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Transient Effects in Low-Temperature Specific Heat of Amorphous Dielectrics

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We show that recent short-time-scale measurements of the specific heat of amorphous dielectrics are not inconsistent with the predictions of the tunneling model if the associated heat diffusion problem is properly treated. This requires taking into account the kinetics of energy transfer between the phonons and the tunneling modes.

In a recent Letter Goubau and Tait¹ presented short-time-scale ($t \sim 100 \mu\text{sec}$) measurements of the specific heat of some amorphous dielectrics, which agree with the earlier long-time results^{2,3} within the experimental uncertainty. They concluded that these results contradict the tunneling model^{4,5} in that the latter would require the long-time specific heat to exceed the short-time value¹ by a factor of 3 to 4. The tunneling model assumes the existence of localized two-level structural states in amorphous dielectrics and was introduced previously to interpret the thermal properties of these systems.^{4,5}

The purpose of the present Comment is twofold. First we show that the above measurements are indeed consistent with the tunneling model provided that the heat diffusion problem is treated correctly, taking into account the kinetics of the energy transfer between the phonons which carry the heat and the localized two-level tunneling systems. Secondly, for an ideal situation of uniform spatial heating of the sample, we derive explicitly the intrinsic time dependence of the specific heat in the dominant-phonon approximation and discuss some limiting cases. By "intrinsic" we refer to the time dependence arising entirely from the delayed transfer of energy⁴⁻⁶ from the phonons to the two-level systems in the absence of heat diffusion.

We consider the experimental situation where a slab of unit cross-sectional area confined to the region $0 < x < L$ is heated by a heat pulse at $x=0$, at $t=0$. The temperature gradient $\partial T(x,t)/\partial x$ is maintained zero¹ at $x=0$ and $x=L$ for all

$t > 0$. The heat transport is governed by

$$\partial Q(x,t)/\partial t = \kappa \partial^2 \Delta T(x,t)/\partial x^2, \quad (1)$$

where $\partial Q(x,t)/\partial t$ is the rate of accumulation of heat per unit volume and κ is the thermal conductivity. This heat is taken up instantaneously by the phonons which then slowly transfer part of it to the local tunneling states. We describe the kinetics of this heat transfer in the dominant-phonon approximation in which the thermal phonons are replaced by an effective number, N_p , of phonon modes per unit volume, having energy $E_p \equiv E = 3k_B T$. The latter are assumed to interact only with an effective number N_l of pairs of resonant tunneling states per unit volume, of energy splitting $E_l \equiv E$. We denote by $n_p(x,t)$ the phonon occupation number density per mode and assume that the phonon subsystem is always locally in thermal equilibrium. Thus the local (phonon) temperature is defined and a change $\Delta n_p(x,t)$ corresponds to a change ΔT in the measurable temperature given by ($\beta = 1/k_B T$)

$$\Delta n_p = \frac{\beta E}{4T \sinh^2(\frac{1}{2}\beta E)} \Delta T \equiv a \Delta T. \quad (2)$$

The time evolution of $n_p(x,t)$ is determined by

$$\frac{\partial n_p}{\partial t} = \frac{a}{\rho c_p(T)} \frac{\partial Q(x,t)}{\partial t} + \left(\frac{\partial n_p}{\partial t} \right)_l, \quad (3)$$

where the first term gives the change in the phonon occupation due to the inflow of heat $\partial Q(x,t)/\partial t$ into an element of thickness Δx and $(\partial n_p/\partial t)_l$ represents the rate of change of the phonon occupation due to resonant interaction with the lo-

calized tunneling levels and is given by

$$(\partial n_p / \partial t)_i = \tau_p^{-1} [(n_p + 1)N_+ - n_p N_-]. \quad (4)$$

In the above equations ρ denotes the mass density; $c_p(T)$ the phonon specific heat per unit mass [$c_p(T) = N_p \rho^{-1} E a$ in the dominant-phonon approximation]; and N_{\pm} the occupation number densities of the upper and lower levels of an isolated tunneling pair [$N_+ = N_- \exp(-\beta_i E)$, $N_+ + N_- = 1$, $\beta_i = (k_B T_i)^{-1}$, $T_i = T + \Delta T_i$] of splitting E . The relaxation time τ_p is given by⁶

$$\frac{1}{\tau_p} = \frac{\pi M^2 E}{\hbar \rho v_{\text{Deb}}^2} \frac{dN_{\pm}}{dE}, \quad (5)$$

where v_{Deb} is the sound velocity and M is related to⁶ the deformation potential B and to the off-diagonal matrix element Δ , which couples the unperturbed states of a tunneling pair, through $M = B\Delta/E$. Since the tunneling modes do not conduct heat their population changes only as a result of their local coupling to the phonons. From energy conservation for this process we obtain.

