Thermodynamic and kinetic properties of amorphous dielectrics at low temperatures

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It is shown that it is important to take account of the influence of vibrations of the medium on the tunneling of heavy particles in a two-level system when studying relaxation processes in glasses. Zero-point vibrations increase the probability of tunneling by several orders of magnitude. As the temperature is raised, single-phonon processes first give a contribution and then multiphonon processes. The periodic reduction in the potential barrier by vibrations of the medium plays an appreciable role. With this mechanism the double-peaked temperature dependence of the inverse ultrasonic attenuation length can be explained and also the temperature dependence of the thermal conductivity and of the luminescence intensity (the so-called "inverse Arrhenius law").

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INTRODUCTION

The discovery of anomalous low-temperature behavior of the heat capacity and thermal conductivity of amorphous dielectrics[1–4] required a radical reconsideration of the structure of low-frequency vibrations in such systems. For explaining these anomalies the hypothesis was put forward[5,6] that the low-temperature behavior of dielectric glasses is mainly determined by so-called two-level systems. Its main assumption is that as a result of reordering of the crystal lattice it is possible for a few atoms (or a group of atoms) to tunnel between two states which are close together in energy. Excitation of such two-level systems produces a contribution linear in temperature to the heat capacity. Scattering of phonons by them determines the low-temperature behavior of thermal conductivity and ultrasonic damping, while the attenuation of an electromagnetic field determines anomalies in the temperature dependence of the real and imaginary parts of the dielectric susceptibility.[7,8] A similar model was used to explain some unusual properties of quantum liquids.[9] A more complete list of the literature can be found in a recent review.[10]

In spite of the considerable successes of the theory based on the model of two-level systems, however, the overall situation can still not be considered satisfactory. The absence of a consistent microscopic model of the two-level systems themselves is a great shortcoming of the theory. This is in spite of the fact that many different variants have up to now been proposed. For example, Phillips[11] discusses five types of two-level systems, while Duffy and Rivier[12] even consider a highly exotic model based on the Yang-Mills theory. There is, nevertheless, so far no serious basis for choosing one of these variants. As a result, a certain arbitrariness remains in the choice of the parameters of the two-level system and in interpreting the observed phenomena.

A quantitative comparison of the deductions from theory and the experimental data also gives not altogether satisfactory results. For example, Anderson *et al.*[6] pointed out that they were forced to use a very low value of the height of the potential barrier ($V_b < 0.2$ eV for an oxygen atom) to obtain agreement with the results of measuring heat capacity.[3] Stephens[13] collected and discussed in detail results on the heat capacity and thermal conductivity of a large number of glasses and indicated a number of difficulties he encountered in interpreting these data. For example, on introducing impurities into such glasses as As_2S_3, B_2O_3 and $CaK(NO_3)_3$, the heat capacity was changed by a factor of one and a half to two, while the thermal conductivity did not change at all. It is difficult to understand this from the point of view of the standard two-level system theory,[5,6] according to which both quantities should be produced by the same mechanism. By calculating the density of two-level systems from results on heat capacity and then finding the probability of interaction between a phonon and the separate system, Stephens[13] concluded that this probability must be anomalously high. The plateau in the temperature dependence of the thermal conductivity in the region of a few Kelvins also requires an explanation. We note that Matey and Anderson[14] found an analogous plateau in the phonon part of the thermal conductivity of a metallic glass (an alloy of palladium and silicon).

A peculiar double-peaked curve of the temperature dependence of inverse attenuation length was found in studies of ultrasonic attenuation in glasses.[15–17] The model proposed by Jäckle *et al.*[17] to explain it seems unconvincing to us and contains too many artificial assumptions. We should remember that there is yet another experimental fact which is not explained by standard two-level system theory, namely the unusual temperature dependence (inverse Arrhenius law) of the intensity of luminescence in g-As_2S_3 glass.[18]

It seems to us that one of the important reasons for such a situation must be the application of an inadequate theory of tunneling transitions in two-level systems. Because of this not nearly all the observed effects can be analyzed with the model.[5,6] In particular, difficulties thus arose in interpreting the temperature dependence of the inverse ultrasonic attenuation length[17] and in discussing the temperature dependence of the luminescence intensity.[19,20] In describing tunneling transitions in two-level systems, the model developed by Sussmann[21] is usually used, in which tunneling processes

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involving only a single phonon are considered, while the possibility of two or more phonons taking part were only considered in connection with transitions taking place via an intermediate real state. The role of zero-point vibrations was not taken into account at all. In addition, out of several different means of exciting two-level systems discussed by Sussman,[20] one was chosen without a particular basis, corresponding to "diagonal perturbation" of the potential under the action of a phonon wave[22] (see also Refs. 10 and 17). To first order in the interaction only a change in particle energy in a separate well takes place then, while transitions between wells appear in second order (the so-called "relaxation mechanism").

In actual fact there is besides this mechanism a much stronger "nondiagonal" interaction which corresponds to a change in the penetrabiltiy of the barrier for vibrations of the two-level system. The wells then periodically get close and because of the exponential dependence of the tunneling probability on the distance between the wells, this can lead to a noticeable increase in it.[23] As a result, the one-phonon approximation hardly ever works. Just considering zero-point vibrations can increase the probability of tunneling even for $T = 0$ by several orders of magnitude.[24] For these reasons its temperature, frequency and other dependences also differ greatly from Sussman's results.[21] This difference becomes specially marked at relatively high temperatures ($T > 10$ K), when short-wave and optic modes of vibration start to be excited, which lead to very strong approaches of the wells. At even higher temperatures they can approach so much that the potential barrier disappears. We note that this mechanism is very similar to the fluctuational barrier "preparation" mechanism which was discussed by Kagan and Klinger[25] in the problem of quantum diffusion of heavy particles along a regular lattice of equivalent wells.

