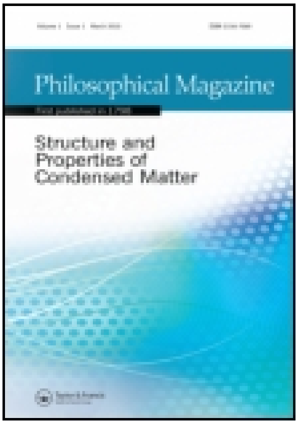


Philosophical Magazine
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tphm19

# Anomalous low-temperature thermal properties of glasses and spin glasses

P. w. Anderson [a] [b], B. I. Halperin [a] & c. M. Varma [a]
[a] Bell Laboratories, Murray Hill, New Jersey, 07974
[b] Cavendish Laboratory, Cambridge, England

To cite this article: P. w. Anderson , B. I. Halperin & c. M. Varma (1972): Anomalous low-temperature thermal properties of glasses and spin glasses, Philosophical Magazine, 25:1, 1-9

To link to this article: http://dx.doi.org/10.1080/14786437208229210

THE

PHILOSOPHICAL MAGAZINE

A JOURNAL OF THEORETICAL, EXPERIMENTAL
AND APPLIED PHYSICS

First Published in 1798

[EIGHTH SERIES—VOL. 25]

# Anomalous Low-temperature Thermal Properties of Glasses and Spin Glasses

By P. W. ANDERSON†, B. I. HALPERIN and C. M. VARMA
Bell Laboratories, Murray Hill, New Jersey 07974

[Received 27 September 1971]

## ABSTRACT

We show that a linear specific heat at low temperatures for glass follows naturally from general considerations on the glassy state. From the same considerations we obtain the experimentally observed anomalous low-temperature thermal conductivity, and we predict an ultrasonic attenuation which increases at low temperatures. Possible relationships with the linear specific heat in magnetic impurity systems are pointed out. We suggest experimental study of the relaxation of thermal and other properties.

## § 1. INTRODUCTION

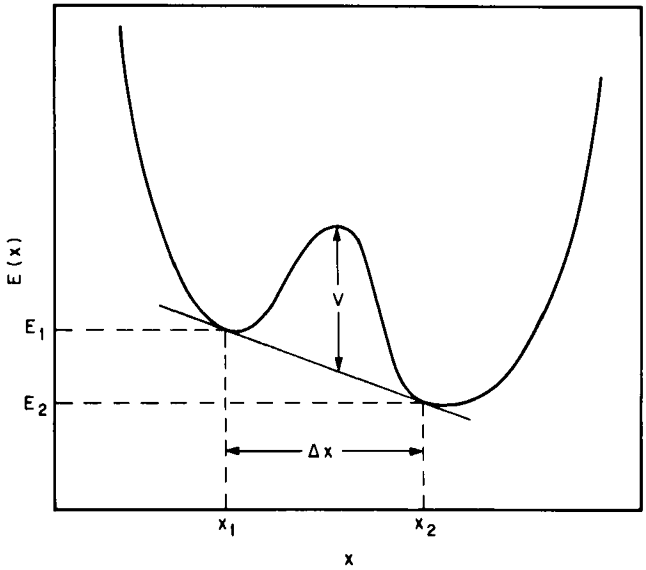
Zeller and Pohl (1971) have recently discovered a contribution to the low-temperature specific heat varying linearly with temperature in a variety of glasses. It is remarkable that a linear specific heat is observed (Anderson 1970) also in 'spin glasses'; i.e. alloys like Cu–Mn where a random configuration of spins condenses at low temperature. We propose here an explanation for the linear specific heat, based on a statistical distribution of localized 'tunnelling levels', which suggests that a linear specific heat should be a universal feature of glass systems at low temperatures. Our model also predicts the observed anomalous thermal conductivity, and predicts an ultrasonic attenuation which increases at low temperatures.

## § 2. THE MODEL

The central hypothesis of our model is that in any glass system there should be a certain number of atoms (or groups of atoms) which can sit more or less equally well in two equilibrium positions. In terms of an

---

† Also at Cavendish Laboratory, Cambridge, England.