to lowest order in ΔT_i ,

$$\frac{\partial N_{\pm}}{\partial t} = \frac{N_p E a}{\rho c_i(T)} \tanh^2\left(\frac{\beta E}{2}\right) \left(\frac{\partial n_p}{\partial t}\right)_i, \quad (6)$$

where $c_i(T)$ is the specific heat per unit mass associated with the tunneling states. Equations (3), (4), and (6) form a closed system from which the occupation numbers $n_p(x, t)$ and $N_{\pm}(x, t)$ may be obtained by linearizing with respect to the changes Δn_p and ΔN_{\pm} [$\Delta N_{\pm}(x, 0) = 0$] of these quantities produced by the source term $\partial Q(x, t) / \partial t$. The explicit solution for the Laplace transform $\Delta n_p \sim(x, s)$ of $\Delta n_p(x, t)$ is

$$\begin{aligned} \Delta n_p \sim(x, s) &= \frac{a}{\rho c_p(T)(s + s_1)} \left(1 + \frac{1}{\tau s} \coth \frac{\beta E}{2}\right) \left(\frac{\partial Q}{\partial t}\right) \sim, \quad (7) \end{aligned}$$

where $[c(T) = c_p(T) + c_i(T)]$

$$\frac{1}{\tau} = \frac{N_p E a}{\rho c_i(T)} \tanh^2\left(\frac{\beta E}{2}\right) \frac{1}{\tau_p}, \quad (8)$$

$$s_1 = \frac{1}{\tau} \frac{c(T)}{c_p(T)} \coth\left(\frac{\beta E}{2}\right). \quad (9)$$

According to Eqs. (4) and (6), τ^{-1} represents the relaxation rate of the two-level systems. At this stage it may be remarked that τ^{-1} has a distribution⁶ and eventually physical quantities must be averaged with respect to this distribution. Combining Eqs. (1), (2), and (7) we obtain the following equation for $\Delta T \sim(x, s)$:

$$\left(1 + \frac{c_p(T)}{c(T)} \frac{s_1}{s}\right) \left[\frac{\partial^2 \Delta T \sim(x, s)}{\partial x^2} + \frac{\rho c_p(T)}{\kappa} \Delta T(x, 0)\right] = \frac{\rho c_p(T)}{\kappa} (s + s_1) \Delta T \sim(x, s). \quad (10)$$

This equation, which is central to our treatment, differs from the usual heat-diffusion equation in that it incorporates explicitly the effect of the transfer of energy from the heat-carrying phonons to the two-level tunneling states which do not transport heat. In the time domain Eq. (10) represents an integro-differential equation for $\Delta T(x, t)$ which may be solved after converting it into a differential equation, whose general solution is then required to satisfy the original integral equation. Using the above boundary conditions and the steady-state condition

$$\lim_{t \rightarrow \infty} \Delta T(x, t) = Q_0 / \rho L c(T) \equiv \Delta T_m,$$

where Q_0 is the total amount of heat supplied impulsively at time $t = 0$ at $x = 0$, we arrive at the final result ($\eta = \rho c_p(T) / \kappa$)

$$\begin{aligned} \frac{\Delta T(x, t)}{\Delta T_m} &= 1 + \left(\frac{c(T)}{c_p(T)} - 1\right) \exp(-s_1 t) \\ &\quad + 2 \frac{c(T)}{c_p(T)} \sum_{n=1}^{\infty} \cos \frac{n\pi x}{L} \exp(-b_n t / 2) [f_n \exp(a_n t / 2) + (1 - f_n) \exp(-a_n t / 2)], \quad (11) \end{aligned}$$

where

$$b_n = s_1 + \frac{\pi^2 n^2}{\eta L^2}, \quad (12)$$

$$a_n = \left(b_n^2 - \frac{4}{\tau} \coth \frac{\beta E}{2} \frac{\pi^2 n^2}{\eta L^2}\right)^{1/2}, \quad (13)$$

and

$$f_n = (b_n^2 - a_n^2)(2s_1 + a_n - b_n)[4a_n(b_n - s_1)(b_n + a_n)]^{-1}.$$

One may easily verify that at $t=0$, $\Delta T(x, 0)$ vanishes inside the sample except for a δ -function pulse of strength $\Delta T_m^0 = Q_0/\rho L c_p(T)$ at $x=0$, as required since the initial heat Q_0 is taken up by the phonons.⁷ The temperature profile given by Eq. (11) is plotted in Fig. 1 for fused silica and polymethyl methacrylate (PMMA), for various values of $k = \pi x/L$ taking $L = 1$ mm.¹ The effective number of phonon modes N_p is defined by equating the phonon specific heat in the dominant-phonon approximation to the Debye expression.³ The quantity M^2 is estimated from the measured thermal conductivity,³ using the Debye model expression for κ and the above form for the phonon relaxation rate⁶ $\tau_p^{-1} \tanh(\frac{1}{2}\beta E)$. Finally, the values of the remaining parameters are taken from Table I of Ref. 3.

