

Thermal expansion of glasses at low temperatures

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(Submitted 24 July 1984)

Pis'ma Zh. Eksp. Teor. Fiz. **40**, No. 7, 283–286 (10 October 1984)

The thermal-expansion coefficient of a glass varies linearly with the temperature at low temperatures and is governed by the presence of two-level systems in the glass. The Grüneisen constant Γ is anomalously large ($\sim 10^2$), because of the softness of the local atomic potentials in which the two-level systems occur. The primary component of the thermal-expansion coefficient is nonstationary, i.e., it depends on the experimental time t .

Previous research has shown that most of the low-temperature properties of glasses can be explained under the assumption of so called two-level systems in the glasses. The model for two-level systems, which was proposed independently by Anderson, Halperin, and Varma¹ and by Phillips² (the AHVP model), has made it possible to interpret experimental data on the specific heat, thermal conductivity, ultrasonic absorption, etc. On the other hand, this model has not explained some very interesting experiments on the thermal expansion of glasses.³ According to these experimental

results, the thermal-expansion coefficient α_T of the glass at a low temperature ($T \lesssim 1$ K) is proportional to T , so that the Grüneisen relation $\alpha_T = \Gamma C / K$ holds, where C is the specific heat, and K^{-1} is the bulk modulus. The temperature-independent Grüneisen constant Γ is negative, on the order of a few tens in magnitude. In contrast, the direct use of the AHVP model (in which there is no correlation between the strain energy and other parameters of the two-level system) leads to an α_T which is independent of the temperature.

In the present letter we propose a theory for the thermal expansion of glasses which explains the experimental data. At low temperatures the thermal-expansion coefficient is governed by two-level systems and can be written in the form

$$\alpha_T = - \frac{1}{K} \sum_{2LS} \frac{E}{4T^2 \text{ch}^2 \frac{E}{2T}} D; \quad D = \frac{\partial E}{\partial \epsilon}, \quad (1)$$

where $\epsilon = \text{div} u$ is the dilatation, E is the distance between the levels of the two-level system, the summation is over all the two-level systems in a unit volume of the gas, and the number of such systems is assumed to be independent of the external pressure and temperature.

To calculate the strain energy D and to carry out the summation in (1), we use the model of two-level systems proposed by Karpov, Klinger, and Ignat'ev⁴ (the KKI model), in which a correlation between D and the other parameters of the two-level system arises in a natural way. According to the KKI model, the two-level system is described by an anharmonic oscillator potential

$$V(x) = \mathcal{E}_0 \left[\eta \left(\frac{x}{a} \right)^2 + t \left(\frac{x}{a} \right)^3 + \left(\frac{x}{a} \right)^4 \right], \quad (2)$$

where \mathcal{E}_0 is an energy on the order of atomic energies, and a is a distance on the order of the average interatomic distance. The Schrödinger equation for the tunneling of an atom of mass M in potential (2) has a characteristic energy $W = \mathcal{E}_0 \eta_L^2 \sim 30$ K, where $\eta_L = (\hbar^2 / 2Ma^2 \mathcal{E}_0)^{1/3} \sim 10^{-2}$. In order of magnitude, this is the distance to the third level.⁵ Since we are interested in two-level systems with low energies, $E \ll W$, we should consider regions in the parameters η and t , which are small in terms of phase volume, in which such states occur. There are two such regions⁴: in the η, t plane, the vicinity of the ray $t = 0, \eta < 0$ (two-level systems of type I) and the vicinity of the parabola $\eta = t^2/4$ (two-level systems of type II). In the spirit of the KKI model, we assume that the state densities along η and t vary only slightly in these regions, and we denote these state densities by ψ_I and ψ_{II} , respectively. It is convenient to characterize the two-level systems by an asymmetry parameter Δ and a tunneling splitting Δ_0 ; here $E = (\Delta^2 + \Delta_0^2)^{1/2}$. The latter parameters should be expressed in terms of η and t by solving the Schrödinger equation. Corresponding expressions for the systems of types I and II are given in Ref. 4.