In view of everything said above it is essential to carry out afresh an analysis of the main propositions of the model of two-level systems[5,6] since there is every reason to think that many of them are changed appreciably by taking account of the mechanism discussed above.[23–25] We have given[26] some preliminary results of such an analysis and demonstrated the large influence exerted on the process of ultrasonic attenuation by interaction of two-level systems with vibrations of the medium. In the present work we consider the temperature and time dependence of the heat capacity of amorphous dielectrics, and also the temperature dependence of thermal conductivity, ultrasonic attenuation, and luminescence intensity. In doing this we shall start from the same basic assumptions about the role of two-level systems in low-temperature processes which take place in amorphous dielectrics, as previous authors,[5,6] but will take more correct account of the influence of vibrations of the medium on the probability of tunneling transitions. This will allow us to rid the theory of a number of difficulties mentioned above, and also to explain many features of the behavior of thermodynamic and kinetic characteristics of glasses without introducing any additional assumptions.

2. GENERAL RELATIONS

We shall calculate below the constants of the tunneling transition rate in a two-level system, taking account of vibrations of the medium. Suppose a particle of mass m moves in the two-well potential shown in Fig. 1. Since we have no adequate microscopic model of the two-level systems, we shall suppose that in talking about a particle we are referring to the motion along some generalized coordinate Q which is appropriate to the mass m. We assume that we can divide our system into three subsystems: a fast electron subsystem, a slower subsystem corresponding to oscillations of a particle in the potential of Fig. 1, and a still slower phonon subsystem. In that case we can make use of the double adiabatic approximation and separate the variables corresponding to the three susbsystems. The rate constant for a transition from well 1 to well 2 can then be written in the form

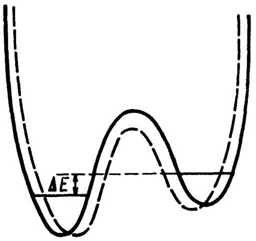

FIG. 1. Potential energy of a tunneling particle. The dashed line shows the change in the potential barrier as the wells approach one another.

$$K=\frac{2\pi}{\hbar}Av_i\sum_f|\langle\{\nu_f\};2|\hat{M}|1;\ \{\nu_i\}\rangle|^2\delta(E_i-E_f). \tag{1}$$

Here $|\alpha', \{\nu\}>$ indicates in which well the particle is and the state of the phonon subsystem then; E_i and E_f are the initial and final energies of the whole system. We neglect changes taking place in the characteristics of the phonon subsystem during the transition of the particle from well to well.

The form of the operator $\hat{M}$ depends on just which process interests us. If it is a fluctuational (without external interaction) transition, it can be for example the matrix element of an operator nonadiabatic in the electron wave functions. We shall also be interested in particle tunneling processes from one well to the other, accompanied by absorption or emission of a certain long-wave phonon in an interaction, for example, with an ultrasonic wave. During the passage of such a wave both wells shift practically parallel to one another, i.e., the interaction of a phonon with the two-level system due to the approach of the wells is small in this case. The attenuation of long-wave phonons will, therefore, only be related to the first terms in the expansion of operator $\hat{M}$ in the corresponding phonon coordinates q_λ. Strictly speaking, terms corresponding to mode λ should simultaneously be excluded from the sum in Eq. (1). We shall not however do this because the corresponding corrections are small on the macroscopic scale. There is an appreciable correction because the energy of the absorbed (emitted) external phonon must be taken into account in the energy balance explicitly, i.e., in Eq. (1) $\delta(E_i - E_f)$ must be replaced by $\delta(E_i - E_f \pm \hbar\omega_\lambda)$.

Independently of the type of process, the matrix element of the operator can be written in the form

$$\langle 1|\hat{M}|2\rangle=V\exp[-{}^1/{}_2J(\{q_\mu\})], \tag{2}$$

where a smooth function of its variables occurs in the exponent. This function is large for tunneling of a heavy particle; its change, because of phonon vibrations, can therefore lead to a very great change in the matrix element of Eq. (2). In principle a cross-over situation can then arise when the main contribution to the tunneling process comes from the region of values of $\{q_\mu\}$ which are far from equilibrium.[25] As a result, calculation of the tunneling transition rate constant meets with great technical difficulties, especially if we are interested in a wide temperature range. We shall therefore consider a simplified model of the situation when the exponent can be represented in the form of a function of second order in the variable q_μ[27]:

$$J(\{q_\mu\})=\sum_\mu A_\mu q_\mu+{}^1\!/_2\sum_{\mu\mu'} B_{\mu\mu'}q_\mu q_{\mu'}. \tag{3}$$

The quantity V then characterizes a process in which phonon vibrations are neglected. With this approximation, the calculations can be carried out to the end, preserving all the main qualitative features of the processes studied. One has to exercise caution, however, in interpreting Eq. (3) as an expansion of the function $J(\{q_\mu\})$ in a Taylor series, since it can lead to noticeable quantitative errors, especially at high temperatures.

Representing the phonon subsystem in the form of a collection of independent oscillators, we can rewrite Eq. (1) in the form

$$K=\frac{V^2}{\hbar}\int_{-\infty}^{\infty} dv\prod_{\mu\mu'}\int dq_{1\mu}dq_{2\mu}\rho_\mu(\beta+iv;\, q_{1\mu},\, q_{2\mu})\rho_\mu(iv;\, q_{1\mu},\, q_{2\mu})$$

$$\times Z_\mu^{-1}(\beta)\,e^{iv\Delta\tilde{E}}M_{12}(q_{1\mu})M_{21}(q_{2\mu}), \tag{4}$$

where

$$\rho_\mu(\beta;\, q_{1\mu},\, q_{2\mu})=\sum_{n_\mu=0}^{\infty}|n_\mu\rangle\exp(-\beta E(n_\mu))\langle n_\mu|$$

the equilibrium density matrix corresponding to phonon mode μ at temperature $kT=1/\beta$; k is Boltzmann's constant and $Z_\mu(\beta)$ the corresponding partition function. In deriving Eq. (4) we have used the integral representation of the δ-function.[28] The choice of the magnitude of $\Delta\tilde{E}$ depends on which process is being considered. For a fluctuational transition $\Delta\tilde{E}=\Delta E=E_2-E_1$, where ΔE is the change in energy of a particle on going from well 1 to well 2. In the case of a transition accompanied by the capture (emission) of an external phonon, $\Delta\tilde{E}=\Delta E\pm\hbar\omega_\lambda$.

