Physics, Clark Hall, Cornell University, Ithaca, New York 14853
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We study the low-temperature properties of glasses in a model consisting of elastic dipoles placed randomly in an elastic continuum. We use Monte Carlo annealing to find glassy minimum-energy states and then determine the density of states for small angular oscillations of the dipoles. The coupling of these modes to the phonon strain fields is shown to lead to a frequency-dependent velocity shift and lifetime for the phonons. We find a bump in C/T^3 and a plateau in the thermal conductivity, in quantitative agreement with experimental data for the orientational glass KBr:KCN.

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Glasses have a number of striking universal properties at low temperatures. Experiments below 1 K have been explained by the phenomenological two-level–system model[1] and we shall treat this regime as understood. Between 1 and 20 K, glasses have other equally universal properties which have not yet been satisfactorily explained and which we will address in this paper. The first is an excess specific heat over that predicted by the Debye model, seen most easily as a bump in C/T^3. The second property is a plateau in the thermal conductivity between about 1 and 10 K. In addition, all glasses show a rather broad distribution of relaxation times at temperatures well below the glass transition—a phenomenon which, as we shall argue below, is closely related to the "intermediate"-temperature thermal properties.

We have chosen to study the mixed crystal $KBr_{1-x}KCN_x$ since it is a glassy material whose microscopic structure is well characterized. It exhibits all the usual glassy properties[2] over the range of CN concentrations (x between about 0.1 and 0.6) for which there is no long-range orientational order. Two of us have recently argued[3] that the intermediate-temperature properties in KBr:KCN are due to small-angle oscillations of the cyanides, and that the dielectric-loss peak is due to thermally activated 180° reorientations of these same cyanides. Within the simple approximations needed for the analytic work, we were able to explain the dielectric loss and the thermal conductivity; however, the specific-heat agreement was at best qualitative. In this paper we include the cyanide-cyanide interactions in a simple numerical simulation and are able to explain all of these phenomena using only experimentally measured parameters.

We take as our model[4] elastic dipole defects (the cyanides) place randomly in an isotropic elastic continuum (representing the long-wavelength excitations of the host lattice). The dipoles, characterized by $Q_{ij} = Q_0(\hat{n}_i\hat{n}_j - \frac{1}{3}\delta_{ij})$, where Q_0 is the dipole moment and $\hat{\mathbf{n}}$ a unit vector, interact with one another through their long-range strain fields via the Hamiltonian

$$H = -\frac{1}{2}\sum_{\mathbf{r}_1\neq\mathbf{r}_2} Q_{ij}(\mathbf{r}_1)J_{ijkl}(\mathbf{r}_1-\mathbf{r}_2)Q_{kl}(\mathbf{r}_2). \qquad (1)$$

$J_{ijkl}(\mathbf{r}_1-\mathbf{r}_2)$ is an anisotropic coupling[5] which dies off like $1/r^3$. The energetically favorable arrangement for two dipoles is a "tee," with one dipole parallel and the other perpendicular to the vector connecting them. Simplification of the detailed interactions in this way has conceptual as well as computational advantages. Since the properties we are trying to understand occur in all glasses as well as KBr:KCN, one hopes that details of the interaction do not play a crucial role.

We have studied the ground states, the spectrum of relaxation times, and the density of states (DOS) of the defect Hamiltonian (1) via an extensive numerical simulation. Using the numerically estimated DOS, we have analytically studied the interaction between the excitations of (1) and low-frequency acoustic phonons. This allows us to calculate the low-temperature thermodynamics and transport in our model glass, details of which will be published elsewhere.[6]

In our Monte Carlo simulation[7] of (1) we randomly place elastic dipoles with probability $x=0.5$ on sites of an fcc lattice. (We focus on the case $x=0.5$ for which the most extensive data are available.) Our largest runs have had approximately 250 dipoles. We have used periodic boundary conditions, cutting off the interaction at the size of the box. The initial cooling from ≈ 1000 to 0 K in about 2000 time steps per dipole is followed by a $T=0$ anneal (where we align the dipoles with the local strain field) until the system converges into a local minimum of the energy (a "ground state"). Since the positions of the dipoles are random, and the interaction in Eq. (1) is frustrated, we find that the ground states do not have long-range orientational order. To determine the quantities of interest, we typically average over twenty configurations.