To analyze the thermal expansion, we need to determine how the parameters η and t (and thus the energy E) of the two-level systems depend on the dilation ϵ . As

Karpov and Parshin have shown, it is extremely important to take into account the high-frequency (in comparison with W/\hbar) phonon field ϵ_0 , the so-called zero-point vibrations of the glass atoms. We write the Hamiltonian for the interaction of the two-level system with the static strain field ϵ and the rf strain field ϵ_0 as follows:

$$\mathcal{H}_{\text{int}} = a_1 \mathcal{E}_0 \left(\frac{x}{a}\right)^2 (\epsilon + \epsilon_0) + a_2 \mathcal{E}_0 \left(\frac{x}{a}\right) (\epsilon + \epsilon_0)^2, \quad (3)$$

where a_1 and a_2 are constants. We now take an average of (3) over the fast motions (as we may, since the scale frequency for the motions in soft potentials W/\hbar is much lower than the Debye frequency ω_D) and we use $\langle \epsilon_0 \rangle = 0$, $\langle \epsilon_0^2 \rangle = b\eta_L^{3/2}$. Here b is a number on the order of unity. A term which is linear in x appears in this average Hamiltonian. We shift the origin of the x scale to put the potential energy in form (2) again. As a result, we develop increments in the coefficients η and t ; some of these increments do, and others do not, depend on ϵ . The increments of the first type are renormalizations of the parameters η and t . It is logical to assume that these renormalizations have already been incorporated in the parameters of the Hamiltonian for $\epsilon = 0$. The increments proportional to ϵ account for the effect of interest here. Using expressions for these increments and equations relating η and t to Δ and Δ_0 for the systems of types I and II, we find the following expressions for the strain potential of the two-level system:

$$D_{\text{I}} = \frac{a_1 W}{\eta_L} \left\{ 1.10 \lambda_1 \sqrt{1-p} \frac{\text{sign } t}{L^{1/3}} + 0.91 \frac{E}{W} \left[p L^{1/3} - \frac{(1-p)}{L^{2/3}} - 0.22 \lambda_1^2 \frac{(1-p)}{L^{8/3}} \right] \right\}, \quad (4)$$

$$D_{\text{II}} = \frac{a_1 W}{\eta_L} \left\{ 3.30 \sqrt{1-p} L^{2/3} \text{sign} \left(\eta - \frac{t^2}{4} \right) + 0.038 \lambda_1^2 \frac{E}{W} \left[\frac{p}{L^{5/3}} + 0.67 \frac{(1-p)}{L^{8/3}} \right] \right\}. \quad (5)$$

Here $\lambda_1 = a_2 b$; $L = \ln(W/E\sqrt{p})$; and $p = (\Delta_0/E)^2$. When the summation is carried out in (1), the sign function causes the contributions of the first terms in (4) and (5) to the thermal-expansion coefficient to vanish. We have written them out, however, since these terms are the ones which basically govern all the kinetic coefficients that are proportional to D^2 . The other terms can be seen from (4) and (5) to be smaller than the first terms (by a factor on the order of the parameter E/W) and to be proportional to E . Accordingly, when these terms are substituted into (1) they lead (with logarithmic accuracy) to the Grüneisen relation.

The contributions of the two-level systems are summed by integrating over the parameters E and p in expression (1). The distribution function of these parameters in the lowest approximation in L^{-1} is (cf. Refs. 4 and 7)

$$N_{\text{I, II}}(E, p) = 0.61 \psi_{\text{I, II}} \frac{\eta_L^{3/2}}{W} \frac{1}{p \sqrt{1-p} L^{4/3}}. \quad (6)$$

It can be seen that the product of the first two terms in (square) brackets in (4) and $N_I(E, p)$ is the derivative of p of some function of E and p that vanishes at $p = 0$ and at $p = 1$. This actually means that the corresponding contribution of the two-level centers of type I to the thermal-expansion coefficient depends on the experimental time. The point is that thermodynamic relation (1) holds only for those two-level systems that manage to undergo transitions during the experimental time t , i.e., those systems for which the relaxation time satisfies $\tau < t$. Since $\tau \sim p^{-1}$, we should integrate over p only in the interval $1 > p > p_0(E) = \tau_{\min}(E)/t$, where $\tau_{\min}(E)$ is the minimum relaxation time of two-level systems with a given energy E . The net result is that this contribution is the lower limit of the integration over p , and it falls off logarithmically with increasing t . At values of t that are not too large, this contribution may be greater than or on the order of the steady-state contribution, which is described by the last term in (4). For two-level systems of type II, the time-varying contribution is small in comparison with the steady-state contribution (which is on the same order of magnitude as the steady-state contribution for the two-level systems of type I, but it has the opposite sign).

