Strain interactions and the low-temperature properties of glasses

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It is shown that the anomalous low-temperature specific heat of amorphous materials may arise from strain interactions between two-level tunneling states. The calculation relates the specific heat to the elastic constants of the glass. The result suggests a reason for widely different glasses having very similar low-temperature properties.

The anomalous linear temperature dependence of the specific heat[1,2] C, the T^2 dependence of the thermal conductivity[1,2] κ, and the temperature, frequency, and nonlinear effects[3,4] found in the ultrasonic properties of glassy materials at low temperatures are most successfully explained by a model presented by Anderson, Halperin, and Varma[5] and by Phillips[6] (AHVP). In this model, the unusual properties are due to a broad band of two-level excitations that are attributed to tunneling. It is assumed that some of the units of the glass reside in double-well potentials resulting in ground-state energy splittings of $E = (\epsilon^2 + \Delta^2)^{1/2}$, where ϵ is the asymmetry energy of the double well. The overlap energy due to tunneling, $\Delta \approx (2V/\lambda)e^{-\lambda}$, with $\lambda = d(2mV)^{1/2}/\hbar$, depends on the height V and width $2d$ of the potential barrier and the mass m of the tunneling unit. A specific heat approximately linear in T requires that the probability distribution $p(E)$ of the tunneling states be continuous and nearly constant over at least the range of energies ≈ 0.01–1 K.

It was originally assumed that the tunneling states were essentially isolated. However, it has been shown[7,8] that the strain interactions between tunneling states should be considered in order to understand the relaxation phenomena observed in phonon-echo[4] and "hole-burning"[9] experiments. The relaxation phenomena are believed to occur because of a fluctuating strain field at a given tunneling site caused by thermal transitions between the two levels at other tunneling sites. The transitions occur only if $E \lesssim kT$, and hence only a fraction of the total density of tunneling states contributes to the relaxation phenomena at very low temperatures. Nevertheless, those tunneling sites for which $E > kT$ also contribute static strain fields at neighboring sites that can modify the distribution $p(E)$ and hence influence the thermal properties at low temperature. It is the purpose of this

paper to examine the effect of the static strain interactions on the low-temperature properties of glassy materials. We find that the strain interactions alone can give rise to a continuous energy distribution of tunneling states extending from $E = 0$ even for cases where $p(\epsilon)$, in the absence of interactions, is not continuous and where $p(\epsilon) = 0$ for small ϵ. As an example, the arbitrary $p(\epsilon)$ shown in Fig. 1 by the solid curve is modified to give the dashed distribution when strain interactions of a given strength are included. In addition, we find that the inclusion of the static strain interaction suggests a possible explanation for the similar magnitudes of the thermal properties of widely different glasses.

The physical idea of the static strain interaction is as follows. As in the AHVP model, it is assumed that some of the units of the glass reside in double-well potentials. When the strain interactions are turned on, the strain tensor $\tilde{\lambda}^0$ located at an arbitrary origin 0 interacts with the strain fields arising from all other tunneling units in the
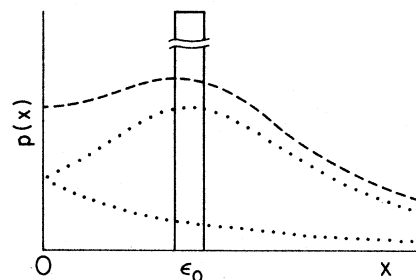

FIG. 1. Distribution of tunneling states $p(x)$ for the case where $p(\epsilon)$ in the absence of strain interactions is a narrow distribution centered at $\epsilon = \epsilon_0$. The dotted lines show the probability distribution of the strain interaction $p(\xi)$ centered about $\xi = \epsilon_0$, with the negative values reflected to $+\xi$. The resultant distribution of tunneling states is shown by the dashed line.