If we limit ourselves to the harmonic approximation for phonon vibrations, we can use for the density matrix ρ_μ the well known expression (see, for example, Feynman[29]). Substituting Eqs. (2) and (3) into Eq. (4) and integrating over the variables $q_{1\mu}$ and $q_{2\mu}$ we find the tunneling transition rate constant[27]

$$K=\frac{V^2}{\hbar}\int_{-\infty}^{\infty} dv\{\det\Phi\}^{-1/2}$$

$$\times\exp\left\{\Delta\tilde{E}\left(v+\frac{i\beta}{2}\right)+\frac{1}{4}\sum_{\mu\mu'}A_\mu C_{\mu\mu'}^{-1}A_{\mu'}\right\}, \tag{5}$$

where

$$C_{\mu\mu'}={}^1\!/_2B_{\mu\mu'}+2\delta_{\mu\mu'}\,\mathrm{sh}(\hbar\beta\omega_\mu/2)\,[\mathrm{ch}(\hbar\beta\omega_\mu/2)-\cos(\hbar v\omega_\mu)]^{-1}.$$

$$\Phi=\{\delta_{\mu\mu'}+{}^1\!/_4B_{\mu\mu'}[\mathrm{ch}(\hbar\beta\omega_{\mu'}/2)+\cos(\hbar v\omega_{\mu'})]\,[\mathrm{sh}(\hbar\beta\omega_{\mu'}/2)]^{-1}\}$$

$$\times\{\delta_{\mu\mu'}+{}^1\!/_4B_{\mu\mu'}[\mathrm{ch}(\hbar\beta\omega_{\mu'}/2)-\cos(\hbar v\omega_{\mu'})]\,[\mathrm{sh}(\hbar\beta\omega_{\mu'}/2)]^{-1}\}.$$

If we take $B_{\mu\mu'}=0$ and $\Delta\tilde{E}=0$ in Eq. (5) and understand Eq. (3) as an expansion in small displacements near the crossing point, then the magnitude of Eq. (5) coincides with expressions (3.3) and (3.10) of Kagan and Klinger[25] under the condition that we neglect the polaron effect.

Equation (5) can be simplified in two cases. First, for temperatures low compared with the Debye temperature, the quantity $B_{\mu\mu'}$ can be neglected; then

$$K=\frac{V^2}{\hbar}\exp\left\{-\frac{\beta\Delta\tilde{E}}{2}+\frac{1}{8}\sum_\mu|A_\mu|^2\,\mathrm{cth}\left(\frac{\hbar\beta\omega_\mu}{2}\right)\right\}$$

$$\times\int_{-\infty}^{\infty}dv\exp\left\{+i\Delta\tilde{E}v+\frac{1}{8}\sum_\mu|A_\mu|^2\cos(\hbar v\omega_\mu)/\mathrm{sh}\left(\frac{\hbar\beta\omega_\mu}{2}\right)\right\}. \tag{6}$$

At higher temperatures it is essential to take $B_{\mu\mu'}$ into account, but we can then use the Einstein model of the phonon spectrum and obtain

$$\begin{gathered}K=\frac{2\pi V^2}{\hbar\Omega\varphi_3^{1/2}}\exp\left[-\frac{\beta\Delta\tilde{E}}{2}+\varphi_1(1-\varphi_2)\right]I_0(\varphi_1\varphi_2),\\ \varphi_1=\frac{\hbar J'^2}{4M\Omega}\left[\mathrm{th}\left(\frac{\hbar\beta\Omega}{4}\right)+\frac{\hbar J''}{2M\Omega}\right]^{-1},\\ \varphi_2=\frac{2M\Omega}{\hbar J'^2}\frac{\varphi_1\,\mathrm{sh}(\hbar\beta\Omega/4)}{\mathrm{ch}^3(\hbar\beta\Omega/4)},\\ \varphi_3=\left[1+\frac{\hbar J''}{2M\Omega}\mathrm{cth}\left(\frac{\hbar\beta\Omega}{4}\right)\right]\left[1+\frac{\hbar J''}{2M\Omega}\mathrm{th}\left(\frac{\hbar\beta\Omega}{4}\right)\right].\end{gathered} \tag{7}$$

Here $I_0(x)$ is a Bessel function of imaginary argument, Ω is the Einstein frequency, and the primes on J indicate differentiation with respect to $\Delta R=R_2-R_1$, where R_2 and R_1 are the coordinates of the wells of the two-level system and M is a characteristic mass determining the phonon spectrum of the glass.

3. HEAT CAPACITY

The anomalous behavior of heat capacity in amorphous dielectrics, $C\sim T$, observed by Zeller and Pohl[3] served as the main impetus in developing the two-level system model.[5,6] A linear law for heat capacity comes directly from the assumption that the density of two level systems $n(\Delta E)$ with a given value of ΔE is practically constant over some range of values $\Delta E<\Delta E_0$. For sufficiently low temperatures we then have[5,6]

$$C(T)=(\pi^2/6)\,n(0)\,k^2T,\quad kT<\Delta E_0. \tag{8}$$

Heat capacity is a thermodynamic quantity and, strictly speaking, it should be evaluated for a system which has already reached equilibrium. However, it is a feature of amorphous systems that they cannot be characterized by a single relaxation time. Each two-level system with a given ΔE can have its own value for the transparency parameter of the barrier. This means that the value of

$$V=\hbar\nu\exp[-J_0/2] \tag{9}$$

varies as a result of the change in the parameter J_0. (Variations in the parameter $\nu \sim 10^{13}$ s^{-1} play no special role.) If the scatter in J_0 is large enough, then in practice for any observation time two-level systems will be found with such a large value of J_0 that relaxation will still not have had time to take place. The amount of energy accumulated by the two-level systems at a given temperature therefore increases all the time. In this sense, heat capacity is a kinetic quantity, dependent on time.

We shall assume that the glass, originally in equilibrium, is heated "rapidly" to some higher temperature T. In the present case "rapidly" means in a time shorter than the smallest relaxation times in the two-level systems. We are interested in the amount of energy $E(t)$ which the glass absorbs during a time t. The probability of populating the higher-energy state of a two-level system characterized by the parameters ΔE and J_0 is of the form

$$f(t,\ T)=f_0(T)\{1-\exp[-K^*(\Delta E,\ J_0,\ T)t]\}, \tag{10}$$

where

$$f_0(T)=[1+\exp(\beta\Delta E)]^{-1},\quad K^*=K_\uparrow+K_\downarrow,$$

and $K_\uparrow$ and $K_\downarrow$ are transition rate constants for processes with increasing or lowering of the energy of the two-level system.

