Low-Temperature Specific Heat and Thermal Conductivity of Glasses

L. Gil, M. A. Ramos,[(a)] A. Bringer, and U. Buchenau
Institut für Festkörperforschung, Forschungszentrum Jülich, Postfach 1913, D-5170 Jülich, Germany

(Received 17 July 1992)

The soft potential model (an extension of the tunneling model to include soft localized vibrations) is shown to describe the anomalous features of the specific heat C_p and the thermal conductivity of glasses over the entire low-temperature range, up to and including the peak in C_p/T^3 and the second rise of the thermal conductivity above the plateau.

PACS numbers: 63.50.+x, 65.40.−f, 66.70.+f

While the low-temperature properties of glasses cannot be understood in terms of the standard Debye model, they seem to be nonetheless universal [1, 2]. Below 1 K, one finds a linear specific heat and a thermal conductivity increase with T^2 (T temperature). These features can be explained within the tunneling model [3]. Above 1 K, the specific heat C_p rises stronger than the Debye T^3 term and the thermal conductivity shows a plateau. It has recently been shown [4] that a consistent description of these additional anomalous features is possible in terms of the soft potential model [5, 6], an extension of the tunneling model to include soft vibrations into the picture.

What is missing, however, is an explanation of the glassy anomalies at still higher temperatures, namely, the peak in C_p/T^3 and the second rise of the thermal conductivity. In terms of the vibrational density of states $g(\nu)$ and the frequency ν, the peak in C_p/T^3 is due to a maximum in $g(\nu)/\nu^2$, observed universally in Raman and neutron scattering [7]. The maximum appears at a frequency at which the corresponding crystals still have only sound waves with a wavelength of the order of ten to twenty interatomic spacings. In glasses, the soft vibrational modes of the maximum coexist with sound waves of that wavelength [8]. They are more numerous by 2 to 3 orders of magnitude than the tunneling states which dominate the properties below 1 K. Consequently, these vibrational modes do not only appear in the specific heat, but become accessible to neutron and Raman scattering [7, 8] as well as to numerical simulations [9]. A better understanding of these modes is highly desirable, not only for glasses, but also for undercooled liquids [10].

Here we show that a physically plausible assumption, which relates the asymmetry of the soft potentials to thermal strains at the glass temperature, allows one to describe these modes within the framework of the soft potential model without any additional parameter. The resulting vibrational density of states accounts for the peak in C_p/T^3 and the second rise of the thermal conductivity around 10 K. Thus one gets for the first time a simple and consistent description of the glassy anomalies in the specific heat and the thermal conductivity over the entire low-temperature range.

The soft potential model postulates soft localized modes with an effective mass M and a stabilizing fourth-order term in the potential

$$V(x) = W\left[D_1\left(\frac{x}{d}\right) + D_2\left(\frac{x}{d}\right)^2 + \left(\frac{x}{d}\right)^4\right]. \qquad (1)$$

The origin of the configurational coordinate x is chosen such that the third-order term of the potential vanishes. The coefficients D_1 and D_2 are supposed to be random with a density of states $P(D_1, D_2) = P(0,0) \equiv P_s$. The distance d is fixed by the condition $W = \hbar^2/2Md^2$. With this condition, the quantum mechanical balance between potential and kinetic confinement energy leads to level splittings which are greater than W for any single-well potential. Smaller level splittings are only achieved in the double-well tunneling case (see Fig. 1). Consequently, the energy W marks the crossover between tunneling and vibrational states.

We have chosen to formulate the soft potential model in natural units. The connection to Refs. [4–6, 11] is given by $d = a\eta_L^{1/2}$ and $P_s = 2P_0\eta_L^{5/2}$.

In the tunneling case, the above assumptions have been shown [4] to lead to a practically constant density of states, thus reproducing the tunneling model. For the vibrational states, one derives [6] an increase $g(\nu) \sim \nu^4$. Here we present a simple scaling argument for that increase. For the purely quartic potential at $D_1 = D_2 = 0$, the second derivative at the potential minimum is zero. Going away from the origin of the D_1-D_2 plane in any direction, the second derivative at the minimum (or the minima) increases until it determines the splitting of the quasiharmonic levels at the bottom of the well(s). This will happen when the corresponding harmonic level splitting gets larger than W. The coordinate $x_0 = x_{\min}/d$ of the minimum obeys the equation $D_1 + 2D_2x_0 + 4x_0^3 = 0$ and the second derivative, proportional to the square of the harmonic frequency, is $2D_2 + 12x_0^2$. Scaling D_1 with a factor f^3 and D_2 with a factor f^2, one scales both x_0 and the harmonic frequency ν by f. This transformation brings the area of the D_1-D_2 plane with frequencies between ν and $\nu + \Delta\nu$ to a factor f^5 larger area with frequencies between $f\nu$ and $f\nu + f\Delta\nu$. Consequently, as soon as the curvatures at the minimum determine the

