

Parameters of soft atomic potentials in glasses

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The probability distribution of the parameters of random local atomic potentials in glasses is considered. It is argued that the parameters of soft atomic potentials correspond to a probability density proportional to the absolute local quasielastic constant. This behavior results in a very rapid rise of the density of quasilocal vibrations with energy and suggests the possibility of their collectivization. This makes it possible to account for the experimental data on the excess specific heat of glasses.

The concept of two-level systems, identified with tunnel states of atomic particles in two-well potentials, is used widely in the physics of noncrystalline substances.^{1–3} An approach has been proposed^{4,5} to account for the existence of two-well potentials in glasses by fluctuations of microscopic structure parameters. As a result of these fluctuations there is a finite probability for soft atomic potentials to occur for which the quasielastic constant is small for at least one of the local modes. When the local potential is expanded in terms of a soft mode

$$V(x) = \mathcal{E}(\eta x^2 + t x^3 + x^4), \quad (1)$$

an allowance for the anharmonic terms plays a fundamental role because of the smallness of $|\eta|$, $|t| \ll 1$ (here and later the dimensionless displacements x will be expressed in terms of a unit atomic length $a \sim 1 \text{ \AA}$; we then have $\mathcal{E} \sim 10 \text{ eV}$, which is a characteristic atomic energy in a solid). If $\eta < (9/32)t^2$, the potentials described by Eq. (1) are of the two-well type and two-level systems may then occur. An approach based on an expansion of Eq. (1) reproduces all the results of the usual model of two-level systems^{1,2} and also leads to a number of new conclusions.^{4–8} In particular, it predicts the existence of soft one-well atomic potentials [characterized by $\eta > (9/32)t^2$] and in this case excitations are not described by the two-level model.^{5–8}

One of the important topics related to the concept of soft atomic potentials of Eq. (1) is the form of the probability distribution $P(\eta, t)$ the random parameters η and t . The distribution $P(\eta, t)$ as a function of η is assumed to be centered near the value $\eta \sim 1$, corresponding to the standard (nonsoft) atomic potentials which are encountered most frequently. The soft potentials then occur in the region of the tail of the distribution $P(\eta, t)$ falling in the range of low values of η . The distribution $P(\eta, t)$ of the parameter t is assumed to be even because of the absence of preferred directions in a glass. It is also assumed that in the limit $\eta \rightarrow 0$ the distribution $P(\eta, t)$ becomes finite.^{4,6–8}

We shall consider the form of $P(\eta, t)$ in the limit in which the first parameter is small, $|\eta| \ll 1$. We shall give arguments to support the conclusion that

$$P(\eta, t) = |\eta| P_0(\eta, t) \quad \text{for } \eta \rightarrow 0, \quad (2)$$

where $P_0(\eta, t)$ is a smooth function which is finite in the limit $\eta \rightarrow 0$ and we shall consider some consequences of this behavior of $P(\eta, t)$.

Our aim will be to obtain an expansion of the type described by Eq. (1) beginning from a more general expression

$$V(x') = \mathcal{E}(h'x' + \eta'x'^2 + t'x'^3 + x'^4), \quad (3)$$

which contains, in contrast to Eq. (1), random linear terms. We can go over from the expansion of Eq. (3) to that of Eq. (1) by shifting the origin of the reference system: $x' = x + (t' - t)/4$. This gives the following relationship between the parameters:

$$\begin{aligned} \eta - 3/8t^2 &= \eta' - 3/8t'^2, \\ 1/2t(\eta - 1/4t^2) &= 1/2t'(\eta' - 1/4t'^2) - h'. \end{aligned} \quad (4)$$

We shall now replace the distribution $G'(h', \eta', t')$ in the random parameters of the expansion (3) by a distribution $G(\eta, t, t')$ in three other parameters η , t , and t' . The Jacobian of this operation found from Eq. (4) is $1/2|\eta|$. We consequently have

$$G(\eta, t, t') = 1/2|\eta| G'[h'(\eta, t, t'), \eta'(\eta, t, t'), t']. \quad (5)$$

We note now that for given values of η and t the energy spectrum of the potential (1) is independent of the parameter t' . Consequently, we can calculate the average quantities associated with the energy spectrum of an ensemble of the potentials of Eq. (1) using the distribution density averaged over the parameter t' :

$$P(\eta, t) = \frac{1}{2} |\eta| \int_{-\infty}^{\infty} dt' G'[h'(\eta, t, t'), \eta'(\eta, t, t'), t']. \quad (6)$$

The function $G'(h', \eta', t')$ is assumed to be nonsingular on the basis of physical considerations. Therefore, the integral in Eq. (6) is finite in the limit $\eta \rightarrow 0$, in agreement with the result given by Eq. (2).