The curve $k = \pi$ corresponds to the experimental situation and it is seen that our treatment involving no free parameter yields excellent agreement with experiment¹ for fused silica and qualitative agreement for PMMA, without using the fact that τ^{-1} has a distribution⁶ and replacing this quantity by the average value determined above. The overshoot above the equilibrium temperature ΔT_m at points x close to the origin is a general feature related to the sudden nature of the heating process at $x=0$ at $t=0$.

The drastic effects associated with the existence of the two-level systems are best seen by comparing the results of Fig. 1 with the temper-

ature profiles $\Delta T^0(x, t)/\Delta T_m^0$ which would be expected if the phonons were present alone in the system, which corresponds to the limit $\tau \rightarrow \infty$, $c_l(T) \rightarrow 0$, and $\kappa \rightarrow \kappa_{\text{crystal}}$ in Eq. (11). In the case of SiO_2 , for example, one finds that at $T = 0.16$ K (0.88 K) the time \bar{t} required for $\Delta T(L, t)$ to reach half its maximum height ΔT_m changes from $\bar{t} < 1$ μsec in the absence of tunneling states to $\bar{t} = 70$ μsec (38 μsec) in the presence of these states. In the present situation involving mobile phonons coupled to tunneling states, the temperature profiles $\Delta T(x, t)$ have a more direct meaning than the time-dependent specific heat itself.⁷ The effect of the tunneling states on $\Delta T(x, t)$ in Eq. (11) is controlled by the two essentially independent parameters τ and $\alpha \equiv c_l(T)/c_p(T)$, from which one could envisage different limiting situations. In particular, the estimate of τ for SiO_2 as indicated above, using Eq. (8), yields $\tau = 2.54$ μsec at $T = 0.16$ K and $\tau = 0.022$ μsec at $T = 0.88$ K. This shows that in the range of the experimental measurement times (see Fig. 1) the two-level systems are essentially in equilibrium with the phonons and no *intrinsic* time dependence of $\Delta T(L, t)$ can result. This explains why the short- and long-time-scale specific-heat measurements yield the same results, as noted in Ref. 1.

We now consider the intrinsic time dependence of the specific heat in an ideal case where a heating pulse dQ/dt of height $Q_0/\Delta t$ and width Δt is applied uniformly to the entire sample. Our previous equations (3)–(9) remain valid for this case with the difference that the spatial dependence is now suppressed. For this case, the explicit form of $\Delta n_p(t)$ obtained from (7) with $\Delta n_p(0) = 0$ is

$$\Delta n_p(t) = \frac{aQ_0}{\rho c_p \Delta t s_1} \left[\frac{c_l(T)}{c(T)} [\exp(\Delta t s_1) - 1] \exp(-t s_1) + \frac{\Delta t}{\tau} \coth\left(\frac{\beta E}{2}\right) \right], \quad t > \Delta t. \quad (14)$$

From Eq. (14) we obtain the change in phonon temperature using Eq. (2) and hence we find the explicit form of the specific heat $c(t, T) = Q_0/\Delta T(t)$, $t > \Delta t$. In general, however, we must average the physical quantity $\Delta n_p(t)$ with respect to the distribution of τ^{-1} . We recall that $\tau^{-1} \propto \Delta^2$ and that the splitting of the tunneling states is given by⁶ $E = (\epsilon^2 + \Delta^2)^{1/2}$, where $\Delta = \Delta_0 e^{-\lambda}$. Here $\pm \frac{1}{2}\epsilon$ are the unperturbed ground-state energies in the two minima of the asymmetrical potential well and Δ is the resonance integral, Δ_0 being typically the zero-point energy in the potential minima. Both ϵ and λ ⁴ are random quantities which we shall assume to be uncorrelated.⁵ In order to get a line-

ar specific heat it is sufficient to have a smooth density of tunneling states which is nonvanishing down to the lowest energies of interest.⁴⁻⁶ This can be realized⁶ by assuming ϵ and λ to have the following probability density distributions: $p_\lambda(\lambda) = \lambda_m^{-1}$ for $0 < \lambda < \lambda_m$ and $p_\epsilon(\epsilon) = \epsilon_m^{-1}$ for $0 < \epsilon < \epsilon_m$. From these distributions we find the joint distribution $P(E, \omega)$ of E and $\omega = \tau^{-1}$ and the result coincides with that given by Jäckle⁶ except that there are well-defined lower and upper bounds to the allowed values of ω , which ensures that $P(E, \omega)$ is finite for all ω : $\omega_m < \omega < \omega_M$, where ω_M is the maximum value of ω obtained by putting $\Delta = E$ in the