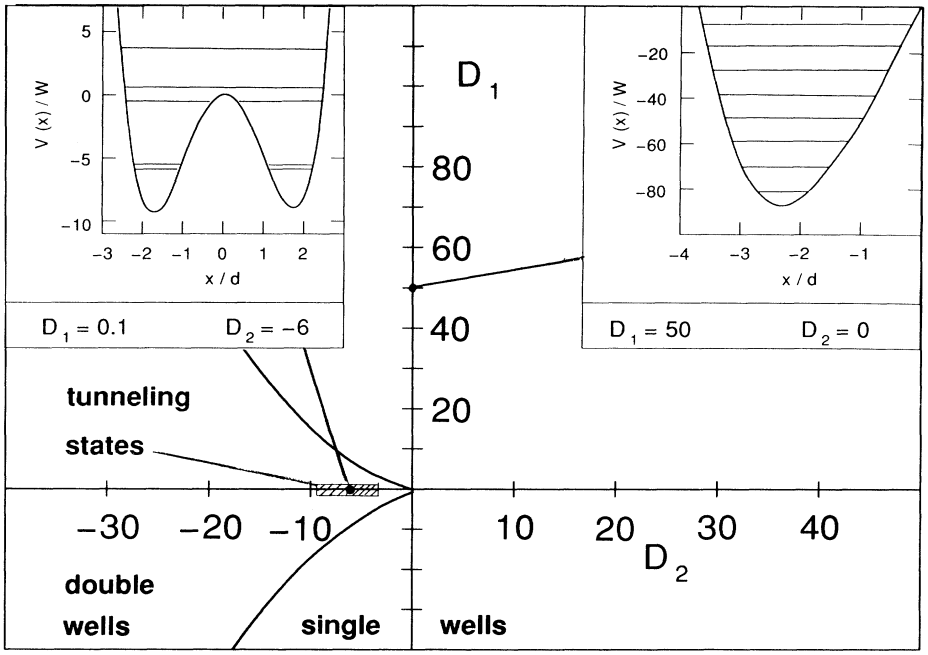

FIG. 1. Single- and double-well regions in the D_1-D_2 plane of the soft potential model. Insets: Potentials and levels of a typical tunneling state (left) and a typical vibrational state (right). The levels were calculated using a numerical search for stationary solutions of the Schrödinger equation.

level splittings, the density of states must increase with the fourth power.

As argued in earlier papers [6, 11], the sum of a constant density of tunneling states, a ν^2 density of sound waves, and a ν^4 density of soft vibrational modes implies the existence of a minimum in $g(\nu)/\nu^2$ and, consequently, C_p/T^3. The temperature $T_{\rm min}$ of the latter is determined exclusively by the energy W. From analytical approximations [11], $W = 1.6 k_B T_{\rm min}$. The numerical calculations reported below gave $W = 1.8 k_B T_{\rm min}$.

From specific heat data (see Table I), $T_{\rm min}$ ranges between 0.6 and 4 K. Using crude estimates for the anharmonic terms [11], one calculates a number of twenty to a hundred atoms participating in a single soft mode (this estimate has been recently confirmed in numerical work on a model glass [9]) and distances d of the order 0.1 to 0.2 Å. With these values, the average atomic displacement of the soft modes up to the glass temperature T_g is still only about one tenth of the interatomic spacings. Thus an expansion of the potential up to the quartic term seems still reasonable.

The description of the maximum in C_p/T^3 or, equivalently, $g(\nu)/\nu^2$, requires some kind of limitation in the D_1-D_2 distribution. Otherwise the soft mode part of $g(\nu)$ would increase $\sim \nu^4$ without end. A limitation in D_1 has in fact been anticipated, since it was introduced as being due to small perturbations [6]. One thus expects something like a Gaussian distribution of D_1 around the origin.