Energy $E$ of the system as a function of a generalized coordinate $x$, measuring position along a line connecting two nearby local minima of $E$.

appropriate position coordinate $x$ for such an atom, or set of atoms, the energy $E$ $(x)$ will then have two local minima, separated by a barrier, as shown in the figure. The figure is a section of the $3N$-dimensional configuration space along the coordinate connecting two such local minima. The atoms of interest for the specific heat will be those for which the energy barrier is sufficiently great so that resonant tunnelling between the two local minima does not occur, but sufficiently small so that tunnelling between the two levels can take place and thermal equilibration can occur during the time span of the specific heat experiment (say $10^{-10}$ sec $< t < 10^3$ sec). Of the atoms with barriers in the acceptable range, those contributing to the specific heat at a low temperature $T$ ($T$ is of the order of 0·1–10°K) will be atoms for which the energies of the two local minima are accidentally degenerate to within an amount of order $kT$. We argue that this must lead to a specific heat proportional to $T$. In general, the energies of the two levels will be more or less random quantities, dependent on such factors as the particular configuration of atoms surrounding the two minima, on local strains, etc. Inasmuch as the positions of the two minima are spatially separated, we would expect that the probability distribution of the energy difference $\Delta E$ between the two levels will vary on the scale of these random energies (perhaps 0·1 ev to 1 ev in a typical glass) *and will be smooth on the scale of* $kT$. In particular, $n(\Delta E)$, the density of levels per unit volume and per unit $\Delta E$, with energy difference $\Delta E$ and with tunnelling time in the acceptable range, should be non-zero and continuous in the vicinity of $\Delta E = 0$. The density of such levels with

$\Delta E < kT$ is then proportional to $T$, leading to an entropy and a specific heat likewise proportional to $T$. The specific heat is given, in fact, by

$$C = k \int_0^\infty n(\Delta E) \times \left\{ \left( \frac{\Delta E}{kT} \right)^2 \frac{\exp(-\Delta E/kT)}{[1+\exp(-\Delta E/kT)]^2} \right\} d(\Delta E)$$

$$\sim \frac{\pi^2}{6} k^2 T n(0). \qquad (1)$$

To make our argument clearer, let us consider a model Hamiltonian which describes the two-level system consisting of the ground states in the two local energy wells. We write

$$H = \begin{pmatrix} E_1 + \hbar\omega_1 & \hbar\omega_0 \exp(-\lambda) \\ \hbar\omega_0 \exp(-\lambda) & E_2 + \hbar\omega_2 \end{pmatrix}, \qquad (2)$$

where $E_1$ and $E_2$ are the energies of the local minima in the potential energy $E(x)$, $\hbar\omega_1$ and $\hbar\omega_2$ are the energies of zero-point motion about these minima, $\hbar\omega_0$ is an energy of the order of the zero-point energy, and the factor $\exp(-\lambda)$ represents the overlap between the wave functions for the two potential wells. For the potential of the figure we have

$$\lambda \approx \tfrac{1}{2} \left( \frac{2mV}{\hbar^2} \right)^{1/2} \Delta x, \qquad (3)$$

where $m$ is the mass of the tunnelling atom or group of atoms. Let

$$\Delta E = E_1 + \hbar\omega_1 - E_2 - \hbar\omega_2 \qquad (4)$$

be the difference between the two diagonal elements of $H$. (We shall arbitrarily choose the indices 1 and 2 so that $\Delta E \geqslant 0$.) The correction to the eigenvalues of the Hamiltonian due to the *off-diagonal* element will be negligible provided

$$\lambda > \lambda_{\min} \equiv \ln(2\hbar\omega_0/\Delta E). \qquad (5)$$

If condition (5) is satisfied, then transitions between the two energy levels can occur only by a process such as phonon-assisted tunnelling, with emission or absorption of a phonon necessary to conserve energy. The rate of such transitions can be written roughly in the form

$$\Gamma \approx \Gamma_0 \exp(-2\lambda), \qquad (6)$$

where we estimate $\Gamma_0$ to be of the order of $10^{12}\,\text{sec}^{-1}$. A more accurate form for $\Gamma$ will be discussed below. The condition $\Gamma^{-1} < t$ can be written