We shall now consider the difference between the expansion (1) and (3). We shall do this by examining an ensemble of slightly different atomic configurations, each of which has a soft local atomic potential. A soft mode

$$x = \sum_{i, \alpha} b_i^\alpha \xi_i^\alpha$$

represents in each configuration a superposition of Cartesian components ξ_i^α of different atomic displacements. In each of the units of this ensemble a mode x , in terms of which the expansion (1) is performed, is characterized by its own set of

coefficients b_i^α because equilibrium positions of atoms in these units are different. We shall select one of the configurations of the ensemble as the reference point and determine the corresponding set of the coefficients b_i^α . This defines uniquely a normal soft mode x' used in the expansion of Eq. (1) for a reference unit. Obviously, in the case of the other (nonreference) units of the ensemble the expansion of the potentials in terms of the selected mode x' contains linear terms, i.e., it is described by Eq. (3). Therefore, Eq. (3) represents the expansion of different soft atomic potentials in terms of the same fixed mode x' , whereas in the expansion of Eq. (1) a soft mode x is specific to each individual potential. Since the mode x in Eq. (1) depends on the parameters of the potential, it follows that in general we cannot regard η and t as statistically independent; this follows directly from Eq. (6). The behavior

$$P(\eta, t) \propto |\eta|$$

also reflects the dependence of the definition of the mode x on the parameters of the soft potential.

We note that the expressions in Eq. (4) describe the combinations $I_1 = \eta - \frac{3}{2}t^2$ and $I_2 = \frac{1}{2}t(\eta - \frac{1}{2}t^2)$, from which the parameters η and t can be found uniquely only if $\eta > (9/32)t^2$, when the potential of Eq. (1) is of the one-well type. If $\eta < (9/32)t^2$, then for each pair of the quantities I_1 and I_2 there is a single form of the two-well potential of Eq. (1), but this form can be described by three different pairs of the parameters (η, t) . This indeterminacy reflects simply the possibility of expansion of two-well potential of Eq. (1) near one of its three extrema. We shall consider the specific case when the origin of x for the two-well potentials of Eq. (1) is selected at the maximum of the barrier. Then the potentials of Eq. (1) correspond in the (η, t) plane to a region defined by $\eta > (9/32)t^2$ (one-well potentials) and by a half-plane $\eta < 0$ (two-well potentials). Using the arguments employed at the beginning of this paper and the results represented by Eq. (2), we can plot the distribution $P(\eta, t)$ as shown in Fig. 1.

We shall now consider some physical consequences that follow from the behavior of $P(\eta, t)$ described by Eq. (2). The energy spectrum of the potential (1) can be represented in the form $E_n = w\varepsilon_n$, where ε_n are the dimensionless eigenvalues of the Schrödinger equation^{6,7}

$$-\psi_n'' + (\alpha y^2 + \beta y^3 + y^4)\psi_n = \varepsilon_n \psi_n, \quad n=1, 2, 3, \dots, \quad (7)$$

$$\alpha = \eta/\eta_L, \quad \beta = t/\eta_L^{1/2}, \quad y = x/\eta^{1/2}.$$

Typical parameters are

$$\eta_L = \left(\frac{\hbar^2}{2ma^2\mathcal{E}} \right)^{1/2} \sim \left(\frac{\hbar\omega_D}{\mathcal{E}} \right)^{1/2} \sim 10^{-2}, \quad (8)$$

$$w = \mathcal{E}\eta_L^2 \sim \hbar\omega_D\eta_L^{1/2} \sim 10\text{K},$$

where $\hbar\omega_D = (\mathcal{E}\hbar^2/2ma^2)^{1/2}$ is the characteristic Debye energy ($\hbar\omega_D \sim E_1$ when $\eta \sim 1$) and m is the mass of an atomic particle in the potential of Eq. (1). An analysis of the spectrum of ε_n given in Refs. 6 and 7 shows that the model of two-level systems is valid if the first energy gap obeys $E_{21} \equiv E_2 - E_1 \ll w$. We then have