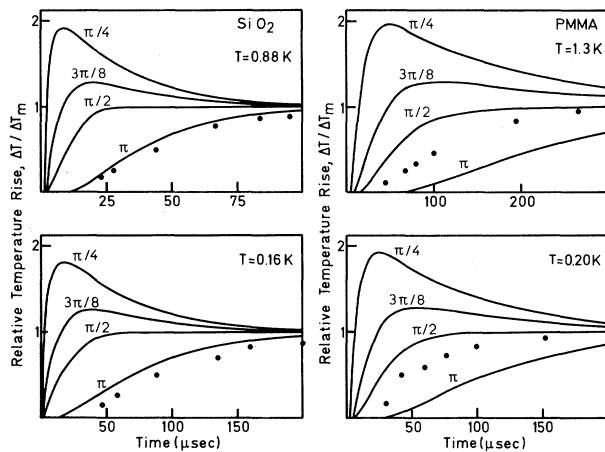


FIG. 1. Temperature profile as a function of time for various positions x in a slab of thickness L subjected to a heat pulse at $x=0$, at $t=0$. The different curves correspond to different values of $k = \pi x/L$ and are normalized to unity at the steady-state value ΔT_m . The dots correspond to measured values of ΔT (Ref.1).

expression of τ_p^{-1} in Eq. (5), while ω_m is the minimum value of ω which corresponds to $\Delta = \Delta_0 e^{-\lambda_m}$. In addition, the constant factor \bar{P} in Jäckle's expression is replaced by $\bar{P} = (\lambda_m \epsilon_m)^{-1}$. Next we average Eq. (14) with the distribution $P(E, \omega)$ assuming $\tau \gg \Delta t$, and substitute the resulting value in Eq. (2). The result for the specific heat $c(t, T)$ at time t is then

$$\frac{1}{c(t, T)} \approx \frac{1}{c(T)} \left\{ 1 + \frac{c_1(T)}{c_p(T)} \left(\ln \frac{t_2}{t_1} \right)^{-1} \left[\text{Ei} \left(\frac{t}{t_2} \right) - \text{Ei} \left(\frac{t}{t_1} \right) \right] \right\}, \quad (15)$$

where $t_1 = c_p(T) [\omega_M c(T) \coth(\frac{1}{2}\beta E)]^{-1}$, $t_2 = (\omega_M / \omega_m) t_1$, and $\text{Ei}(x)$ is the exponential integral. First we note that for $t \rightarrow \infty$, $c(t, T)$ reduces to the steady-state value $c(T)$, as expected. Equation (15) shows that the expression $c(t, T) \propto T \ln(4t\omega_M)$ ($t \gg \omega_M^{-1}$),

which has been used recently,¹ does not follow as such from the tunneling model. Using the data of Ref. 3 for SiO_2 and the typical value $\Delta_0 = 10^{-2}$ eV, we find that for $\lambda_m \lesssim 9$, $c(t = 5 \text{ sec}, T)$ does not exceed $c(t = 100 \text{ } \mu\text{sec}, T)$ by more than 7% in the range $0.2 \text{ K} < T < 1.5 \text{ K}$. On the other hand, for $\lambda_m \gtrsim 10$ the long-time specific heat appreciably exceeds the short-time value at low T and increases rapidly with λ_m .

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⁷Our exact treatment is not directly related to the analysis based on Eq. (3) in Ref. 1. The latter describes the strong-coupling limit where the tunneling states equilibrate instantaneously (i.e., $\tau = 0$) with the phonons at any instant t . In that case the specific heat is clearly time independent and given by $c(T)$, which can be determined from experimental temperature profiles using the solution of Eq. (3) (Ref.1) and the known values of $\kappa(T)$ (Ref.1). On the other hand, in our treatment the specific heat varies continuously from $c_p(T)$ at $t = 0$ [$\Delta N_{\pm}(x, 0) = 0$] to $c(T)$ at $t = \infty$ and its general form could not be found directly from an adaptation of the solutions of our Eq. (10) to the experimental data. Since the tunneling systems are distributed statically in space, the assumption of a resonant interaction with the phonons leading to the instantaneous thermal equilibration implied by Eq. (3) of Ref. 1 is quite unreasonable. However, in practice, for $t \gg \tau$ the exact expression would reduce, of course, to the solution of Eq. (3) in Ref. 1.