$$\lambda < \lambda_{\max} \equiv \tfrac{1}{2} \ln(\Gamma_0 t). \qquad (7)$$

Since we have a situation where $\Gamma_0$ is of the order of $\omega_0$, and $t \gg \hbar\Gamma_0^{-1/2}\Delta E^{-1/2}$, there will be a substantial range of $\lambda$ in the acceptable region between $\lambda_{\min}$ and $\lambda_{\max}$. Furthermore, the limits (5) and (7) of this region depend only weakly (i.e. logarithmically) on the value of $\Delta E$ when $\Delta E \approx kT$, so that this range may be considered constant for our purposes. If $m$ is the mass of an oxygen atom, and $\Delta x \approx 1$ Å, then the acceptable values of $V$ will be $V \lesssim 0{\cdot}2$ ev. If, as is more likely, a whole $SiO_4$ tetrahedron must move, $V$ may have to be even smaller ; this is the most delicate point in the argument. Since the qualitative form of the figure requires that $|\Delta E| \lesssim V$, this implies that the density of levels $n(\Delta E)$ described by our model with $\lambda$ in the 'acceptable range' should actually vary on the scale of 0·1 ev, as it must go to zero for $|\Delta E| > 0{\cdot}1$ ev. This is however quite consistent with our previous assertion, that $n(\Delta E)$ is constant on the scale of $kT$.

It should be emphasized that the density of levels with $\lambda$ in the 'acceptable range' is much smaller than the total density of modes with level splitting $\Delta E$. There are a vast number of modes having small $\Delta E$ which are inaccessible because their energy barriers are too big for tunnelling to occur, or because they require the cooperative motion of too many atoms. The fact that glasses are in a metastable state to begin with implies that there are large numbers of states with arbitrary $\Delta E$ (both positive and negative relative to the occupied state of the system) which are only inaccessible because they are separated from the occupied states by large energy barriers.

We have experimental information about the total number of roughly equivalent *inaccessible* states. Ancient but, apparently, reliable measurements (Gutzow 1926 ; Simon and Lange 1926) of the zero-point entropy of fused $SiO_2$ and of glycerol are available. In the case of $SiO_2$ these suggest that there are of the order of $2^N$ metastable 'ground' configurations, where $N$ is the number of Si tetrahedra. Similarly, glycerol, which has about three or four rigid molecular groups capable of relative rotation, also has of the order of two configurations per rigid group.

The difference in energy between these configurations must be less than the glass transition temperature $T_g$, since at that temperature the glass is still fluid and all configurations are available to it. That is about 0·1 ev. Again it would seem reasonable that the energy differences are otherwise random. Our point of view would be that the states important in the anomalous specific heat are simply the tail of a continuous distribution of alternative states which includes those which give the zero-point entropy, a 'tail' in the sense that there must be a continuous distribution of barrier sizes $V$, and these are the states with relatively low barriers.

If the observed linear spacific heat of fused silica is interpreted according to eqn. (1), one finds that $n(0) \approx 0{\cdot}04$ states per ev per $SiO_2$ group. The total number of level pairs with $\Delta E \leqslant 0{\cdot}1$ ev, and barrier heights in the acceptable range, is thus estimated to be approximately 1/250 of the total number of $SiO_2$ groups. This seems to be a reasonable number, consistent with the information available.

It is not easy to speculate meaningfully on the distribution of the barriers. Most of the simple models we have tried tend to suggest a predominance of rather high barriers ; but the observations, as discussed above, suggest rather that there is a very broad distribution of barrier heights, with low ones as probable as high ones. That is, we require that of the order of 10% of the barriers be ~ 0·2 ev or less, where we would guess that the average barrier involves breaking one or more bonds, ~ several ev. Why the statistics of these barriers is so uniform over a wide spectrum of types of glass remains a mystery. Various situations in which $V$ and $\Delta x$ are sufficiently small can be imagined. For instance, all of the crystalline forms of quartz exhibit 'high–low' transitions in which oxygen bridges between Si tetrahedra bend away from a linear Si–O–Si configuration. Apparently in all crystalline phases the oxygens have a double-minimum potential and the same may be likely for the glass.

The important modes are likely to be quite different in different glasses, and the experimental observation that the magnitude of the linear specific heat is roughly constant in a wide variety of glasses, seems somewhat surprising in the context of this model. The point may be that it is accessibility rather than anything else which determines $n(0)$.