$$E_{21} = (\Delta^2 + \Delta_0^2)^{1/2},$$

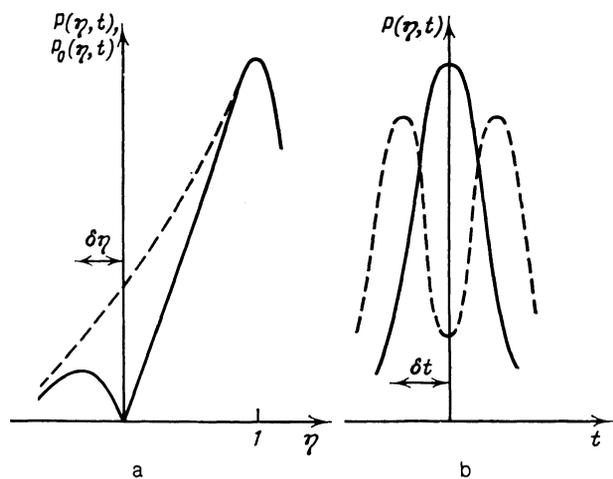


FIG. 1. a) Dependence of the probability distribution $P(\eta, t)$ on η for a fixed value of t . The dashed curve is the corresponding dependence for $P_0(\eta, t)$ taken from Eq. (2). b) Possible form of the dependence of $P(\eta, t)$ on t for a fixed value of η : there are two distributions with a maximum or a minimum at $t = 0$.

$$\Delta = \frac{w}{2^n} \left(-\frac{\eta}{\eta_L} \right)^{n/2} \frac{|t|}{\eta_L^{1/2}}, \quad \Delta_0 \approx w \exp \left[-\frac{2^{1/2}}{3} \left(-\frac{\eta}{\eta_L} \right)^{1/2} \right], \quad (9)$$

where Δ is the asymmetry and Δ_0 is the amplitude of tunneling in a two-well potential. The density of states of two-level systems

$$n(E) = \int_{-\infty}^0 d\eta \int_{-\infty}^{\infty} dt P(\eta, t) \delta(E - E_{21}(\eta, t))$$

is independent of E (as usual, this is based on empirical results¹⁻³) if the scales $\delta\eta$ and δt of the decrease in the distribution $P_0(\eta, t)$ in terms of the parameters η and t are large in the sense that $\delta\eta \gg \eta_L$ and $\delta t \gg \eta_L$. Assuming that in this case we have $P_0(\eta, t) = \text{const}$, we obtain

$$n(E) \approx 2^{1/2} w^{-1} \eta_L^2 (\delta\eta)^{1/2} P_0 \equiv n_0. \quad (10)$$

It therefore follows that the result of Eq. (2) does not alter the conclusion which follows from the concept of soft potentials^{4,7}: the density of states of two-level systems is constant.¹⁾

Moreover, the previous estimate of the deformation potential of a two-level system⁷ is retained:

$$|\gamma| = \left| \frac{\partial E}{\partial u} \right| \sim \frac{w}{\eta_L}, \quad (11)$$

where u is the dilatation. This estimate is obtained in Ref. 7 by a fairly complex process. We shall justify it in a simple manner. We note that

$$\gamma = \frac{\partial E}{\partial \eta} \frac{\partial \eta}{\partial u} + \frac{\partial E}{\partial t^2} \frac{\partial t^2}{\partial u}.$$

The parameters η and t vary by amounts of order unity for a unit dilatation that significantly modifies the potential, i.e., destroys its softness; therefore, $|\partial\eta/\partial u| \sim |\partial t^2/\partial u| \sim 1$. The derivatives are given by $|\partial E/\partial \eta| \sim |\partial E/\partial t^2| \sim w/\eta_L$, because it follows from Eq. (7) that the dimensionless energies ε_n vary by amounts of order unity when α or β^2 is altered by unity. The large value of the deformation potential $|\gamma|$ is on

the order of tenths of electron volts, in agreement with the experimental results reported in Refs. 1–3, and this is due to the softness of the investigated local potentials (in the case of nonsoft potentials, we would have

$$|\gamma| \sim |\partial E / \partial \eta| \sim |\partial E / \partial t^2| \sim \hbar \omega_D \ll w / \eta_L).$$

The behavior $P(\eta, t) \propto |\eta|$ predicted by Eq. (2) has a strong influence on the results relating to excitations in one-well almost-harmonic potentials, which are encountered when $\alpha \gg 1$, i.e., when $\eta \gg \eta_L$ (but still $\eta \ll 1$), and which have the spectrum $E_n = 2w(n - \frac{1}{2})(\eta/\eta_L)^{1/2}$. In Refs. 7 and 8, we found in the case of excitations that the dependence of the excitation density $n(E) \propto E^2$ corresponds to the assumption $P(\eta, t) = \text{const}$ in the limit $\eta \rightarrow 0$. Using Eq. (2), we obtain a different energy dependence of the density of excitations in this part of the spectrum:

$$n(E) = {}^{1/2} n_0 (\eta_L / \delta \eta)^{1/2} (E/w)^4 \quad \text{for } E > 2w. \quad (12)$$

