

Low-Temperature Specific Heat and Thermal Conductivity of Noncrystalline Solids

Peter Fulde

Institut Max von Laue-Paul Langevin, 8046 Garching, Germany,

and

Herbert Wagner

Institut für Festkörperforschung, 517 Jülich, Germany, and Universität zu Köln, Köln, Germany

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We propose a semiphenomenological model for the elementary phonon excitations in noncrystalline solids. This model can explain the low-temperature anomalies in the specific heat and thermal conductivity of amorphous materials which have been found in recent experiments.

In a recent series of experiments Zeller and Pohl¹ and, subsequently, Maynard² and Leadbetter³ have investigated the specific heat C and the thermal conductivity κ of various amorphous materials below 1°K. The specific heat was found to exceed the expected Debye T^3 contribution at the lowest temperatures attained (0.1°K) by as much as 2 orders of magnitude. The thermal conductivity was found to differ from the normal T^3 dependence observed in crystalline solids in the same temperature range. The experimental results indicate that the anomalous behavior of C and κ is independent of structural details of a particular amorphous sample and thus seems to be a general feature of the amorphous state.

The purpose of this note is to suggest a model for the low-lying excitations in a noncrystalline solid that provides an explanation of these data.

One of our basic assumptions about the elementary excitations is contained in the following form of the propagator for low-frequency phonons:

$$D^{-1}(q, z) = z^2 - \omega_0^2(q)[1 - igz\tau/(1 - iz\tau)], \quad (1)$$

with $\text{Im}z > 0$. The function $\omega_0(q)$ describes the phonon dispersion. For small enough values of q we may set $\omega_0(q) = v_0 q$, where v_0 denotes the average acoustic phonon velocity. The third term on the right-hand side of Eq. (1) is similar to a Drude-Maxwell form⁴ for a frequency-dependent bulk viscosity with a relaxation time τ . In our case τ describes the time scale for some kind of structural relaxation, i.e., the time it takes for the random network of molecules in the amorphous solid to adjust itself to the local variations in stress which are caused by the sound waves. Generally, τ is expected to be temperature dependent and to increase as $T \rightarrow 0$. The factor $g > 0$ in Eq. (1) is assumed to be temperature independent but will, in general, depend on

q . It will be seen later that $g(q)$ for $q \rightarrow 0$ must approach a finite value g_0 which determines the thermal conductivity for $T \rightarrow 0$.

The spectral density of states, $-\text{Im}D(q, \omega + i0) \equiv -\text{Im}D_+$, obtained from Eq. (1), is a Lorentzian peaked at frequencies $\omega = v_0 q$ if $\omega\tau \ll 1$. The above form of the phonon spectrum is certainly not specific to the amorphous state. In order to specify the model further for this latter case, we note that in these materials there is no one-to-one correspondence between phonons and the normal modes. One immediate consequence is that the phonons are damped as in anharmonic crystals. In addition, however, there will be, in noncrystalline solids, a spectrum of localized excitations which are expected to contribute to the spectrum at low frequencies a background "noise" extending out to some comparatively large momentum q_m . It is assumed here that these excitations are taken into account in a crude way by the low-frequency, large-momentum part of the above Lorentzian.

To summarize our picture for elementary excitations in amorphous materials we assume (i) a hydrodynamiclike spectrum of vibrational states with tails extending out to some cutoff momentum q_m , and (ii) a structural relaxation time τ which is weakly diverging as $T \rightarrow 0$. We emphasize that the two assumptions are not independent: We expect the large-momentum excitations to be responsible for a comparatively short relaxation time.

The next step is to calculate the specific heat within our model. Because of phonon damping and the tails in the spectrum, it is in general not correct to insert $-\sum_{\vec{q}} \omega \text{Im}D_+$ for the density of states in the Debye formula for the specific heat of phonons. Instead, we use an exact expression for the free energy F as a stationary functional⁵

of D :

$$-2\beta(F - F_0) = \varphi\{D\} - \sum_{\vec{q}, n} \{M(\vec{q}, z_n)D(\vec{q}, z_n) - \ln[-D^{-1}(\vec{q}, z_n)] + \ln[-D_0^{-1}(\vec{q}, z_n)]\}. \quad (2)$$

Here $\beta = T^{-1}$ ($\hbar = k_B = 1$); $z_n = 2\pi i T n$; $n = 0, \pm 1, \dots$; and the sum on \vec{q} with $q \leq q_m$ includes the three polarizations. Formally, the self-energy $M\{D\}$ is defined through $\delta\varphi/\delta D = M$. The correct value of the free energy is obtained by putting $D^{-1} = D_0^{-1} - M$. The functional F is stationary ($\delta F/\delta D = 0$) at this "point" in the D space. Our form for D given by Eq. (1), with $D_0^{-1} = z^2 - \omega_0^2(q)$, defines a self-energy $M = i\omega_0^2(q)gz\tau/(1 - iz\tau)$ and is thus an implicit approximation for φ .