One important consequence of the proposed explanation of the linear specific heat in glasses is the implication that the observed specific heat should depend roughly logarithmically on the length of time over which the observation is made. This feature should be subject to experimental tests.

If the transition between the two levels of the figure involves a net motion of charge, as would be the case of the motion of a single oxygen atom in fused silica, then the modes under consideration should also give a contribution to the dielectric relaxation of the glass which would depend roughly logarithmically on the length of time of observation. Since there appears to be no such contribution to the dielectric response, we assume that the motions responsible for the specific heat involve the rigid rotation or displacement of neutral $SiO_4$ tetrahedra.

## § 3. THERMAL TRANSPORT

Zeller and Pohl (1971) have also found an anomaly in the low-temperature thermal conductivity of glasses. The thermal conductivity varies as $T^2$ which is interpreted as a mean free path for phonons going as $\omega^{-1}$ instead of the $\omega^{-4}$ expected for disordered systems (and which is seen at higher temperatures). It is natural to inquire whether this can be explained in terms of resonant scattering of the acoustic phonons off the same modes which we are invoking to explain the specific heat. The condition that the level pair have a large scattering cross section for a relatively wide frequency range about the resonance $\omega = \Delta E/\hbar$ is that $\lambda$ be approximately equal to the $\lambda_{\min}$ defined in (5), so that there be large overlap between the wavefunctions for the two levels of the model. Thus resonant scattering of phonons will only occur for a small fraction of those configurations which contribute to the linear specific heat. Also, several of the approximations made above will have to be refined when $\lambda \approx \lambda_{\min}$.

The mean free path for a phonon with $\hbar\omega \geqslant kT$ is given by

$$l = (\sigma\nu)^{-1}, \qquad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

where $\sigma$ is the scattering cross section and $\nu$ the number of resonant scatterers per unit volume. For resonant scattering

$$\sigma = 4\pi c^2/\omega^2, \quad \ldots\ldots\ldots\ldots \quad (9)$$

and the frequency $\omega$ of the phonon must coincide with the energy splitting of the two-level systems to within the level width, $\Gamma$.

The density of resonant scatterers will then be given by

$$\nu \approx n(0)\langle\Gamma\rangle, \quad \ldots\ldots\ldots \quad (10)$$

where $\langle\Gamma\rangle$ is the average value of $\Gamma$ for the class of levels we have considered above.

To estimate the width of the two-level system, let us assume that the decay of the upper state occurs with the emission of a longitudinal acoustic phonon, and that the coupling to the phonon can be described as a change in the unperturbed energies $E_1$ and $E_2$, entering the diagonal part of (2), proportional to the local dilation. Then the one-phonon matrix element for transitions between the two eigenstates of (2) can be written

$$M \approx B\left(\frac{\hbar\omega}{2\rho Vc^2}\right)^{1/2}\frac{\omega_0 \exp(-\lambda)}{\epsilon}, \quad \ldots\ldots \quad (11)$$

where $\omega$ is the phonon frequency, $\rho$ is the mass density, $V$ is the volume of the system, $B$ is the difference in the deformation potential constants for the two unperturbed levels, and

$$\hbar\epsilon = [(\Delta E)^2 + [2\hbar\omega_0 \exp(-\lambda)]^2]^{1/2} \quad \ldots\ldots \quad (12)$$

is the actual difference between the two energy eigenvalues of (2). The width of the upper level, due to the spontaneous emission of a phonon of frequency $\omega \approx \epsilon$, is given by

$$\Gamma \approx \frac{3\pi B^2}{Mc^2}\left(\frac{\omega^3}{{\omega_{\mathrm{D}}}^3}\right)\frac{{\omega_0}^2 \exp(-2\lambda)}{\omega^2}, \quad \ldots\ldots \quad (13)$$

where $M$ is the mass per unit cell, and $\omega_{\mathrm{D}}$ the Debye frequency. We must calculate the average value of $\Gamma$ over the ensemble of levels with varying values of $\lambda$, $\Delta E$, $\omega_0$, and $B$, consistent with the condition that $\epsilon = \omega$:

$$\langle\Gamma\rangle = \int p(\Delta E, \omega_0, \lambda, B)\Gamma\delta(\omega - \epsilon)\, dB\, d\lambda\, d\omega_0\, d\Delta E, \quad \ldots \quad (14)$$