A natural excitation in this sysytem is a 180° reorien-

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tation of a dipole. To determine the distribution of barriers to these reorientations we minimize the energy, constraining the dipole of interest to point in a plane perpendicular to its ground-state orientation. To check that there is simply an effective double well seen by the cyanide, we relax the system using steepest descent to see if it falls into the original ground state. In KBr:KCN the broad spectrum of relaxation times observed in dielectric-loss experiments[8] is fitted very well by the assumption that it is due to independent degrees of freedom that are thermally activated over a Gaussian distribution of barrier heights, $p(V)$. Using the experimental value for the dipole moment Q_0 of the cyanide,[9] we obtain a $p(V)$ that agrees quite well with the dielectric-loss data (see Fig. 1).

The study of the vibrational excitations about the orientational glass ground state proceeds in several steps. First, we calculate the normal modes for the small-angle oscillations of the dipoles (called librational modes). Second, we compute their coupling to long-wavelength phonons. Third, we calculate the complex susceptibility of the librations to the acoustic phonons. The real part of this susceptibility leads to a frequency dependence of the macroscopic elastic constants; the imaginary part gives a scattering rate for the phonons. Fourth, we calculate the specific heat. Fifth, we determine the effect of phonon scattering from librations on the thermal conductivity. Finally, we discuss the universality of the plateau within the context of our model.

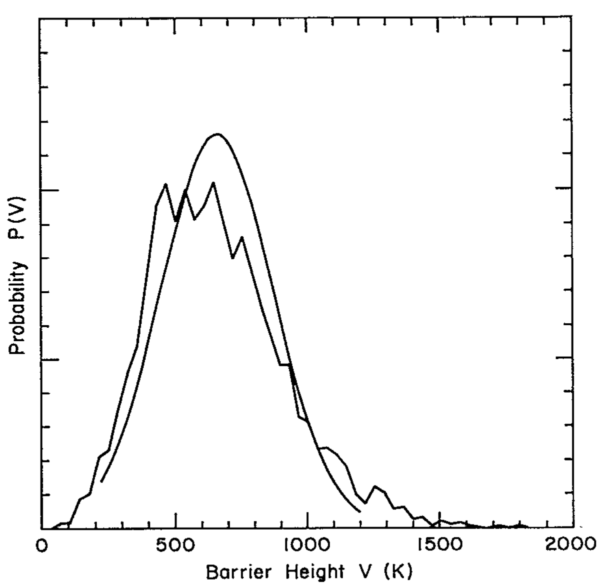

FIG. 1. The smooth curve is a Gaussian distribution of barrier heights, fitted to dielectric-loss data from Ref. 8, in the range probed by experiment. The jagged curve is this distribution obtained from our simulation. The peaks have been scaled to have the same area, since the experimental data are in arbitrary units. The horizontal scale in the simulation is determined by the experimentally known dipole moments and elastic constants. Given the uncertainties in these parameters (Refs. 7 and 9), the excellent agreement in peak position is partially fortuitous.

Since the state we find is a local minimum of the energy, we can diagonalize the dynamical matrix to determine the normal modes of the system. Each dipole has two angular degrees of freedom, ξ_1 and ξ_2. Thus, in a system of N dipoles, there are $2N$ libration modes, with eigenvectors

$$\psi_l = \sum_{\mathbf{x}} \sum_{i=1}^{2} M_{l,\mathbf{x}i} \xi_i(\mathbf{x}),$$

$M_{l,\mathbf{x}i}$ being the amplitude of $\xi_i(\mathbf{x})$ in the lth mode. We should emphasize that the eigenvectors of this highly disordered system are very far from being plane waves. Using the moment of inertia[9] of a defect, we obtain from the corresponding eigenvalue the frequency Ω_l of the lth libration mode. Averaging over different configurations gives us a librational DOS $\rho(\Omega)$, which is peaked at around 10^{13} rad/sec.