We obtain the entropy $S(T)$ from $\delta F = F(T + \delta T) - F(T) = -S(T)\delta T$. The procedure is now to calculate δF for a general M with $D^{-1} = D_0^{-1} - M$ and to insert the approximate form for M in the final expression for S . The calculation is similar to the one for condensed bosons⁶ except that here

we vary F around a fixed temperature $T \neq 0$ because of the T dependence of τ . The final result for $S(T)$ reads

$$S(T) = \frac{1}{\pi} \int_0^\infty d\omega \frac{e^{\beta\omega}}{(e^{\beta\omega} - 1)^2} \frac{\omega}{T^2} \Lambda(\omega, T), \quad (3)$$

where

$$\Lambda = -\sum_{\vec{q}} [\text{Im}M_+ \text{Re}D_+ + \text{Im} \ln(-D_+^{-1})].$$

The specific heat, from Eq. (3), is given by

$$C(T) = \frac{1}{\pi} \int_0^\infty d\omega \frac{e^{\beta\omega}}{(e^{\beta\omega} - 1)^2} \left[\left(\frac{\omega}{T}\right)^2 \frac{\partial \Lambda}{\partial \omega} + \frac{\omega}{T} \frac{\partial \Lambda}{\partial T} \right] \quad (4)$$

The sum on \vec{q} in the expression for Λ , with D from Eq. (1), can be performed analytically, and we arrive at

$$C = \frac{2\pi^2}{5} \left(\frac{T}{v_0}\right)^3 + \frac{1}{\pi^3} \left(1 + T \frac{\partial \ln \tau}{\partial T}\right) (g_0 q_0 \tau T)^3 \int_0^\infty dx \frac{e^x}{(e^x - 1)^2} x^4 \frac{1 - (xT\tau)^2}{[1 + (xT\tau)^2]^4}. \quad (5)$$

The first term is the Debye specific heat C_D . The second term is due to the mass operator $M(q, \omega)$. The momentum q_0 is defined by

$$\int_{q \leq q_m} d^3q g^3(q) \equiv \frac{4}{3}\pi (g_0 q_0)^3.$$

In deriving expression (5) we have neglected terms of the order $g(q \leq q_m)$ as compared to 1 and terms of order $[\omega/\omega_0(q_m)]^n$, $n \geq 4$. It should be noticed that $\omega_0(q)$ does not enter the second term of Eq. (5) so that this result is quite general. We now take $\tau = AT^{-\nu}$, $\nu > 0$. If $\nu \geq 1$, then the second term in Eq. (5) vanishes more rapidly than T^3 as $T \rightarrow 0$, and the specific heat is given by the Debye law. In the case $\nu < 1$, however, the specific heat will be dominated at sufficiently low temperatures by the second term which behaves like $T^{3-3\nu}$ for $T \rightarrow 0$ and which arises from the low-frequency, large-momentum part of the vibrational spectrum. The existence of these states is, in the present model, the distinguishing feature of the amorphous state.

In order to estimate the thermal conductivity we argue that only the propagating acoustic phonons (which contribute the T^3 term to C) carry the heat, and we use the kinetic formula

$$\kappa = \frac{1}{3} \int_0^\infty d\omega C_D(\omega) l(\omega) v_0, \quad (6)$$

where $\int_0^\infty d\omega C_D(\omega) = C_D$, and with the mean free

path l for the acoustic phonons,

$$l(\omega) = \frac{2v_0\tau}{g_0} \left[1 + \left(\frac{1}{\omega\tau}\right)^2 \right], \quad (7)$$

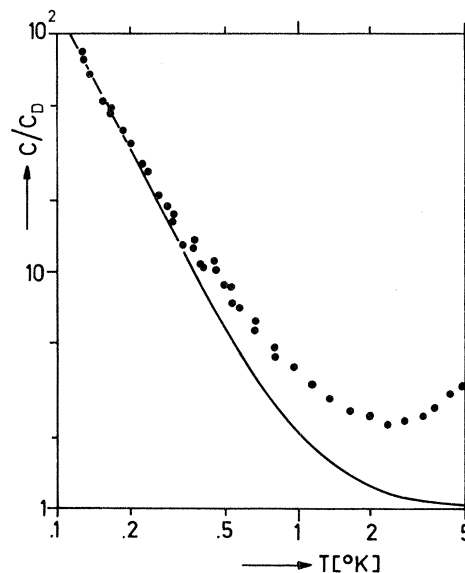


FIG. 1. The specific-heat anomaly in vitreous SiO_2 , plotted as C/C_D vs T , with $C_D = 8.07 \times 10^{-7} T^3 \text{ J g}^{-1} \text{ }^\circ\text{K}^{-1}$, as given in Ref. 1. The data below 2°K are from Ref. 1, those above 2°K from Ref. 10. The solid line is the theoretical curve as described in the text.