5887

glass. Let ξ be the difference in strain energy between the two possible configurations of the tunneling state. The total energy splitting of the tunneling state is then given by

$$E = [(\epsilon + \xi)^2 + \Delta^2]^{1/2} , \qquad (1)$$

with ξ either positive or negative. The strain energy and its probability distribution $p_1(\xi)$ can be derived from fundamental considerations. The calculation is done using the elastic constants for a cubic crystal, since this mathematically simplifies the stress $\tilde{S}$, strain $\tilde{\lambda}$, and elastic constant tensor $\underline{C}$. For simplicity, the tunneling entities are assumed to be elongated in one direction and to be symmetrical in the perpendicular direction.[10] It is also assumed that the net volume change introduced by the distortion of the tunneling unit is zero. Therefore, the tensor $\tilde{\lambda}$ will have only diagonal components[11-13] and a vanishing trace. The diagonal components $\tilde{\lambda}_i^\alpha$ of the strain tensor at site α having its major axis in the direction of l can be written in the form $\tilde{\lambda}_i^\alpha = \mu(3\delta_{il} - 1)$, where $i = 1$, 2, or 3, and μ is the fractional distortion of the unit due to its nonspherical shape. Since $\tilde{\lambda}^\alpha$ is diagonal, only the diagonal components of the strain are of interest so that $\tilde{\lambda}^0 \underline{C} = \underline{C}\,\tilde{\lambda}^0 = (C_{11} - C_{12})\tilde{\lambda}^0$. The strain energy of the tunneling state is[11,12]

$$W_0 = -v_0 \tilde{\lambda}^0 \underline{C}(\tilde{e}_d^0 + \tilde{e}_p^0) \equiv -\tilde{\lambda}^0 \tilde{S}_0 . \qquad (2)$$

Here $\tilde{e}_d^0 = \sum_\alpha \tilde{e}_d^{0\alpha}$, where $\tilde{e}_d^{0\alpha}$ is the strain at site 0 due to a tunneling state located at site α, $\tilde{e}_p^0$ is the strain at site 0 due to elastic waves (phonons), and v_0 is an effective volume of the tunneling unit. The tensor $\tilde{S}_0$, with units of energy, has only diagonal components. The expression for $(\tilde{e}_d^{0\alpha})_i$ in an isotropic system is[12]

$$(\tilde{e}_d^{0\alpha})_i = \sum_{j=1}^{3} v_0(C_{11} - C_{12})D_{ij}^\alpha \lambda_j^\alpha , \qquad (3)$$

with

$$D_{ij}^\alpha = -\frac{\partial^2}{\partial x_i \partial x_j}\left(\frac{A}{r}\delta_{ij} + B\frac{x_i x_j}{r^3}\right)$$

$$= \frac{A-B}{r^3}\delta_{ij} - \frac{B}{r^3} - \frac{3(A-3B)}{r^5}x_i^2\delta_{ij}$$

$$+ \frac{B(x_i^2 + x_j^2)}{r^5} - \frac{15Bx_i^2 x_j^2}{r^7} , \qquad (4)$$

where $A = (C_{11}^{-1} + C_{44}^{-1})/8\pi$, $B = (C_{44}^{-1} - C_{11}^{-1})/8\pi$, and r is the distance between sites 0 and α, $r^2 = \sum_{i=1}^{3} x_i^2$. Note that D_{ij}^α is proportional to r^{-3}, as can be seen from Eq. (4) if x/r is replaced by a direction cosine. Let the tunneling state $\tilde{\lambda}^0$ have two allowable orientations $\tilde{\lambda}_a^0$ and $\tilde{\lambda}_b^0$, and let the difference in strain energy between the two orientations be ξ. Then

$$\xi = (\tilde{\lambda}_a^0 - \tilde{\lambda}_b^0)\langle\tilde{S}\rangle \qquad (5)$$

where $\langle \ \rangle$ indicates thermal average of the strain field $\tilde{S}$. Examining Eqs. (2)–(4), we find that ξ at site 0 depends on the positions as well as the thermal averages for all other tunneling state tensors $\langle\tilde{\lambda}^\alpha\rangle$. Since each of these quantities is a random variable, ξ will also be a random variable with a probability distribution $p_1(\xi)$. To obtain $p_1(\xi)$, we use a modified Bethe-Peierls-Weiss approximation[14] or mean random-field approximation.[15] The distribution is calculated in a manner analogous to that used for dipolar interactions,[16] except that instead of the dipole-dipole interaction we have a strain interaction. The distribution of the tensorial strain fields will have a number of components. However, because $\tilde{\lambda}_a^0$ and $\tilde{\lambda}_b^0$ are fixed in space and because we are interested only in the "projection" of the strain fields upon $\tilde{\lambda}_a^0 - \tilde{\lambda}_b^0$, we have a one-dimensional (Ising-like) distribution. Only the final result of the low-temperature calculation is presented[17]:

$$p_1(\xi) = \pi^{-1}\delta/(\delta^2 + \xi^2) . \qquad (6)$$

Here $\delta = \frac{4}{3}\pi b(N_d/N)$, where N_d is the number of tunneling sites per unit volume, N is the number of units of the glass per unit volume, and b is the strength of the strain interaction, given by

$$b \simeq (C_{11} - C_{12})^2(C_{44}^{-1} - C_{11}^{-1})(v_0\mu)^2 N/2\pi . \qquad (7)$$

Equation (6) will provide the breadth for the distribution of excitations necessary to explain the low-temperature properties of a glass.