where $p$ represents the probability distribution for the varying values of $\Delta E$, $\omega_0$, $\lambda$ and $B$ over the ensemble of levels considered, normalized so that $\int p(0, \omega_0, \lambda, B)\, dB\, d\lambda\, d\omega_0 = 1$. Integrating with respect to $\Delta E$, we find

$$\langle\Gamma\rangle = \int dB\, d\omega_0 \int_{\lambda_{\min}}^{\infty} d\lambda \frac{3\pi B^2}{Mc^2}\frac{\omega^3}{{\omega_{\mathrm{D}}}^3}\frac{{\omega^2}_0 \exp(-2\lambda)}{\omega^2}$$

$$\times \frac{\omega}{[\omega^2 - 4{\omega_0}^2 \exp(-2\lambda)]^{1/2}} p(\Delta E, \omega_0, \lambda, B)\Big|_{\Delta E = \hbar[\omega^2 - 4{\omega_0}^2 \exp(-2\lambda)]^{1/2}}, \quad (15)$$

where $\lambda_{\min}$ is now given by

$$\lambda_{\min} = \ln(2\omega_0/\omega). \qquad (16)$$

(Cf. eqn. (5) above.)

We shall assume that $\omega$ is sufficiently small, and that the distribution of $\omega_0$ is cut off sufficiently rapidly, so that $\omega \ll \omega_0$, for essentially all the levels under consideration. In this case, if we assume $p$ to be a reasonably slowly varying function of its variables, we may carry out the $\lambda$ integration in (15) and write

$$\langle \Gamma \rangle \approx \frac{\pi}{4}\frac{\omega^3}{\omega_D{}^3}\left[\int d\omega_0\, dB\, p(0, \omega_0, \lambda_{\min}, B)\frac{3\pi B^2}{Mc^2}\right]. \qquad (17)$$

The quantity in square brackets, which we shall denote by $D$, depends on $\omega$ only logarithmically, through the variable $\lambda_{\min}$. Combining our previous equations we then find

$$l \approx \frac{4}{\pi}\frac{\omega_0{}^3}{n(0)D}\frac{1}{4\pi c^2}\omega^{-1}, \qquad (18)$$

which has essentially the experimentally observed frequency-dependence. An estimate for $D$ may be obtained if we guess

$$D \approx \frac{1}{\lambda_{\max}}\left(\frac{\lambda_{\min}}{\lambda_{\max}}\right)^{\alpha}\frac{3\pi \bar{B}^2}{Mc^2}, \qquad (19)$$

where $\alpha$ is some unknown exponent describing the $\lambda$-dependence of $p$, and $\bar{B}$ is a typical value of the deformation potential constant. (The dependence of $D$ on $\lambda_{\max}$ must be cancelled by the dependence of $n(0)$ on this quantity.) If we assume $\bar{B} \approx 1$ ev, $\alpha = 1$, $\lambda_{\min} \approx 5$, $\lambda_{\max} \approx 20$, and use the value of $n(0)$, $M$(60 A.U.) and $\omega_D$ (300°K) appropriate to fused silica, we can get the correct order of magnitude for the mean free path, namely $l \approx 10^{-3}$ cm at 1°K.

## § 4. ULTRASONIC ATTENUATION

The formula for $l$ given by eqn. (18) is independent of temperature, and is valid for phonons with $\hbar\omega \gtrsim kT$. For more general values of $\hbar\omega/kT$, we find a decay length

$$l = \frac{4}{\pi}\frac{\omega_D{}^3}{n(0)D}\frac{1}{4\pi c^2}\omega^{-1}\coth\frac{\hbar\omega}{2kT}. \qquad (20)$$

If one thinks of the decay process as a resonant absorption of the acoustic energy by the two-level system, then the factor ($\coth \hbar\omega/2kT$) represents the decrease in the absorption because of the equalization of the occupation of the two levels. Thus for phonons of frequency small compared to $kT$, we find an ultrasonic attenuation proportional to $\omega^2/T$. For fixed frequency, this increases as $T$ is decreased.

If the frequency is decreased sufficiently, at fixed temperature, one should eventually reach a regime where relaxation processes are more important than resonant absorption of the phonon energy, and eqn. (20) will no longer apply.