In order to estimate the width of that Gaussian, we

TABLE I. Test of the relation $R \equiv T_{\rm max}/T_{\rm min}^{3/4} T_g^{1/4} = 1.07$ for several glasses

Glass	$T_{\rm max}$ (K)	$T_{\rm min}$ (K)	T_g (K)	R	Ref.
SiO_2	10.0	2.1	1473	0.93	[1, 8, 15, 16]
$(SiO_2)_{0.65}(NaO)_{0.35}$	13.5	4.0	717	0.92	[17]
GeO_2	8.1	2.1	830	0.87	[1]
B_2O_3	5.4	1.0	523	1.13	[18]
Se	3.1	0.6	305	1.09	[1, 19, 20]
Polybutadiene	5.1	1.4	186	1.07	[21]
Polyethylene	5.0	1.3	240	1.04	[1, 22]
Glycerole	8.0	2.2	185	1.20	[1]
$LiCl \cdot 7H_2O$	10.7	3.3	144	1.26	[23]

have used a limitation scheme based on an idea of Ferrari, Phillips, and Russo [12]. These authors postulate a static thermal strain in each degree of freedom, freezing in at the glass temperature T_g, in order to account for the additional specific heat of undercooled liquids. We ascribe the linear term in the soft mode potential (1) to such a static thermal strain. From the free energy, one derives a differential relation between D_1 and the average displacement

$$\frac{\partial\langle x\rangle}{\partial D_1} = -\frac{W}{k_BTd}(\langle x^2\rangle - \langle x\rangle^2). \qquad (2)$$

From the $\langle x^2\rangle$ value of the pure quartic potential [13], one calculates an energy of $0.169D_1^2W^{3/2}(k_BT)^{-1/2}$ required to generate a small D_1 at $D_2 = 0$. Weighting each D_1 with the corresponding Boltzmann factor at T_g, one gets the distribution function

$$P(D_1, D_2)\,|_{D_2=0}= P_s \exp[-0.169\; D_1^2(W/k_BT_g)^{3/2}]. \qquad (3)$$

We have assumed a Gaussian of the form of Eq. (3) not only for $D_2 = 0$, but for all D_2 values. For D_2, a cutoff at barrier heights of about $k_BT_g/2$ is suggested by low-temperature relaxation data [14], so we did not calculate below $D_2 = -30$. This cutoff, however, had only a small influence on the results of our calculation.

In the numerical integration over the D_1-D_2 plane, the specific heat was calculated from the lowest six levels of each single potential. The levels were calculated by a numerical search for the solutions of the Schrödinger equation. In the double-well case, the lifetime of the tunneling levels was taken into account as in the tunneling model. In all cases, the two lowest levels were used to calculate a density of states.

Having fixed W by its relation to $T_{\rm min}$ and P_s by the specific heat in the tunneling region below 1 K, both the peak position $T_{\rm max}$ and the peak height in C_p/T^3 are reproduced with astonishing accuracy by our crude estimate of the width in D_1. This is illustrated for vitreous silica in Fig. 2(a), where the sum of calculated soft mode contribution (using $P_s = 1.5 \times 10^{-6}$ state/atom and $W/k_B = 3.8$ K) and Debye sound wave contribution is compared to experimental data [1, 8, 15, 16]. The calculated peak in C_p/T^3 appears at a temperature $T_{\rm max}$ with $T_{\rm max} = 1.07\, T_{\rm min}^{3/4}T_g^{1/4}$. Table I shows that this relation is not only fulfilled for vitreous silica, but also for a number of other glasses [17–23] with an average prefactor of 1.06 and a maximum deviation of 19%, well within the error resulting from the experimental determination of the three temperatures. The ratio $T_g/T_{\rm min}$ in Table I varies by a factor 16, showing that W does not depend on T_g.