The strain field of a phonon with wave vector $\mathbf{k}$ and polarization $\hat{\sigma}$ is given by

$$\epsilon_{ij} = \epsilon_0(\mathbf{k},\hat{\sigma}) \exp(i\mathbf{k}\cdot\mathbf{x})(\hat{k}_i\hat{\sigma}_j + \hat{k}_j\hat{\sigma}_i)/2.$$

The interaction energy between an elastic dipole at $\mathbf{x}$ and a phonon is then

$$\epsilon_{ij}Q_{ij} = \epsilon_0 Q_0[(\hat{\mathbf{n}}\cdot\hat{\mathbf{k}})(\hat{\mathbf{n}}\cdot\hat{\sigma}) - (\hat{\mathbf{k}}\cdot\hat{\sigma})/3]\exp(i\mathbf{k}\cdot\mathbf{x}).$$

We linearize this in the libration amplitude and get a bilinear coupling between librational modes ψ_l and phonons,

$$H_{\text{int}} = -Q_0 \sum_{\mathbf{k},\hat{\sigma},l} A_l \psi_l \epsilon_0(\mathbf{k},\hat{\sigma}), \tag{2}$$

where

$$A_l = \sum_{\mathbf{x},i} \exp(i\mathbf{k}\cdot\mathbf{x}) M_{l,\mathbf{x}i} \frac{\partial}{\partial \xi_i(\mathbf{x})} [\hat{n}_\alpha(\mathbf{x})\, \hat{k}_\alpha \hat{n}_\beta(\mathbf{x}) \hat{\sigma}_\beta]$$

is a dimensionless coupling. In order to simplify the subsequent calculation we determine the average[10] of $|A_l|^2$ over all phonon directions $\hat{\mathbf{k}}$ and polarizations $\hat{\sigma}$. We further average over all libration modes in our simulation with frequency $\Omega_l = \Omega$. This defines $\langle A^2\rangle(\Omega)$, the mean squared coupling of libration modes of frequency Ω to long-wavelength phonons.

The susceptibility $\chi(\omega) = \chi'(\omega) - \chi''(\omega)$ of a harmonic libration mode of frequency Ω coupled to the phonon strain field is given by

$$\chi(\omega) = [(\Omega^2 - \omega^2) + i\omega\Gamma(\omega)]^{-1},$$

$$\Gamma(\omega) = Q_0^2 \langle A^2\rangle \omega^2 / 12\pi I \rho v^5. \tag{3}$$

Here Γ is the width of the resonance, I the moment of inertia of the defect, and ρ and v are the density of the material and the average speed of sound, respectively. The imaginary part of χ leads to a finite phonon lifetime,

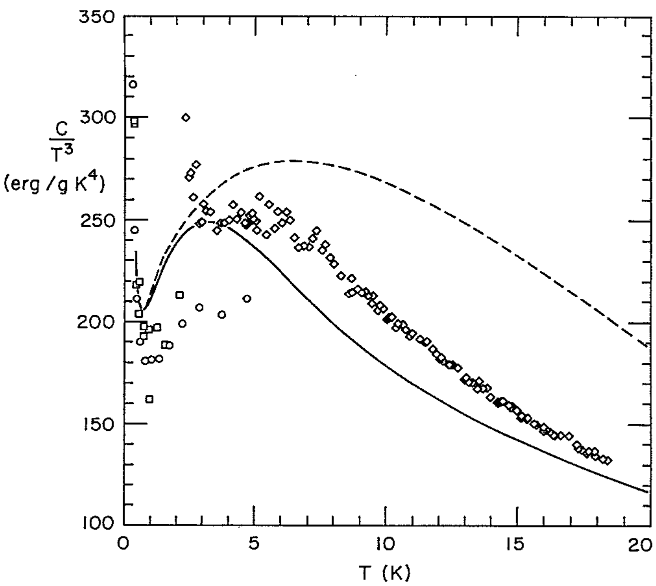

FIG. 2. Specific heat of $KBr_{0.5}KCN_{0.5}$ plotted as C/T^3. The data are from Ref. 2 (squares), Ref. 13 (lozenges), and Ref. 14 (circles). The solid curve is the sum of the contributions from the TLS, acoustic phonons with the modified DOS (see text), and libration modes. The dashed curve differs from the solid one in that it used the Debye density of phonons and also twice the moment of inertia. This shows that the simplest calculation, which does not include the effect of librations on the phonon DOS, is also able to account for the excess specific heat qualitatively.