The total energy $E(t)$ can be found by multiplying Eq. (10) by ΔE and averaging over the parameters ΔE and J_0, which gives

$$E(t)=n(0)\int\limits_0^{\Delta E_0} d(\Delta E)\Delta E\int\limits_{J_{min}}^{J_{max}} dJ_0 f_0(T)\{1-\exp[-K^*t]\}. \tag{11}$$

At low temperatures, when

$${}^1/_8\sum_\mu |A_\mu|^2\cos(\hbar\omega_\mu v)/\mathrm{sh}(\beta\hbar\omega_\mu/2)\ll 1,$$

the exponential under the integral in Eq. (6) can be expanded in a series. (A quantitative evaluation of this temperature region will be carried out below). Carrying out the integration over v then, we obtain

$$K=\frac{2\pi V^2}{\hbar}\exp\left[-\frac{\beta\Delta E}{2}+\sum_\mu |A_\mu|^2\,\mathrm{cth}\left(\frac{\beta\hbar\omega_\mu}{2}\right)\right]$$

$$\times\left\{\delta(\Delta\tilde{E})+\frac{1}{16}\sum_\mu\frac{A_\mu|^2[\delta(\Delta\tilde{E}-\hbar\omega_\mu)+\delta(\Delta\tilde{E}+\hbar\omega_\mu)]}{\mathrm{sh}\left(\frac{\beta\hbar\omega_\mu}{2}\right)}\right\}. \tag{12}$$

Only fluctuational transitions contribute to the heat capacity, i.e., $\Delta\tilde{E}=\Delta E$. The term in Eq. (12) is then proportional to $\delta(\Delta E)$. Further,

$$A_\mu=\mathbf{J}'(\partial\mathbf{R}_2/\partial q_\mu-\partial\mathbf{R}_1/\partial q_\mu)=\mathbf{J}'(\hbar/M\omega_\mu)^{1/2}[\mathbf{a}_\mu{}^2-\mathbf{a}_\mu{}^1], \tag{13}$$

$$\mathbf{a}_\mu{}^n=\frac{\mathbf{e}_\mu}{N^{1/2}}\exp(ik\mathbf{a}_n),\qquad \mathbf{a}_n=(a_xn_x,\ a_yn_y,\ a_zn_z).$$

Here $\mathbf{e}_\mu$ is the polarization vector of the phonon, N the number of atoms, $a_{x,y,z}$ is the interatomic distance. The sum over μ in Eq. (12) can be found in the Debye approximation. The first sum is

$$J_1=\frac{1}{8}\sum_\mu |A_\mu|^2\,\mathrm{cth}\left(\frac{\beta\hbar\omega_\mu}{2}\right)=\frac{3\hbar J'^2}{4Mq_D{}^3}\int\limits_0^{q_D} dk\frac{k^2}{\omega_k}$$

$$\times\left[1-\left(\frac{q_D}{\pi k}\right)\sin\left(\frac{\pi k}{q_D}\right)\right]\mathrm{cth}\left(\frac{\beta\hbar\omega_k}{2}\right) \tag{14}$$

or at $T=0$

$$J_1=\frac{3}{8}\left(1-\frac{4}{\pi^2}\right)\frac{\hbar J'^2}{Mq_Ds}.$$

The second sum is

$$\frac{1}{16}\sum_\mu |A_\mu|^2[\delta(\Delta E-\hbar\omega_\mu)+\delta(\Delta E+\hbar\omega_\mu)]/\mathrm{sh}\left(\frac{\beta\hbar\omega_\mu}{2}\right)$$

$$=\frac{\pi^2J'^2|\Delta E|^3}{8\hbar^3M(sq_D)^5}[\exp(\beta|\Delta E|)-1]^{-1}\exp\left(\frac{\beta|\Delta E|}{2}\right). \tag{15}$$

In these latter equations q_D is the Debye momentum and s the velocity of sound.

The appearance of the quantity J_1 in the expression for the rate constant for a tunneling transition is due to the influence of zero-point phonon vibrations. In Eqs. (9) and (10) J_0 must be replaced by an appreciably smaller quantity $J^*=J_0-J_1$. The corresponding growth in K arises because the wells approach one another under the influence of zero-point vibrations of short-wave or optic phonons and the transparency of the barrier increases.

We transform Eq. (11) with the help of Eqs. (12) to (15) into

$$E(t)=n(0)\int\limits_0^{\Delta E_0} d(\Delta E)\,\Delta E f_0(\beta\Delta E)$$

$$\times\int\limits_{J^*_{\min}}^{J^*_{\max}} dJ^*\{1-\exp[-\hbar^2\nu^2\alpha e^{-J^*}\Delta E^3\times\mathrm{cth}(\beta\Delta E/2)\,t]\}, \tag{16}$$

where $\hbar\alpha/2\pi$ is equal to the coefficient in Eq. (15), independent of ΔE. The expression in curly brackets in Eq. (16) can be approximated by a step function, which is equal to unity for $J^*<J_b$ and zero for $J^*>J_b$, where

$$J_b=\ln[\hbar^2\nu^2\alpha\Delta E^3\,\mathrm{cth}(\beta\Delta E/2)\,t]. \tag{17}$$