## § 5. SPIN GLASSES

Marshall (1960), Herring (private communication) and Klein and Brout (1963) have pointed out that the linear specific heat in spin glasses follows naturally from two assumptions. The first is highly plausible : that the distribution of local magnetic fields on the spins has a width linear in the concentration of spins, of order $T_N$, the 'glass transition temperature'. The second has never been adequately justified : that only one component $H^z$ of the local field is important, and (by similar handwaving arguments to ours about $E$) that there is no singularity in its distribution at $H^z{}_{\mathrm{loc}}=0$, so that there is a constant $(dN/dH)|_{H_z=0}$.

But undoubtedly the other components of $H_{\mathrm{loc}}$, which provide off-diagonal matrix elements connecting the states of different $M_z$, are not to be neglected ; if they have the same distribution as $H_z$, the density of states →0 as $H \to 0$ and we get no linear specific heat. We can make contact with our present point of view, however, by noting that the proper starting point for understanding the spin glass is not so much the energy levels of a spin in some fixed random magnetic field, but rather the classical potential energy as a function of the simultaneously specified orientations of all of the spins. The metastable states of the spin glass will then correspond to local minima in the energy of the spin configuration. The primary effect of the quantum mechanical uncertainty principle, which forbids exact knowledge of the orientation of a spin, is to cause a zero point motion of the spin system about the local energy minimum. Tunnelling between one local minimum and another can occur only if the separation in configuration space is not too great, or if the transition involves the rearrangement of a small number of spins. The energy diagram of the figure can be applied to such a rearrangement if we interpret $x$ as a generalized coordinate appropriate to the simultaneous motion of a small number of spins. The remainder of the reasoning, leading to the linear specific heat, should go through unchanged in the present case. Note that the linear specific heat of the spin glass is again predicted to have roughly logarithmic dependence on the observation time. Note also that if the interaction between the spins varies as the inverse cube of the distance between the spins, the specific heat will remain independent of concentration of the spins, provided that the time of experimental observation, as well as the rate of cooling through the 'glass transition', are appropriately scaled. In particular, if the concentration is increased by a factor of $\nu$, the system will be isomorphic to the original if we scale temperatures, frequencies, tunnelling rates, and energies per spin by the same factor $\nu$.

## ACKNOWLEDGMENTS

The authors would like to acknowledge enlightening conversations with J. Krumhansl, J. Wilkins, D. Turnbull, S. Hunklinger, T. Geballe, and A. Leggett. Professor Leggett, in particular, has independently proposed explanations which are similar to those presented here.

R. J. Rollefson has observed a linear specific heat at low temperatures in crystalline NaBr : F, which he has explained in terms of the tunnelling of a fluoride impurity ion between a group of localized levels whose degeneracy is split by random strains. (References to various other calculations of the effects of tunnelling levels on the properties of imperfect crystals may be found in Rollefson's thesis (1970) and in a review article by Narayanamurti and Pohl (1970).) A suggestion that similar kinds of defect states could be responsible for the anomalous thermal properties of glasses is also contained in Zeller and Pohl (1971 a, b).

## REFERENCES

ANDERSON, P. W., 1970, *Mater. Res. Bull.*, **5,** 549.
GUTZOW, I., 1926, *Z. phys. Chem.*, **221,** 153.
HERRING, C. (private communication).
KLEIN, M. W., and BROUT, R., 1963, *Phys. Rev.*, **132,** 2412.
MARSHALL, W., 1960, *Phys. Rev.*, **118,** 1519.
NARAYANAMURTI, V., and POHL, R. O., 1970, *Rev. mod. Phys.*, **42,** 201.
ROLLEFSON, R. J., 1970, Ph.D. Thesis, Cornell Materials Science Center Report No. 1382.
SIMON, F., and LANGE, F., 1926, *Z. Phys.*, **38,** 227.
STEPHEN, R. B., ZELLER, R. C., and POHL, R. O., 1971, *Bull. Am. phys. Soc.*, **16,** 377.
ZELLER, R. C., and POHL, R. O., 1971 a, *Phys. Rev.* (to be published) ; 1971 b, *Bull. Am. phys. Soc.*, **16,** 377.