We can now write the final expression for the Grüneisen constant according to these calculations:

$$\Gamma = - \frac{0.55 a_1}{1 + A} \frac{1}{L^{2/3} \eta_L} \left[\frac{L}{L + \frac{1}{2} \ln \frac{t}{\tau_{\min}(T)}} - \frac{0.04 \lambda_1^2}{L^2} \left(1 - \frac{11}{16} A \right) \right]; L = \ln \frac{W}{T}, A = \frac{\psi_{II}}{\psi_I}. \quad (7)$$

Let us discuss this result. The physical reason for the functional dependence $\Gamma(t)$ is that an increase in the parameter $|\eta|$ due to compression of the glass for the case of two-level systems of type I (with $a_1 > 0$) leads to a decrease in the tunneling transparency Δ_0 and, in contrast, an increase in the asymmetry Δ . For this reason, two-level systems with $\Delta < \Delta_0$ make a negative contribution to the thermal-expansion coefficient, while those with $\Delta > \Delta_0$ make a positive contribution. Correspondingly (as $t \rightarrow \infty$), parts arise that cancel each other completely. This cancellation¹⁾ occurs at a constant distribution function of the parameters η and t , for the contribution to the thermal expansion from the term in $\partial\eta/\partial\epsilon$ that does not depend on η . Since the relaxation time (τ) of the two-level centers increases with increasing Δ (at a given energy E), however, and since there are always two-level systems for which $\tau \sim t$, this cancellation does not occur over a finite experimental time. The glass therefore initially contracts during heating, but then it slowly begins to expand.

The sign of the Grüneisen constant after a long time is determined by two factors: the ratio (A) of the state densities of the two-level systems and the sign of the constant a_1 . This sign is apparently sensitive to the microscopic structure of the two-level systems. In estimating an absolute value of Γ , we should take into account the fact that the values of the constants a_1 and λ_1 are a few units (they are third derivatives of the potentials which act between the atoms of the glass and which depend on the coordinates in a power-law manner, with rather large powers). We ultimately find $\Gamma \sim \eta_L^{-1} \sim 10^2$, in agreement with the experimental data of Ref. 3.

The discussion above is adequate for dielectric glasses. In metal glasses the contri-

bution of two-level systems to α_T is added to the contribution from conduction electrons, which is positive in the free-electron model. The latter contribution is also proportional to T and is comparable in magnitude to the contribution of two-level systems. This circumstance may explain why α_T in metal glasses is of the same order of magnitude as in dielectric glasses but has a positive sign. As a test of this explanation, it would be interesting to see experiments on the thermal expansion of amorphous superconductors, in which the contribution of quasiparticles could be substantially reduced by choosing a temperature below the superconducting transition temperature T_c . In this situation, if the two-level systems in the metal and dielectric glasses have similar structures (if they have identical—negative—signs of a_1), α_T would change sign with decreasing temperature.

We wish to thank V. G. Karpov for a detailed discussion of these questions.

¹The addition of impurities to a glass could disrupt this cancellation, because of the appearance of two-level systems with a fixed tunneling transparency Δ_0 but a broad spread in the asymmetry Δ , which would apparently be more sensitive to the random surroundings of the atoms in the glass than the tunneling barrier would be. Since the asymmetric two-level systems make a positive contribution to the thermal-expansion coefficient, the thermal-expansion coefficient of a "dirty" glass might be several times lower than that of a chemically pure glass, and this is what is found experimentally.³

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Translated by Dave Parsons

Edited by S. J. Amoretty