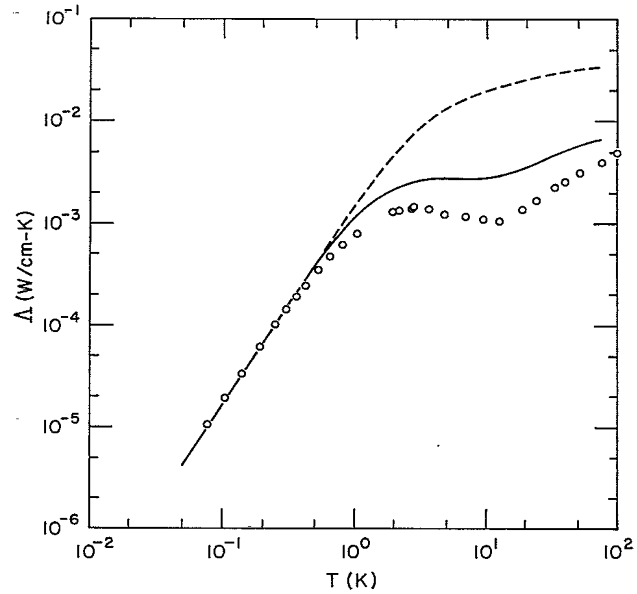

FIG. 3. Thermal conductivity of $KBr_{0.5}KCN_{0.5}$. The dashed curve includes scattering from TLS and the calculated Rayleigh scattering (see Ref. 3). The solid curve, which exhibits the plateau, includes librational scattering. The data are from Ref. 2.

due to resonant scattering[3] from the libration modes, given by

$$\tau^{-1}(\omega)=\frac{Q_0^2\omega}{\rho v^2 I}\int d\Omega\, p(\Omega)\langle A^2\rangle\chi''(\omega). \tag{4}$$

This scattering rate is a highly peaked function of ω reflecting the peak in the librational DOS.

At low frequencies the real part of χ acts to soften the material and reduce the speed of sound,[11] since the dipoles can relax and reduce the stress in the medium. The change in the elastic constants λ and μ are given by

$$\delta C(\omega)=\frac{Q_0^2}{I}\int d\Omega\, p(\Omega)\langle A^2\rangle\chi'(\omega), \tag{5}$$

with $\delta\mu=-\frac{1}{5}\delta C$ and $\delta\lambda=\frac{2}{15}\delta C$.

We calculate the specific heat from the total DOS in the system, given by the sum of the librational and phonon DOS. The density of phonon modes is modified from a Debye DOS due to the frequency-dependent elastic constants. At each frequency we calculate a mean sound velocity and calculate the phonon DOS using

$$g(\omega)=\frac{k^2(\omega)}{2\pi^2}\frac{dk}{d\omega}.$$

For the two-level system we add a low-temperature linear term[1] to the specific heat whose magnitude is fitted to experiment. In a plot of the total specific heat over T^3 we get a bump due to the librational modes in reasonable agreement[12] with experiment (see Fig. 2).

The librations have been assumed to be localized and contribute to thermal resistance[15] by scattering the phonons. The thermal conductivity given by the phonon Boltzmann equation is

$$\Lambda(T)=\int_0^{\omega_D} d\omega\, C_{ph}(\omega,T)v^2\tau(\omega,T), \tag{6}$$

where C_{ph} is the phonon specific heat and ω_D is the Debye frequency. The total scattering rate $1/\tau$ for phonons is computed with use of Matthiesen's rule of adding rates from independent scattering mechanisms. There are various mechanisms which have been traditionally studied in glasses: (1) resonant scattering from the TLS (which gives the T_2 conductivity for $T<1$ K), (2) relaxational scattering from the TLS, and (3) Rayleigh scattering calculated[3] from density fluctuations. These have proved inadequate to explain the plateau in the thermal conductivity.[1,3] When we add the strongly peaked resonant scattering from the libration modes [Eq. (4)], we get a plateau which agrees well with experiment (see Fig. 3). We find that thermal transport in the plateau region is dominated by low-energy phonons ($\hbar\omega \ll k_BT$), as discussed in Ref. 3.