Both vibrational and tunneling states are assumed to interact with the sound waves, in order to explain the universal anomalies in the acoustic properties and the thermal conductivity of glasses [14, 24]. In the long wavelength limit, the sound waves can be characterized by elastic strains, a uniaxial strain ϵ_l in the longitudinal and a shear strain ϵ_t in the transverse case. The interaction with the soft modes is assumed to be bilinear

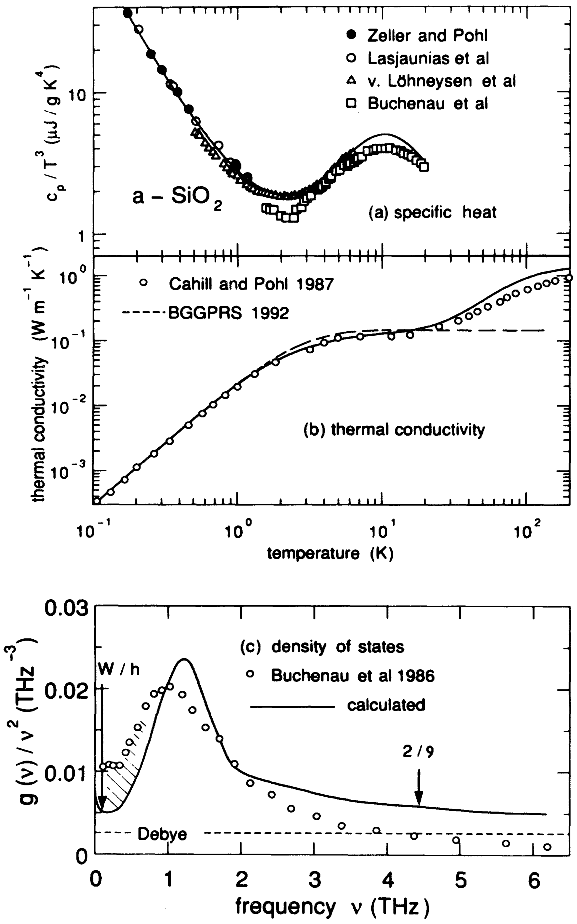

FIG. 2. Comparison of the model calculations (continuous lines) to experimental data in vitreous silica. (a) Specific heat [1, 8, 15, 16], plotted as C_p/T^3 vs T. (b) Thermal conductivity [1, 26] vs T (dashed line: earlier calculation [4]). (c) Density of states [8], plotted as $g(\nu)/\nu^2$ vs frequency ν. The shaded area shows an estimate [8] of the relaxational contribution to the experimental data.

$$\delta V_l = \Lambda_l \frac{x}{d}\epsilon_l, \quad \delta V_t = \Lambda_t \frac{x}{d}\epsilon_t, \qquad (4)$$

with coupling constants Λ_l and Λ_t. It has recently been shown [4] that this assumption explains both the initial T^2 rise of the thermal conductivity and the subsequent plateau in terms of the combined scattering of tunneling, relaxational, and soft vibrational states. The plateau is mainly due to the resonant scattering of the sound waves by the soft localized vibrations. That calculation [4] assumed a density of soft vibrations increasing with ν^4, without any limitation (with this condition, the resonant scattering from the harmonic part of the soft modes has the same temperature and frequency dependence as the Rayleigh scattering). We have modified that calculation by inserting the calculated density of soft vibrations of Fig. 2(c) and obtained the calculated thermal conductivity curve of Fig. 2(b). The calculation assumed $\Lambda_l = 0.64$ eV and $\Lambda_t = 0.4$ eV, calculated from tunneling model fits [25] via the relation $P_s\Lambda_j^2/W = 0.9\bar{P}\gamma_j^2$ between the parameters of the two models ($j = l,t$). That relation, derived from our numerical results in the tunneling regime, differs by the prefactor 0.9 from the one derived from analytical approximations [4].

Though our calculation overestimates the thermal conductivity at higher temperatures, it shows the onset of the second rise at the right temperature, linking the form of the specific heat curve to the form of the thermal conductivity curve in a consistent way (similar to an earlier approach [27]). In fact, the universal condition [24] $l \approx \lambda$ for this onset in our case turned out to be reasonably well fulfilled at and above the peak in $g(\nu)/\nu^2$.

At higher frequencies, our simple scheme begins to fail. This is clearly seen in the comparison of the calculated density of states to neutron data [8] in Fig. 2(c), which show that failure at about 3 times the peak frequency. There, however, the Debye scheme itself begins to fail as well, not only in the glasses, but also in the corresponding crystals, for well-known reasons. A "golden-rule" calculation based on Eq. (4) shows that the frequency at which the soft modes and the sound waves begin to be overdamped because of their mutual interaction is also of the same order.

In summary, the soft potential model accounts for the density of states of glasses, from the tunneling and relaxational states treated in earlier papers up to the THz range treated here. Though still mainly phenomenological, such a description may pave the way for a genuine microscopic theory.

