

Thermal expansion of glasses at low temperatures: sensitivity to the two-level-system model

Yu. M. Galperin, V. L. Gurevich, and D. A. Parshin

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The theory of low-temperature thermal expansion of glasses is discussed. It is demonstrated that the expression for the thermal expansion coefficient is sensitive to the model of two-level systems. In particular, from the time dependence of the thermal expansion coefficient one can obtain information on the distribution function of the two-level system parameters.

1. Most of the low-temperature properties of glasses are well described within the framework of the Anderson-Halperin-Varma-Phillips two-level-system (TLS) model.^{1,2} At the same time, as the present authors have demonstrated,^{3,4} the AHVP model in its original form is insufficient to explain such important properties as the thermal expansion of glasses.

In Refs. 3 and 4, a theory of the coefficient of thermal expansion was constructed, based on the model of two-level systems proposed by Karpov, Klinger and Ignat'ev⁵ (the KKI model). It includes the TLS concept in the form of an anharmonic oscillator with two stochastic parameters, plus an assumed distribution of these parameters. The KKI model is a more concrete approach than the AHVF model, and it gives a well-defined correlation between the deformation potential and the other TLS parameters. The theory^{3,4} allows one to explain the large value of the Grüneisen parameter and predicts the observed dependence of the thermal expansion on the time τ_{exp} . However, the question remains open as to how model-dependent these results are. Specifically, to what degree are they sensitive to the distribution of TLS parameters?

With this goal, we have calculated the coefficient of thermal expansion for another distribution of these parameters, proposed by Il'in, Karpov and Parshin.⁶ We shall see that from this there arises a different time-dependence. Thus, looking at experimental results for the thermal expansion, we can judge the form this distribution has in reality.

2. We shall begin with an illustrative example. We take as our illustration the concrete example of a TLS composed of three atoms linearly arranged and interacting by means of a Lennard-Jones potential. To model the asymmetry, we will consider the force constants for both pairs of atoms to be somewhat different. We have

$$U(r) = \frac{A_1}{(r-a)^{12}} - \frac{B_1}{(r-a)^6} + \frac{A_2}{(r+a)^{12}} - \frac{B_2}{(r+a)^6} \quad (1)$$

($2a$ is the distance between the atoms on the ends); r is the coordinate of the central atom (see Fig. 1). We take

$$|A_1 - A_2| \ll A_{1,2}, \quad |B_1 - B_2| \ll B_{1,2}.$$

Expanding around $r = 0$, we have ($x \equiv r/a$)

$$U(x) = 2(A-B) + (6\beta - 12\alpha)x + (156A - 42B)x^2 + (-364\alpha + 56\beta)x^3 + (2630A - 252B)x^4. \quad (2)$$

Here

$$A = (\frac{1}{2}a^{12})(A_1 + A_2), \quad \alpha = (A_1 - A_2)/a^{12}, \\ B = (\frac{1}{2}a^6)(B_1 + B_2), \quad \beta = (B_1 - B_2)/a^6. \quad (3)$$

We shall be interested in weak potentials, i.e., potentials near the critical value.⁵ The critical potential is determined from the existence of an inflection point at $x = 0$, that is, by equating to zero the coefficient of x^2 :

$$B = (26/7)A.$$

Then the coefficient of x^4 is $1694A = \mathcal{E}_a$; we neglect fluctuations of this value and move it outside the average. We have

$$U(x) = U_0 + \mathcal{E}_a(h'x + \eta'x^2 + t'x^3 + x^4). \quad (4)$$

The fluctuating coefficients for the linear, quadratic and cubic terms are determined by the expressions

$$h' = (6\beta - 12\alpha)/1694A, \quad \eta' = (78A - 21B)/847A, \\ t' = (-182\alpha + 28\beta)/847A. \quad (5)$$

The root-mean-square fluctuation in bond lengths in a glass is of the order of 10%. In this case, the corresponding fluctuations of the coefficients A and B are of the same order. Then the typical fluctuations of the coefficients h' and t' are, correspondingly, 10^{-3} and 10^{-2} . We emphasize that for our use of x , the coefficient of the quadratic term, η' , can have either sign.