The boundary value of J_b separates the two-level systems in which relaxation has already taken place from systems still in equilibrium. With this approximation we can carry out the integration in Eq. (16) and find the energy accumulated in the glass during times for which

$$J^*_{min}<J_b(t)<J^*_{max}.$$

By differentiating with respect to temperature, we find an expression for the heat capacity

$$C(T,t)=(\pi^2/6)n(0)k^2T\ln[t/\tau^*(T)], \tag{18}$$

where

$$1/\tau^*(T)=\alpha\hbar^2\nu^2(kT)^3\exp[-J^*_{min}+3]. \tag{19}$$

In deriving Eqs. (18) and (19) we assumed that

$$J^*_{min}>2\ln(\hbar\nu/\Delta E),$$

i.e., that renormalization of the energy difference ΔE, due to tunneling of particles between wells in the two-level system, is small. Such a situation is possible if there is a lower limit to J_0, $J_0 \gg J_{\text{str}}$, because of the properties of the macroscopic structure of the two-level systems. Expression (19) obtained above, in which $J^*_{\text{str}} = J_{\text{str}} - J_1(T)$ had to be substituted for $J^*_{\min}$, will then be valid at temperatures

$$kT > \hbar\nu \exp[-J^*_{str}/2].$$

At lower temperatures, renormalization of the magnitude of ΔE due to tunneling of particles between the wells becomes large and it is necessary to make use of the approach developed by Jäckle *et al.*[17] A different coefficient of proportionality then appears in Eq. (19). It is, however, necessary for this that there should not be a structural lower limit to the spread of ΔE, i.e., two-level systems should exist with

$$\Delta E < \hbar\nu \exp[-J^*_{str}/2].$$

Such a limit can arise if the distribution of values of J_0 has a sufficiently sharp peak near J_{str}. The fact that in many cases a time dependence of the heat capacity is generally not observed, or only observed for very small times $t < 10\,\mu\text{s}$,[30] is evidence in favor of this assumption (see the discussion by Smolyakov and Khaĭmovich[10]). As we shall see below, there are other experimental facts which indicate the existence of J_{str}. We can already give a quantitative evaluation however. From the fact that the temperature dependence of Eq. (19) is followed down to a temperature ~ 20 mK, there follows the inequality $J_{\text{str}} \gtrsim 15$.

This requirement is realized if a typical two-level system is characterized by the following parameters: barrier height $V_b \approx 0.5$ eV, mass of the tunneling particle $m \approx 16$ (carbon) mass units, Debye temperature $\Theta \approx 150$ K, characteristic mass determining the phonon spectrum, $M \approx 60$ mass units, barrier width $\Delta R \approx 0.5$ Å. Then $J_0 \approx 50$, $J' \approx 200$ Å^{-1} and $J^* \approx 20$. The renormalization of the barrier penetration parameter J_0 due to zero-point vibrations is then so large that to calculate it one must make use of Eq. (7) for $T = 0$ obtained for $J'' \neq 0$ (assuming $J'' \approx 400$ Å^{-2}). We shall use these parameters below for quantitative calculations. The main parameter of our problem is then the large dimensionless quantity

$$R = \hbar J'^2 / M\omega_D \approx 200,$$

which characterizes the coupling of phonons to the two-level system.

4. ULTRASOUND ATTENUATION

The attenuation of the ultrasound in glass at low temperatures is due to its absorption by the two-level systems. We shall confine ourselves below only to the case of relatively low frequencies when on the passage of the sound wave the two-level system is displaced parallel to itself, while the form of the potential well is hardly distorted. The sound then interacts weakly with the two-level system and Eq. (4) can be used with $\Delta\tilde{E} = \Delta E \pm \hbar\omega_\lambda$. Such an approximation can prove unsatisfactory at high frequencies since the attenuation by the two-level system becomes nonlinear due to the strong oscillation of the wells. This regime will be considered separately.

Expression (12) can be used at low temperatures to calculate the probability of capture of an ultrasonic phonon $\hbar\omega_\lambda$ by the two-level systems. The first term in it, proportional to $\delta(\Delta E \pm \hbar\omega_\lambda)$, corresponds to resonant absorption (emission) of a phonon $\hbar\omega_\lambda$. Such processes determine the finite ultrasound attenuation at $T = 0$. The corresponding inverse attenuation length is of the form

$$l_\lambda^{-1}(T) = s^{-1}(2\pi/\hbar)\overline{V}_\lambda^2 n(\hbar\omega_\lambda) e^{J_1(T)} \operatorname{th}(\beta\hbar\omega_\lambda/2). \tag{20}$$

To find the amplitude, V_λ, of the interaction of phonon $\hbar\omega_\lambda$ with a two-level system it is sufficient to expand the matrix element of Eqs. (2) and (9) in terms of the corresponding normal coordinate. Averaging $|V_\lambda|^2$ over the orientations of the axis of the two-level system, we obtain

$$\overline{V_\lambda^2} = \gamma\hbar^2\nu^2 e^{-J_0}, \qquad \gamma = (\pi^2/20)(\omega_\lambda/\omega_D). \tag{21}$$

As the temperature increases, nonresonant single-phonon ultrasound absorption starts to become appreciable besides the resonant processes of Eq. (20). Then $\hbar\omega_\lambda \neq |\Delta E|$ and the energy defect is covered by absorption or emission of a single phonon from the thermal reservoir. Four different elementary processes are possible, differing from one another in whether a lowering or raising of the energy of the two-level system occurs and whether an ultrasonic phonon is emitted or absorbed.

Summing all these processes with the corresponding statistical weights, we obtain for two-level systems with a given ΔE:

$$l_\lambda^{-1}(T) = l_{\lambda 1}^{-1}(T) + l_{\lambda 2}^{-1}(T),$$

$$\begin{aligned} l_{\lambda 1}^{-1} &= s^{-1}[K_{\lambda\uparrow}(\hbar\omega_\lambda) - K_{\lambda\downarrow}(-\hbar\omega_\lambda) \\ &\quad \times \exp(-\beta|\Delta E|)][1+\exp(-\beta|\Delta E|)]^{-1} \\ &= n(\Delta E)\frac{\pi^3 R\overline{V_\lambda^2} e^{J_1}}{4\hbar s(\hbar\omega_D)^4}|\Delta E - \hbar\omega_\lambda|^3[\exp(\beta\hbar\omega_\lambda) - 1] \\ &\quad \times [1-\exp(-\beta|\Delta E - \hbar\omega_\lambda|)]^{-1}[1+\exp(\beta|\Delta E|)]^{-1}. \end{aligned} \tag{22}$$

The expression for $l_{\lambda 2}^{-1}(T)$ differs from $l_{\lambda 1}^{-1}(T)$ by the change in sign of $\hbar\omega_\lambda$ which at the same time indicates that an ultrasonic phonon $\hbar\omega_\lambda$ is absorbed (+) or emitted (−).