There may be a question as to the validity of a probability distribution of the form $p_1(\xi)$ given in Eq. (6). It has been argued in connection with the spin-glass problem that the probability distribution $p(H)$ of the internal magnetic fields H must tend to zero as H goes to zero.[18] If this argument is valid, the tunneling-states model should also have a "hole" in $p(E)$ at $E = 0$ if strain interactions are present. Since there is good evidence that strain interactions indeed do exist between tunneling sites,[7-9] the distribution of Eq. (6), or that assumed in the origional AHVP model should then contain a hole at $E = 0$, and the calculated low-temperature properties would be modified. Indeed, the apparent distribution $p(E)$ of many glassy materials does vary as[2,19] E^m, $m \gtrsim 0$.

Recognizing that Eq. (6) may be only an approximation to the actual distribution, we proceed to a calculation of some low-temperature properties of glassy materials when strain interactions are present. First, however, we briefly review previous work to provide a comparison. The original AHVP model assumes an energy-independent density of states,[5-7,20] $P(\epsilon, \lambda) = N_d/(\epsilon_{max}\eta) = p(\epsilon)p(\lambda)N_d$, where

$\eta \approx \lambda_{max} - \lambda_{min}$. $P(\epsilon, \lambda)$ depends on the number of tunneling units N_d and the widths of the distributions over ϵ and λ. The energy-independent density of states gives a specific heat proportional to T

$$C = \tfrac{1}{6}\pi^2 k^2 T(N_d/\epsilon_{max}) \tag{8}$$

in the long-time limit, where[7,19] $\eta(t)/\eta_{max} \approx 1$. This density of states also gives a mean free path for a phonon of frequency ω

$$l^{-1} = (\pi\gamma^2/\rho v^3)\omega \tanh(\hbar\omega/2kT)(N_d/\epsilon_{max}\eta), \tag{9}$$

which results in a thermal conductivity varying as T^2. The mean free path depends on the density ρ of the glass, the phonon velocity v, and the strength of the coupling parameter γ between the two-level states and the phonons. The last quantities in parentheses in Eqs. (8) and (9) are both referred to as densities of states. The difference in the densities of states deduced from thermal conductivity and specific-heat experiments indicates[7,19] that η is roughly 10.

The specific heat from our formulation is

$$C = N_d(4kT^2)^{-1} \int_{-\infty}^{+\infty} d\xi \int_0^{\epsilon_{max}} d\epsilon \int_{\lambda_{min}}^{\lambda_{max}} d\lambda \, p_1(\xi)p(\epsilon)p(\lambda)[(\xi+\epsilon)^2 + \Delta^2] \operatorname{sech}^2\left(\frac{[(\xi+\epsilon)^2 + \Delta^2]^{1/2}}{2kT}\right). \tag{10}$$

For an experiment of sufficiently long time duration so that all sites with $\Delta \leq kT$ have had time to relax to thermal equilibrium, the specific heat is approximately

$$C \approx N_d(4kT^2)^{-1} \int_0^{+\infty} dE\, p(\epsilon)$$

$$\times \int_{-\infty}^{+\infty} d\xi\, p_1(\xi)E^2 \operatorname{sech}^2\left(\frac{E}{2kT}\right). \tag{11}$$

In the low-temperature limit, only the values near $E = 0$ contribute to the integral. Thus $p(\epsilon)$ can be replaced by $p(-\xi)$, giving

$$C \approx \frac{N_d\pi^2 k^2 T}{6} \int_{-\infty}^{+\infty} p_1(\xi)p(-\xi)\, d\xi. \tag{12}$$