We are interested in only those cases when the potential $U(x)$ is weak, that is, corresponds to the TLS with not-too-high barriers, which a particle can pass over in a time less than that of experiment. The conditions on the weakness of the potential have the form

$$|\eta'| \ll \eta_L, \quad |t'| \ll \eta_L^{1/2}, \quad |h'| \ll \eta_L^{1/2}, \quad (6)$$

where

$$\eta_L = (\hbar^2/2Ma^2\mathcal{E}_a)^{1/2},$$

and M is the mass of the central atom.

The characteristic energy scale W , given by the potential (4), for which the conditions (6) are fulfilled is of the order of¹⁾

$$W \approx \mathcal{E}_a \eta_L^{1/2} \ll \mathcal{E}_a. \quad (7)$$

An estimate for the triatomic molecule with a 2 eV bond energy, $a = 2 \text{ \AA}$ and M that of oxygen gives $\eta_L = 2 \times 10^{-3}$. Thus we see that in the case considered, of fluctuations in h'

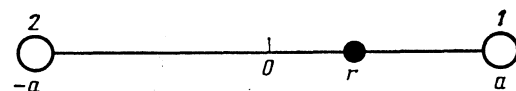


FIG. 1.

(due to fluctuations in atomic bond lengths) greater than $\eta_L^{3/2}$, and fluctuations in t' less than $\eta_L^{1/2}$, there are no great disparities.

For the energy W in Eq. (7) we find an estimate of 100 K. This is a comparatively large energy. If we look at other TLS models, taking into consideration that they are related to, for example, the bending of a certain bond or the rotation of some atomic cluster as a whole (for example, the rotation of a tetrahedron in melting quartz, which Buchinau⁷ considered) this energy can be smaller.

We go over now from Eq. (4) for the potential energy to the standard form (not containing the linear term⁵), by shifting the reference origin:

$$U(x) = \mathcal{E}_0 [\eta(x-\delta)^2 + t(x-\delta)^3 + (x-\delta)^4] + \text{const}, \quad (8)$$

where

$$\delta = (t-t')/4.$$

The relation between the coefficients of the Hamiltonians has the form

$$h' - \frac{t'}{2} \left(\eta' - \frac{t'^2}{4} \right) = -\frac{t}{2} \left(\eta - \frac{t^2}{4} \right), \quad \eta - \frac{3}{8} t^2 = \eta' - \frac{3}{8} t'^2. \quad (9)$$

To work with the Hamiltonian of Eq. (8), we need to know the distribution function of the parameters η and t . We will relate it to the distribution of the parameters h' , η' , t' . Since in our example the t' distribution is narrow (compared to $\eta_L^{1/2}$) we will set $t' = 0$. The Jacobian of the transformation is

$$\left. \frac{\partial(h', \eta')}{\partial(\eta, t)} \right|_{t'=\text{const}} = \frac{\eta}{2}. \quad (10)$$

Let the distribution of the parameters h' and η' have the form

$$\Psi(h', \eta'). \quad (11)$$

Then, in agreement with Eq. (10), the distribution of the parameters η and t is

$$\left| \frac{\eta}{2} \right| \Psi \left[\frac{t}{2} \left(\eta - \frac{t^2}{4} \right), \eta - \frac{3}{8} t^2 \right], \quad (12)$$

that is, the new distribution function contains $|\eta|$ as a multiplier and for a nonsingular function $\Phi(h', \eta')$ goes to zero at $\eta = 0$. This is a general statement and according to the derivation does not depend on the choice of the double-well potential model under consideration.⁶ The specific example given serves only as an illustration. The distribution function goes to zero for the parameter $\eta = 0$ because the form of the potential in Eq. (4) with $\eta' = t' = 0$ is unusually sensitive to any external influence. The values of the parameters η and t after the displacement in Eq. (8) are expressed as nonanalytic functions of the parameter h' : $\eta \sim (h')^{2/3}$, $t \sim (h')^{1/3}$.