Two limiting cases should be distinguished in Eq. (22). For $kT \ll \hbar\omega_\lambda$ only one of the four processes gives an appreciable contribution in which capture of an ultrasonic phonon takes place, accompanied by lowering of the two-level system's energy. In this case the inverse attenuation length grows linearly with temperatures, since only systems with $\Delta E \lesssim kT$ take part and their number is proportional to T. We have, after averaging over ΔE

$$l_\lambda^{-1}(T) = \frac{\pi^3 \ln 2}{4} n(0) R \frac{\overline{V_\lambda^2}}{\hbar s}\left(\frac{\omega_\lambda}{\omega_D}\right)^3 \frac{T}{\Theta} e^{J_1(T)}. \tag{23}$$

(At the end of this section we shall consider questions related to averaging over the barrier-transparency parameter J_0.)

A different situation arises for $kT \ll \hbar\omega_\lambda$. We can then expand in terms of the small parameter $\beta\hbar\omega_\lambda$ in Eq. (22), in this case

$$l_{\lambda 1}^{-1}(T) = l_{\lambda 2}^{-1}(T)$$

and

$$l_\lambda^{-1} = \frac{\pi^7}{32} n(0) R \frac{\overline{V_\lambda^2}}{\hbar s} \frac{\omega_\lambda}{\omega_D} \left(\frac{T}{\Theta}\right)^3 e^{J_1(T)}. \tag{24}$$

This relation can be explained in the following way. Two-level systems with $\Delta E \lesssim kT$ give a contribution to the attenuation, and their number is proportional to T. In view of the inequality $\hbar\omega_\lambda \ll kT$, a phonon with energy $\hbar\omega_\mu \approx kT$ must be absorbed from the thermal reservoir (or emitted) in a one-phonon process. The total number of such phonons is proportional to T^2, so that we obtain the relation $l_\lambda^{-1} \sim T^3$ observed in experiments.[15–17]

We proposed earlier[26] that the increase in ultrasound absorption according to the T^3 law would stop in the region of a few Kelvins because there is a limit to the distribution $\Delta E/k \lesssim (2 \text{ to } 3)$ K, although it would be more natural to assume that this limiting value is connected to the glass-forming temperature.[6] In actual fact there is no necessity to make such a rigorous assumption about the distribution of values of ΔE, which can actually extend to arbitrarily large values. This is because the temperature dependence of the inverse ultrasonic attenuation length is described by Eq. (24) only at temperatures

$$T \ll (4/\pi^6 R)^{1/4} \Theta \approx 10 \text{ K},$$

for which the single-phonon approximation used in deriving Eq. (12) is valid. As the temperature rises, both the characteristic energy of the thermal phonons and their number increases and their effect on the two-level system becomes strong. Another approximation, equivalent to the method of steepest descent, can be used in this case.

We expand $\cos(\hbar\omega_\mu v)$ in a series up to terms of second order in v, after which the integral in Eq. (6) is easily found, and we obtain

$$K_\lambda = n(0) \Delta E_0 (\overline{V_\lambda^2}/\hbar) [2\pi/F(T)]^{1/2} \exp[-\beta\Delta \tilde{E}/2 + J_2(T)],$$

$$F(T) = \frac{1}{16} \sum_\mu |A_\mu|^2 \frac{(\hbar\omega_\mu)^2}{\mathrm{sh}(\beta\hbar\omega_\mu/2)},$$

$$J_2 = \frac{1}{8} \sum_\mu |A_\mu|^2 \,\mathrm{cth}\left(\frac{\beta\hbar\omega_\mu}{4}\right). \tag{25}$$

The parameter in this approximation is the quantity $(kT)^2/F(T)$. Comparing it to unity, we can verify that Eq. (25) is valid at temperatures

$$T \gg (\pi^8 R)^{-1/4} \Theta \approx 4 \text{ K}. \tag{26}$$

As in deriving Eq. (22), it is necessary to sum the contributions from the four processes and average the result over ΔE in order to find the ultrasonic attenuation in this regime. Then

$$l_\lambda^{-1}(T) = \frac{2n(0)\overline{V_\lambda^2}}{\pi^2 \hbar s (2\pi R)^{1/2}} \frac{\omega_\lambda}{\omega_D} \left(\frac{\Theta}{T}\right)^3 e^{J_2(T)}. \tag{27}$$

In Eqs. (26) and (25) we used the expression

$$F(T) = 2\pi^8 R (T/\Theta)^6 (\hbar\omega_D)^2,$$

which is obtained in the Debye approximation for the phonon spectrum.

The increase in l_λ^{-1} with temperature is thus changed to a decrease in proportion to T^{-3}. We do not have any formula to describe the transition region where the inverse attenuation length can pass through a maximum at $T = T_1$. Equations (24) and (27) only describe two slopes of the curve of the temperature dependence of l_λ^{-1} on either side of this maximum which lies in the temperature interval $4\text{K} < T_1 < 10$ K. This result agrees quite satisfactorily with experiment,[15–17] where the value $T_1 \approx 5$ K was obtained.

As the temperature increases, there is an increase in the number of two-level systems which take part in the scattering process. This growth, however, is offset by the factor

$$2\,\mathrm{sh}(\,\text{[illegible]}\,) \approx \hbar\omega_\lambda/kT. \tag{28}$$

On the other hand, the large number of thermal-reservoir phonons which take part only inhibits the satisfaction of the energy conservation law in elementary acts of absorption (emission) of ultrasonic phonons. They can be said to upset the resonance in the two-level system. For this reason the increase in the number of phonons with increasing temperature weakens the attenuation in proportion to T^{-3}. There is a definite similarity between this process and the process of "dynamical band destruction" which was discussed by Kagan and Maksimov.[31] It should be pointed out that the discussion there was about coherent one-phonon processes for which the state of the phonon subsystem does not change.