Using an arbitrary sum of δ functions from which a specific $p(\epsilon)$ could be constructed, namely $p(\epsilon) = (1/n)\sum_{i=1}^n \delta(\epsilon - \epsilon_i)$, for δ of Eq. (6) greater than all ϵ_i we obtain

$$\int_{-\infty}^{+\infty} p_1(\xi)p(-\xi)\, d\xi = \frac{\delta}{\pi n} \sum_{i=1}^n (\delta^2 + \epsilon_i^2)^{-1}$$

$$\leq \frac{3N}{4\pi^2 bN_d}. \tag{13}$$

This is equivalent to replacing the density of states $P(\epsilon, \lambda)$ by $P(\epsilon + \xi, \lambda) = 3N/4\pi^2 b\eta$. Thus the specific heat for this case depends solely on the strength of the strain interaction and is independent of N_d

$$C \leq Nk^2 T/8b. \tag{14}$$

This expression is valid provided the interaction is sufficiently strong, or that the density of tunneling states N_d/N is sufficiently large. The strength of the coupling between phonon and tunneling state can be expressed using the same parameters. From Eq. (5), we obtain an average coupling constant

$$\gamma \equiv \frac{1}{2}\frac{\partial(\epsilon+\xi)}{\partial e_p} = \tfrac{1}{2}v_0(\bar\lambda_a^0 - \bar\lambda_b^0)\underline{C}.$$

Thus, we estimate the magnitude of the coupling to be $\gamma = \tfrac{1}{2}v_0\mu(C_{11} - C_{12})$, which also gives $\gamma^2/b = \tfrac{1}{2}\pi N^{-1}(C_{44}^{-1} - C_{11}^{-1})^{-1}$. Equation (14) can then be rewritten

$$C \leq \tfrac{1}{16}\pi k^2 T(C_{44}^{-1} - C_{11}^{-1})^{-1}\gamma^{-2}. \tag{15}$$

Comparing Eq. (8) with Eq. (15) shows the difference brought about by inclusion of strain interactions. Previously the specific heat was explicitly proportional to the number of tunneling states N_d, whereas in the present description the specific heat is, at least for some forms of $p(\epsilon)$, independent of N_d. The result of Eq. (15) may be compared with published data for vitreous silica. Using $\gamma \approx 1.6$ eV from phonon-echo measurements,[4] the upper bound on the specific heat is[21] $\approx 300\, T$ (erg/cm^{3}K), a factor of 7 larger than obtained experimentally.[2] The magnitude of γ and the density of tunneling states,[2,19] $N_d/N \gtrsim 0.1\%$, should be sufficient for Eq. (15) to be applicable to fused silica. The distortion parameter μ for fused silica, assuming the tunneling units to be SiO_2, would be ≈ 0.1, or similar to values found for impurities in crystals.[10]

Consideration of other properties, such as the thermal conductivity, requires a knowledge of the distribution over Δ in Eq. (1). A broad distribution in Δ is needed to describe the apparent spectrum of relaxation times between tunneling states and the phonon bath. For example, a single, discrete value of Δ would give a thermal conductivity proportional to T^4 for temperatures greater than Δ/k. Although the strain interactions could provide (note added in proof [see, for example, H. U. Beyeler, Phys. Rev. B 11, 3078 (1975)]) the required breadth in Δ, we have so far not carried out the calculations. We therefore, with AHVP, make the ad hoc but reasonable assumption that a distribution over Δ does exist. The trans-

verse phonon mean free path then becomes

$$l^{-1} \lesssim \tfrac{3}{8} v^{-1}(1 - C_{44}/C_{11})^{-1}\eta^{-1}\omega \, \tanh(\hbar\omega/2kT). \quad (16)$$

If the dependence of $p(E)$ on Δ is similar for different amorphous materials, the mean phonon lifetime $\tau = l/v$ would be nearly independent of material parameters as, in fact, is observed experimentally.

If there does exist a broad spectrum in Δ, the magnitude of the specific heat in the AHVP (or present) calculation should depend on the duration of the measurement.[5-7] The recent "fast" heat-capacity measurements of Kummer et al.[22] suggest that such a time dependence may not exist. However, there is some question of interpretation at the lowest temperatures (where ballistic phonons and the Debye contribution are not masking the sought-for effect). First, the phonons to which the tunneling states relax in that experiment were initially an order of magnitude higher in (effective) temperature than the ambient temperature.[22] Second, the effect of cross relaxation in enhancing the flow of heat between the phonons and the complete set of tunneling states was not considered. The calculations of Ref. 7 do reflect on the mechanism of cross relation via strain interactions to those tunneling states that interact strongly with phonons. However, it appears to us that the magnitude of cross relaxation would not be sufficient to explain the data of Kummer et al. In brief, there remain some important questions concerning the distribution in Δ.