3. Thus, from our point of view, there are two types of glasses. In glasses of type I there is a broad distribution of asymmetry parameters h' in comparison with the size of $\eta_L^{3/2} T/W$ (T is temperature). In these glasses it is natural to take the distribution Φ to be smooth, and then the distribution function is proportional to $|\eta|$.

In type II glasses $\Phi(h', \eta')$ is a sharply peaked function of the first argument. In this case it is possible to put the

distribution function in the form given in Ref. 5 and used in Refs. 3 and 4.

Exactly which of these situations is realized in fact depends on the specific form of the glass. The only way to answer this question is to experimentally investigate those properties that depend on the detailed behavior of the distribution function, such as the specific heat, thermal expansion and several others (for example, thermal radiation).

In conclusion we present results for a type I glass which was found by the same method as in Refs. 3 and 4. The coefficient of thermal expansion is

$$\alpha = -\frac{\gamma \Psi(0, 0) k_B^2 T \eta_L^{1/2}}{KW} \times \left[\frac{1}{\ln^{1/2}(W/k_B T)} - \frac{\gamma_1}{[\ln(W/k_B T) + 1/2 \ln(\tau_{\text{exp}}/\tau_{\text{min}})]^{1/2}} \right]. \quad (13)$$

Here γ and γ_1 are dimensionless constants of order unity; γ may have either sign; K is the modulus of hydrostatic compression and τ_{min} is the minimum relaxation time for a TLS with a level separation $k_B T$. The specific heat is

$$C \propto T \left(\ln \frac{W}{k_B T} + \frac{1}{2} \ln \frac{\tau_{\text{exp}}}{\tau_{\text{min}}} \right)^{1/2}, \quad (14)$$

so that the Grüneisen parameter $\Gamma = \alpha K / C$ tends to zero for $\tau_{\text{exp}} \rightarrow \infty$, if there is no cutoff in the η -distribution function for η large in absolute value and negative (cf. Ref. 1).

Thus, in the present work and in Refs. 3 and 4 we have considered the low-temperature thermal expansion of glasses on the basis of two different models. Both models yield a large value for the Grüneisen coefficient. This is an essential difference between glasses and crystals, which have in theory (as in experiment) small values of the Grüneisen coefficient. The chief reason for this difference is that in the theory of glasses there appear large logarithmic terms as well as large values of η_L^{-1} , which determine a large Grüneisen parameter. The physics of this is tied to the weakness of the potentials which give rise to a TLS, which inescapably leads to a large anharmonicity.

As Anderson *et al.*^{8,9} correctly note, various values of Γ —from several tens to unity—are observed in experiment. Therefore it is natural to ask the questions: which is more surprising, from the theoretical point of view, and which is in need of more explanation—large or small values of Γ ? In our opinion, on the basis of what has been said, an explanation of small values of Γ in glasses is needed.

One possible explanation is the presence in glasses of several types of TLS, which could give contributions of different signs to Γ , and cancel each other. Another explanation would be the presence of defects. As shown by a series of experiments,⁹ the introduction of defects in a glass reduces the value of Γ . The physics of this influence of defects is still unclear, but there is no doubt as to the facts. In this connection, we feel that it would be extremely desirable, in those cases when the Grüneisen parameter is small, to independently control the defect concentration. Such experiments could then be used to analyze why the low-temperature thermal expansion of glasses (as opposed to such properties as, for instance, the specific heat or sound absorption) is so sensitive to defect concentration.

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¹Since we are interested in the resolution of the TLS with $E \approx T \ll W$, coefficients proportional to the power of $\ln W/T$ may arise on the right-hand side of the inequality (6).

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