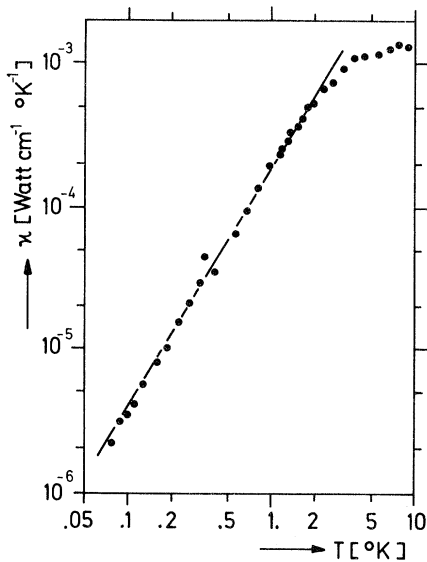


FIG. 2. Comparison of the experimental thermal conductivity of vitreous SiO_2 (Ref. 1) with the theoretical curve (solid line).

as obtained⁷ from Eq. (1). The result for κ is

$$\kappa = \frac{4}{15\pi^2} \frac{T^3\tau}{v_0g_0} + \frac{1}{6\pi} \frac{T}{v_0g_0\tau}. \quad (8)$$

With our assumption $\tau = AT^{-\nu}$, $\nu < 1$, the second term in Eq. (8) dominates at low temperatures, giving $\kappa \propto T^{1+\nu}$ for $T \rightarrow 0$.

In Fig. 1 we compare the excess specific heat C/C_D as obtained from Eq. (5) with the measurements for vitreous SiO_2 . The integral in Eq. (5) was calculated numerically. We have chosen $\tau = 3.6 \times 10^{-13} T^{-2/3}$ sec ($\nu = \frac{2}{3}$). The factor $g_0q_0v_0 = 7.7 \times 10^{12}$ sec⁻¹ was determined by the fit to the experimental data at $T = 0.15^\circ\text{K}$. Below 1°K we have $C/C_D - 1 \propto T^{-2}$ and thus $C \propto T$ for $T \rightarrow 0$ indicated experimentally. We remark that the deviations at higher temperatures result from neglecting phonon dispersion in the Debye specific heat.

With the above choice for τ , the first term on the right-hand side of Eq. (8) for κ is less than

the second term by a factor of 10^{-3} at 1°K . Hence $\kappa \propto T^{5/3}$ for $T \leq 1^\circ\text{K}$. In Fig. 2 the experimental results for κ in vitreous SiO_2 are compared with the theoretical curve, where we used¹ $v_0 = 4.1 \times 10^{-5}$ cm/sec and $g_0 = 3.4 \times 10^{-3}$.

The mean free path of phonons in vitreous SiO_2 at a frequency $\omega = 1.65 \times 10^{11}$ sec⁻¹ and temperatures slightly above 1°K was estimated from light-scattering experiments⁹ to be between 1 and 0.1 cm. For this frequency and for $T = 1^\circ\text{K}$ we find, with our parameters, $l = 3 \times 10^{-2}$ cm. This is surprisingly large but still an order of magnitude, at least, below the experimental value.¹⁰

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¹R. C. Zeller and R. V. Pohl, to be published

²R. Maynard, private communication.

³A. Leadbetter, private communication.

⁴See, for example, L. P. Kadanoff and P. C. Martin, *Ann. Phys. (New York)* **24**, 419 (1963).

⁵C. De Dominicis and P. C. Martin, *J. Math. Phys.* **5**, 31 (1964); see also W. Götze, *Phys. Rev.* **156**, 951 (1967).

⁶The explicit temperature expansion for the free energy of a Bose system around $T = 0$ has been worked out by W. Götze and H. Wagner, *Physica* **31**, 475 (1965). The generalization required here for the expansion around $T = T_0 > 0$ is straightforward.

⁷A mean free path $l \propto \omega^{-2}$ of phonons in noncrystalline solids at low temperatures has been predicted by P. G. Klemens, *Proc. Roy. Soc., Ser. A* **208**, 108 (1951).

⁸P. Flubacher, A. J. Leadbetter, J. A. Morrison, and B. P. Stoicheff, *J. Phys. Chem. Solids* **12**, 53 (1959).

⁹W. Heinicke and G. Winterling, *Appl. Phys. Lett.* **11**, 231 (1967).

¹⁰K. Dransfeld (private communication) has pointed out that saturation effects in the light-scattering experiments of Ref. 8 can lead to an apparent mean free path which might well be too large by an order of magnitude.