Finally, we have tried a wide range of parameters and noticed that this model always seems to give a plateau. It turns out that the peak in the scattering due to the *li-*

bration modes always has $\omega\tau$ of order 1. To see this, assume that the width of the resonance is much less than that of the librational DOS (an assumption which is only moderately good for KBr:KCN). We can then integrate (4) to get $\tau^{-1}(\omega)=\pi Q_0^2 p(\omega)/6\mu I$. Since the only energy scale in the model is the elastic interaction between dipoles, both the peak frequency and the width of $p(\Omega)$ are proportional to $\bar{\omega}\sim(Q_0^2/\mu I a^3)^{1/2}$, where a is a typical distance between dipoles. The density of modes is proportional to $p(\bar{\omega})\bar{\omega}\sim 1/a^3$. Therefore at the peak of the DOS, $\bar{\omega}\tau(\bar{\omega})\sim 1$ independent of all the parameters, and the scattering is always sufficiently strong to lead to a plateau. As a check, this argument implies that for $KBr_{1-x}KCN_x$ the temperature of the plateau should scale as $\sqrt{x}$, and this seems to be the case[2] for x in the glassy range.

We have shown that we can get a quantitative understanding of the intermediate temperature properties of an orientational glass using a simple model of elastic dipole defects embedded in an elastic continuum.

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[a]Present address: Department of Physics, University of Illinois, 1110 W. Green St., Urbana, IL 61801.

[1]For a review, see *Amorphous Solids: Low Temperature Properties*, edited by W. A. Phillips (Springer-Verlag, Berlin, 1981).

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[3]M. Randeria and J. P. Sethna, to be published; M. Randeria, Ph.D. thesis, Cornell University, 1987 (unpublished).

[4]Our approach is rather different from that taken by K. H. Michel, Phys. Rev. Lett. **57**, 2188 (1986), to describe the orientational freezing within a mean-field theory.

[5]The strain field in an isotropic medium at **r** due to an elastic dipole at the origin is given by $\epsilon_{kl}(\mathbf{r})=J_{ijkl}(\mathbf{r})Q_{ij}(0)$, where

$$J_{ijkl}(\mathbf{r})=(8\pi\mu)^{-1}\{-\tfrac{1}{2}(\delta_{ik}\partial_{jl}+\delta_{il}\partial_{jk}+\delta_{jk}\partial_{il}+\delta_{jl}\partial_{ik})r^{-1}+[(\lambda+\mu)/(\lambda+2\mu)]\partial_{ijkl}(r)\};$$

λ and μ are the Lamé coefficients of the material and we have defined $\partial_{ij}\equiv\partial^2/\partial x_i\,\partial x_j$.

[6]E. R. Grannan, M. Randeria, and J. P. Sethna, to be published.

[7]The elastic constants in our simulation are not determined unambiguously from those of KBr:KCN (see Ref. 2) since we must go from the three elastic constants of a cubic medium to two for an isotropic one. We have used $\lambda=2.0\times10^{11}$ and $\mu=0.61\times10^{11}$ dyne/cm^2 for all the results presented here. We have tried other values and obtained similar results.

[8]N. O. Birge, Y. H. Jeong, S. R. Nagel, S. Bhattacharya, and S. Susman, Phys. Rev. B **30**, 2306 (1984).

[9]Using the shape factor and rotational constant measured by H. Beyeler, Phys. Rev. B **11**, 3078 (1972), we arrive at values $Q_0=1.1$ eV and $I=2.8\times10^{-39}$ g cm^2, respectively. While we use these values in this paper, note that the uncertainty in these quantities is rather large; R. Spitzer, Ph.D. thesis, Cornell University, 1987 (unpublished), estimates $I=6.5\times10^{-39}$ g cm^2.

[10]We assume that the wavelength of the phonons important for thermal transport is much larger than the spatial extent of the librations. This allows us to evaluate the angular averages exactly; see Ref. 6. $\langle A^2\rangle$ is a rather slowly varying function of Ω and simply approximating $\langle A^2\rangle(\Omega)=1$ does not materially alter the results.

[11]Our choice of elastic constants was made to give the measured Debye speed of sound at low frequencies.

[12]In our earlier phenomenological model (Ref. 3) we were unable to obtain quantitative agreement with the specific-heat data. This problem is resolved by our present analysis which takes into account the collective motion of the librations and also the change in the phonon DOS due to relaxation of the dipoles.

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[14]D. Moy, J. N. Dobbs, and A. C. Anderson, Phys. Rev. B **29**, 2160 (1984).

[15]We have so far ignored any direct energy transfer through these modes in calculating the thermal conductivity. Note that although the interacting phonon-librations system is harmonic, it is random and thus has finite thermal conductivity, since the phonon momentum is not conserved in a system without translational symmetry.