[(a)] Permanent address: Laboratorio de Bajas Temperaturas, Departamento de Fisica de la Materia Condensada C-III, Universidad Autonoma de Madrid, 28049 Madrid, Spain.

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

[2] *Amorphous Solids: Low Temperature Properties*, edited by W. A. Phillips (Springer, Berlin, 1981).

[3] W. A. Phillips, J. Low. Temp. Phys. **7**, 351 (1972); P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. **25**, 1 (1972).

[4] U. Buchenau, Yu. M. Galperin, V. L. Gurevich, D. A. Parshin, M. A. Ramos, and H. R. Schober, Phys. Rev. B **46**, 2798 (1992).

[5] V. G. Karpov, M. I. Klinger, and F. N. Ignat'ev, Zh. Eksp. Teor. Fiz. **84**, 760 (1983) [Sov. Phys. JETP **57**, 439 (1983)].

[6] M. A. Il'in, V. G. Karpov, and D. A. Parshin, Zh. Eksp. Teor. Fiz. **92**, 291 (1987) [Sov. Phys. JETP **65**, 165 (1987)].

[7] V. K. Malinovsky, V. N. Novikov, P. P. Parshin, A. P. Sokolov, and M. G. Zemlyanov, Europhys. Lett. **11**, 43 (1990).

[8] U. Buchenau, M. Prager, N. Nücker, A. J. Dianoux, N. Ahmad, and W. A. Phillips, Phys. Rev. B **34**, 5665 (1986); U. Buchenau, H. M. Zhou, N. Nücker, K. S. Gilroy, and W. A. Phillips, Phys. Rev. Lett. **60**, 1318 (1988).

[9] B. B. Laird and H. R. Schober, Phys. Rev. Lett. **66**, 636 (1991); H. R. Schober and B. B. Laird, Phys. Rev. B **44**, 6746 (1991).

[10] *Dynamics of Disordered Materials*, Springer Proceedings in Physics Vol. 37, edited by D. Richter, A. J. Dianoux, W. Petry, and J. Teixeira (Springer, Berlin, 1989).

[11] U. Buchenau, Yu. M. Galperin, V. L. Gurevich, and H. R. Schober, Phys. Rev. B **43**, 5039 (1991).

[12] L. Ferrari, W. A. Phillips, and G. Russo, Europhys. Lett. **3**, 611 (1987).

[13] U. Buchenau, Philos. Mag. B **65**, 303 (1992).

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

[15] J. C. Lasjaunias, A. Ravex, M. Vandorpe, and S. Hunklinger, Solid State Commun. **17**, 1045 (1975) (this work was erroneously attributed to Hunklinger and Raychaudhuri in Ref. [11]).

[16] H. v. Löhneysen, H. Rüsing, and W. Sander, Z. Phys. B **60**, 323 (1985).

[17] J. Krüger, Phys. Chem. Glasses **13**, 9 (1972); G. K. White, J. A. Birch, and M. H. Manghnani, J. Noncryst. Solids **23**, 99 (1977).

[18] G. K. White, S. J. Collocott, and J. S. Cook, Phys. Rev. B **29**, 4778 (1984).

[19] J. C. Lasjaunias, C. R. Acad. Sci. Paris **269**, 763 (1969); J. C. Lasjaunias, R. Maynard, and D. Thoulouze, Solid State Commun. **10**, 215 (1972).

[20] O. Brand and H. v. Löhneysen, Europhys. Lett. **16**, 455 (1991).

[21] H. v. Löhneysen, E. Ratai, and U. Buchenau, in *Phonon Scattering in Condensed Matter V*, Proceedings of the Fifth International Conference, Urbana, 1986, edited by A. C. Anderson and J. P. Wolfe (Springer, Berlin, 1986), p. 35.

[22] B. Wunderlich and H. Baur, Adv. Polymer Sci. **7**, 151 (1970).

[23] W. A. Phillips (private communication).

[24] J. J. Freeman and A. C. Anderson, Phys. Rev. B **34**, 5684 (1986).

[25] J. F. Berret and M. Meissner, Z. Phys. B **70**, 65 (1988).

[26] D. G. Cahill and R. O. Pohl, Phys. Rev. B **35**, 4067 (1987); D. G. Cahill, Ph.D. thesis, Cornell University, 1989.

[27] C. C. Yu and J. J. Freeman, Phys. Rev. B **36**, 7620 (1987).