As the temperature increases further the $l_\lambda^{-1}(T)$ dependence passes through a minimum at

$$T_2 = \frac{2}{\pi} \left(\frac{15}{64\pi^2 R}\right)^{1/4} \Theta \gtrsim 10 \text{ K} \tag{29}$$

and starts to rise due to the exponential factor $e^{J_2}(T)$ in Eq. (27). Physically, this increase is due to the growth in the vibration amplitude of the wells in the two-level system as the temperature rises, leading to an effective lowering of the barrier. This mechanism is strong enough to produce eventually an increase in ultrasound attenuation, in spite of the stronger detuning from resonance, as discussed above. At temperatures $kT > \hbar\omega_D/4$, we already enter the classical region and $J_2(T)$ is proportional to the first power of the temperature:

$$J_2(T) = T/T_0, \quad T_0^{-1} \equiv k \sum_\mu |A_\mu|^2 (2\hbar\omega_\mu)^{-1}. \tag{30}$$

As a result, the inverse ultrasound attenuation length increases like e^{T/T_0}. For the two-level systems we have considered, $T_0 \approx 1$ K. It follows from experiments[15–17] that the increase in $l_\lambda^{-1}(T)$ should proceed more slowly. However, recognizing that one is talking about temperatures between 15 and 40 K, where the vibrations can still not be considered classical, and also the certain arbitrariness in the choice of parameters, then the agreement can be considered quite satisfactory.

The function $J_2(T)$ cannot continue to increase with temperature indefinitely according to Eq. (30) since the parameter characterizing the transparency of the barrier, $J^* = J_0 - J_2$, cannot be negative. In fact, the relation (30) changes at sufficiently high temperatures. The well-oscillation amplitude becomes so great that it is no longer possible to confine the expansion of Eq. (3) to linear terms, and quadratic terms must also be taken into account. Strictly speaking, terms of all orders must be taken into account in the expansion of the function $J(\{q_\mu\})$. However, by using a function of second order in q_μ [Eq. (3)], in the calculations we can describe the high-temperature behavior of ultrasound attenuation qualitatively correctly, and by regarding J'' as an adjustable parameter we can reach satisfactory quantitative agreement.

The following expression for the inverse ultrasonic attenuation length is obtained from Eq. (7):

$$l_\lambda^{-1}(T)=\frac{4\pi n(0)\overline{V_\lambda^2}}{s\varphi^{1/2}}\left(\frac{\omega_\lambda}{\Omega}\right)\exp[\varphi_1(1-\varphi_2)]I_0(\varphi_1\varphi_2)\int\limits_0^{\beta\Delta E_0/2}\frac{dx}{\operatorname{ch}x}. \tag{31}$$

For temperatures satisfying the condition

$$4kT<\hbar\Omega[\operatorname{arcth}(\hbar J''/2M\Omega)]^{-1}, \tag{32}$$

the quantity J'' can be neglected in Eq. (31). A result analogous to Eq. (25) obtained in the Debye approximation follows then from Eq. (31). The magnitude of l_λ^{-1} initially decreases with increasing temperautre, passes through a minimum at

$$T_2'=\hbar\Omega/2k\ln(\hbar J'^2/M\Omega) \tag{33}$$

($\Omega = 100$ K) ans starts to rise, reaching at temperatures $kT>\hbar\Omega/4$, the asymptotic law $\sim e^{T/T_0}$ where $T_0 = 2M\Omega/kJ'^2$. We then obtain the same quantitative estimate for T_0 as earlier [see Eq. (30)]. In this case the Einstein and Debye models thus give results which are close together both qualitatively and quantitatively.

However, it is impossible to ignore the quantity J'' at sufficiently high temperatures when the condition (32) is not satisfied. The increase in the function $l_\lambda^{-1}(T)$ then slows down, passes through a maximum at

$$T_3=J'^2M\Omega^2/4kJ''^2 \tag{34}$$

and starts to fall. In this regime, as a result of oscillation of the wells, the effective potential barrier becomes so low that a particle passes above it from one well to another, and the temperature dependence of the attenuation has the activation form $\sim e^{-T_3/T}$. The characteristic temperature T_3 has nothing in common with the equilibrium height of the potential barrier. It is determined by the work expended against elastic forces when the wells come so close that the barrier disappears.

According to experiment[15-17] we have $T_3 \approx 50$ K, from which it follows that $J'' \approx 1200$ Å^{-2}. If J'' is considered as the second derivative of the function $J(\{q_\mu\})$, then $J'' \approx 400$ Å^{-2}. This shows that a large nonlinear deformation of the potential barrier takes place at large vibrations of the wells, and the effective value of J'' increases.

We have so far said nothing about averaging over the transparency parameter of the barrier, J_0, although the method of averaging plays the fundamental part in the present case. Two-level systems with the smallest value of J_0 make the main contribution to the attenuation process. If it is assumed that there is a sufficiently precise lower limit J_{str} to the distribution of J_0, then an attractive and physically intuitive picture is obtained which agrees well with experiment. In this case we must assume that $J_0 \approx J_{\text{str}}$ in all the equations of this section. In evaluating J_{str} it must not be forgotten that in the actual description of the physical processes the effective value $J^*(T)$ is used and it is required that it nevertheless remains large enough at $T<T_3$. The maximum of the ultrasound attenuation at $T \approx T_3$ is due to the sharp reduction in $J^*(T)$ caused by the vibration of the wells. This fact indicates directly the existence of a structural restriction on the set of values of J_0 and makes possible a quantitative estimate of J_{str}.

If, however, we adopt the opposite point of view and consider that the distribution of J_0 is only limited from below by the inequality (19), then the possibility of such a description is lost. In this case, two-level systems with a very small potential barrier are the determining factor at all temperatures, and the transition of a particle from well to well even at temperatures less than T_3 takes place not by tunneling but is activated by the mechanism considered above. As a result, one cannot obtain the described picture of the high temperature behavior of ultrasound attenuation, especially at high temperatures.

5. THERMAL CONDUCTIVITY

The standard expression is used to evaluate the thermal conductivity of a dielectric glass,

$$\varkappa=\Omega_0^{-1}s\sum_\mu\frac{(\hbar\omega_\mu)^2}{4kT^2}\frac{1}{\operatorname{sh}^2(\beta\hbar\omega_\mu/2)}l(\omega_\mu), \tag{35}$$

where Ω_0 is the volume of the specimen. The phonon mean free path is determined from equations derived in the previous section. The main contribution to the integral of Eq. (35) comes from the frequency region $\hbar\omega_\mu \sim kT$, i.e., the parameter $\beta\hbar\omega_\mu$ [see, for example, Eq. (28)] cannot be considered small. In addition, the interaction of a phonon with the two-level system can become strong at relatively high temperatures, and the frequency dependence of the matrix element $V_\lambda(\omega)$ [Eq. (21)] changes. We will not consider this effect in the present work, so that our values of the thermal conductivity in the high temperature region are somewhat overestimated.