In conclusion, we review the description of a glass (i) without and (ii) with strain interactions. Both assume a set of two-level tunneling states. For (i) the ad hoc assumption is made that $p(\epsilon)$ is constant for small ϵ. Both C and κ are proportional to N_d, which might be expected to vary appreciably from material to material. For (ii) the final $p(E)$ is essentially constant at small E even for $p(\epsilon)$ (in the absence of strain interactions) zero for small ϵ. Both C and κ are approximately independent of N_d for a range of concentrations N_d/N and for a variety of $p(\epsilon)$. Also, the upper limit of C for vitreous silica, using no adjustable parameters, lies within an order of magnitude of the measured value.[23] In brief, these low-temperature properties of glasses can be explained by considering the energy distribution caused by strain interactions alone. It is possible, of course, that some other mechanism also contributes to the distribution in $p(E)$.

ACKNOWLEDGMENTS

[1] R. C. Zeller and R. O. Pohl, Phys. Rev. B 4, 2029, (1971).

[2] The precise temperature dependences vary from glass to glass. See J. C. Lasjaunias, A. Ravex, M. Vandorpe, and S. Hunklinger, Solid State Commun. 17, 1045 (1975), and papers cited therein.

[3] S. Hunklinger and W. Arnold, in Physical Acoustics, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1976), Vol. 12, p. 155, and papers cited therein.

[4] B. Golding and J. E. Graebner, Phys. Rev. Lett. 37, 852 (1976).

[5] P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. 25, 1 (1972).

[6] W. A. Phillips, J. Low Temp. Phys. 7, 351 (1972).

[7] J. L. Black and B. I. Halperin, Phys. Rev. B 16, 2879 (1977), and papers cited therein.

[8] P. Hu and L. R. Walker, Solid State Commun. 24, 813 (1977).

[9] W. Arnold, C. Martinon, and S. Hunklinger, J. Phys. (Paris) 39, C6-961 (1978).

[10] We suggest this as an appropriate abstraction of any asymmetric tunneling site. Such a description was discussed previously for CN⁻ dissolved in alkali halides by N. E. Beyer and H. S. Sack, Phys. Status Solidi 30, 579 (1968). For CN⁻ in KC1, μ is approximately 0.15.

[11] J. D. Eshelby, in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic, New York, 1956),

Vol. 3, p. 79.

[12] K. C. Lie, Ph.D. thesis (University of Illinois, 1967) (unpublished).

[13] M. B. Grant and M. V. Klein (private communication). These authors also derived Eq. 4 for the strain interaction between two strain tensors.

[14] T. Plefka, J. Phys. F 6, L327 (1976); P. Shukla and M. W. Klein (unpublished). When the range of the interaction between the tunneling states approaches z, where z is the number of the effective neighbors, and the strength of the interaction is proportional to z^{-1}, the mean random-field distribution is equivalent to that obtained from the Bethe-Peierls-Weiss approximation for a random system when $z \rightarrow \infty$.

[15] M. W. Klein, Phys. Rev. 173, 552 (1968).

[16] M. W. Klein, C. Held, and E. Zuroff, Phys. Rev. B 13, 3576 (1976).

[17] M. W. Klein, Phys. Rev. B 14, 5008 (1976). For $N_d/N \gtrsim 5\%$ $p(\xi)$ becomes Gaussian with width proportional to $N_d^{1/2}$. Similarly the wings of $p(\xi)$ become Gaussian-like even for small N_d/N.

[18] S. Kirkpatrick and C. M. Varma, Solid State Commun. 25, 821 (1978), and papers cited therein.

[19] T. L. Smith, P. J. Anthony, and A. C. Anderson, Phys. Rev. B 17, 4997 (1978).

[20] J. Jäckle, Z. Phys. 257, 212 (1972).

[21] The parameter b of Eq. 7 corresponds to the interaction strength J_{ij} of Ref. 7 for a nearest-neighbor position. The two parameters are numerically equal for

SiO_2 using $\Delta/E \approx 0.5$ and $r_{ij} \approx N^{-1/3}$ for the nearest-neighbor distance.

[22]R. B. Kummer, R. C. Dynes, and V. Narayanamurti, Phys. Rev. Lett. 40, 1187 (1978).

[23]The discussion thus far has considered only a constant density of states $P(E)$ resulting from strong strain interactions. Experimental data of Refs. 2 and 19 indicate that $P(E)$ actually increases with increasing E. An increase with E can be a natural consequence of the present model (see Fig. 1), but the precise behavior does depend on both $p(\epsilon)$ and δ.