At low temperatures, when the one-phonon approximation can be made, we obtain with the help of Eqs. (20) and (22)

$$\varkappa=\frac{5k\omega_D}{8\pi^7 s\hbar Rn(0)}\exp\{J_{str}-J_1(T)\}\left(\frac{kT}{\hbar\nu}\right)^2\phi(T), \tag{36}$$

where

$$\phi(T)=\int\limits_0^\infty dy\,y^3\frac{1}{\operatorname{sh}^2(y/2)}\left\{\operatorname{th}(y/2)+\frac{\pi^3R}{8}\left(\frac{T}{\Theta}\right)^4\varphi(y)\right\}^{-1},$$

$$\varphi(y)=\int\limits_0^\infty dx\left[\frac{(x-y)^3(e^y-1)}{(1-e^{y-x})(e^x+1)}+\frac{(x+y)^3(1-e^{-y})}{(1-e^{-y-x})(e^x+1)}\right].$$

If we retain only the first term in the curly brackets, we obtain the well known law $\varkappa \sim T^2$. It is due to resonant phonon scattering by the two-level systems. The second term in the curly brackets, corresponding to nonresonant one-phonon processes, causes the conductivity to increase more slowly than T^2, and even start to fall at sufficiently high temperatures. Experimentally this is reflected in the plateau

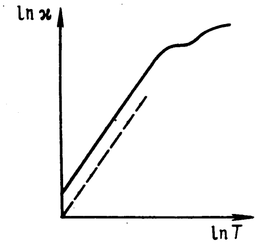

FIG. 2. Temperature dependence of thermal conductivity. The dashed line represents the $\varkappa \sim T^2$ law.

in the temperature dependence of $\varkappa$.[13,14]

At such temperatures, however, multiphonon processes start to become important and one should now use Eq. (31), in which the factor $\beta\hbar\omega_\lambda$ is replaced by $2\sinh(\beta\hbar\omega_\mu/2)$ [Eq. (28)]. Then

$$\varkappa=\frac{5}{\pi^4 s}\frac{\Omega\omega_D k}{\hbar v n(0)}\frac{kT}{\hbar v}\frac{\varphi_3^{1/2}}{I_0(\varphi_1\varphi_2)}\exp[J_{str}+\varphi_1(\varphi_2-1)]\int\limits_0^\infty dy\frac{y^3}{\mathrm{sh}^3 y}. \tag{37}$$

In this temperature region the thermal conductivity thus starts to increase again, owing to the weakening of the phonon scattering by the two-level systems as a result of the destruction of resonance in multiphonon processes, and then starts to fall exponentially like $\varkappa \sim e^{-T/T_0}$, since the phonon scattering increases again as a result of the vibration of the wells. The conductivity passes through a minimum at temperatures $\approx T_3$ and starts to increase.

The general form of the temperature dependence of the thermal conductivity is shown in Fig. 2. We note that as the temperature rises anharmonic processes can start to contribute to the thermal conductivity. Then $\varkappa$ falls with increasing temperature, at first exponentially and then according to a power law (see, for example, Ref. 32) and this can mask the high temperature part of this picture. This will probably pose the problem of experimentally separating the two contributions.

6. CONCLUDING REMARKS

The results given above clearly demonstrate how important it is to take account of vibration of the wells in two-level systems when considering phonon relaxation and scattering processes in dielectric glasses. This mechanism changes appreciably all our ideas about low-temperature phenomena in glasses. Taking account only of zero-point vibrations accelerates all processes by several orders of magnitude. Therefore the necessity of strong limitations on the barrier parameters, for example, falls away. In our calculations we used $V_b \sim 0.5$ eV for the height of the barrier, while Anderson *et al.*[6] called for $V_b < 0.2$ eV. It also becomes clear that two-level systems scatter phonons much more strongly than appeared earlier (see the discussion by Stephens[13]).

It is possible, without introducing any additional mechanisms, to explain fully both qualitatively and quantitatively the unusual nonmonotonic temperature dependence of the inverse ultrasonic attenuation length on the basis of the assumptions discussed. In turn, the thermal conductivity, whose behavior is closely related to the temperature dependence $l_\lambda^{-1}(T)$, exhibits a large number of peculiarities apart from the well known $\varkappa \sim T^2$ law.

The physical processes which we have considered by no means exhaust the list of effects in which two-level systems play some part or another. These include the attenuation of sound at high frequencies, renormalization of the velocity of sound is low and high frequencies, dielectric relaxation, etc. The effect of intramolecular vibrations, on the tunneling-transition rate can also become appreciable for these processes. However, the discussion falls outside the framework of the present work.

In the Introduction we mentioned the temperature dependence of the luminescence intensity in the glass g-As_2S_3 (Ref. 18)

$$I(T) \sim e^{-T/T_0}, \tag{38}$$

which has been called the "inverse Arrhenius law." By comparing Eq. (38) with Eqs. (27), (30), or (31) it is easy to see that this dependence is caused by vibration of the wells, the amplitude of which increases linearly with temperature. However, the question then arises as to why $T_0 \approx 28$ K is an order of magnitude higher than in other glasses (see Sec. 4) and also why the relation (38) should be observed over a wide temperature range up to 280 K, which indicates a very large value for the temperature T_3. To all appearances this is due to the clustering peculiar to g-As_2S_3 glass.[11] In this case the characteristic mass M, which appears in Eqs. (27), (31) and (34) will be equal to the mass of a cluster, which also explains such a large increase in the characteristic temperatures T_0 and T_3.

One of the main conclusions of the present work can be considered to be the empirical basis for asserting the existence of a lower limit J_{str} to the distribution of the barrier transparency parameter J_0. It is possible that the effect observed by Stephens[13] is connected with this. We assume alloying produces two-level systems with J_0 larger than the J_{str} characteristic of the given glass. They then contribute to the heat capacity and increase it, but do not contribute to the thermal conductivity which is determined by scattering of phonons by the wells with the lowest values of J_0. However, the important question of the physical causes of such a limit is still open.

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