We can expect the strong dependence $n(E)$ of Eq. (12) to be manifested in the temperature dependence of the specific heat $c(T)$. Figure 2 shows the temperature dependence of the reduced specific heat c/T^3 , which is calculated by numerical solution of Eq. (7). In the limit of low temperatures $T \rightarrow 0$ the behavior of c/T^3 to the left of the minimum represents the contribution of two-level systems. To the right of the minimum the behavior of c/T^3 is due to the dependence $n(E)$ of the type described by Eq. (12). The existence of a minimum in the temperature dependence of c/T^3 has been demonstrated experimentally (usually at $T \sim 2\text{--}10$ K) for those materials which at the very lowest temperatures $T \lesssim 1$ K exhibit a linear temperature dependence of the specific heat $c \propto T$ due to the presence of two-level systems.³ The origin of this minimum has not yet been explained.

Measurements demonstrate also that the rise of c/T^3 to the right of the minimum is followed by a fall, as shown schematically by the dashed curves in Fig. 2, i.e., the dependence c/T^3 exhibits a maximum (usually at $T \sim 10\text{--}30$ K), as reported in Ref. 3. A possible explanation of this maximum is as follows. An increase in E increases the density $n(E)$ of quasilocal vibrations of Eq. (12) and their width $\Gamma \propto E^4 (\hbar \omega_D)^{-3}$ so much⁹ that vibrations become collectivized. The energy E_d at which this happens can be estimated roughly from the condition

$$\lambda^3 \Gamma(E) n(E) = 1,$$

where $\lambda = 2\pi s / \omega$ is the characteristic wavelength of a quasilocal vibration of frequency $\omega = E/\hbar$; s is the velocity of sound.¹⁰ For $n(E)$ described by Eq. (12) and typical experimental values $n_0 \sim 10^{33} \text{ erg}^{-1} \text{ cm}^{-3}$ (Ref. 3), this gives $E_d \sim 3w$. Delocalization of vibrations in the range $E \gtrsim E_d$ suppresses the dependence $n(E)$ of Eq. (12), so that the density of states now obeys the usual Debye law. Since vibrations characterized by $E > E_d$ make practically no contribution to the excess (compared with the Debye value) specific heat, the rise in the temperature dependence of c/T^3 changes to a fall when $T \gtrsim E_d/5$ [this estimate is obtained if, subject to Eq. (12), the spectrum of quasilocal vibrations is replaced by a monoenergetic peak at $E = E_d$]. Our estimates of the positions of the minimum and the maximum in the temperature dependence of c/T^3 are in qualitative agreement with the experimental data for typical values $w \sim 10$ K.

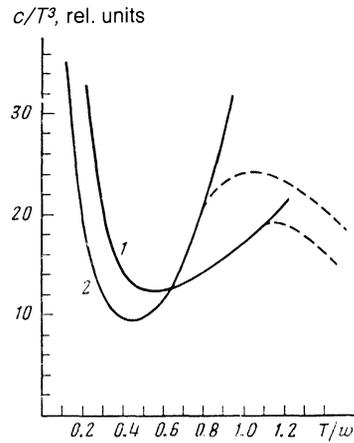


FIG. 2. Temperature dependences of the reduced specific heat for a system of oscillators, described by Eq. (1) with a probability distribution in the parameters given by Eq. (2): the curves are calculated by numerical solution of Eq. (7). The dashed curves represent the fall, which agrees with the experimental results. The calculations were made for two different forms of the distribution of Eq. (2): curve 1 corresponds to $P_0(\eta, t) = \text{const}$ and curve 2 corresponds to $P_0(\eta, t) \propto \exp(\eta/\delta\eta)$, where $\delta\eta = 0.1$. We can see that the positions of the minima are not very different for these two distributions.

If the dependence (2) is obeyed,²⁾ allowance for this dependence may alter some of the results of earlier investigations^{6–8} based on the assumption that $P(\eta, t) = \text{const}$ in the limit $\eta \rightarrow 0$. We have demonstrated this for the density of quasilocal vibrations. Moreover, instead of a logarithmic Van Hove singularity predicted in Ref. 6 for the density of excitations $n(E_{21})$ corresponding to the first interlevel gap E_{21} , when Eq. (2) is allowed for, there is only a singularity in the derivative $dn(E_{21})/dE_{21}$. On the other hand, the conclusion about a discontinuity of the excitation density at E_{31} , corresponding to transitions between the first and third levels,⁶ is still retained. Moreover, the conclusion about the predominant role of subthermal phonons⁷ in the thermal conductivity and its temperature dependence $\chi \propto T$ in the range $T > w$ still remains valid.

There are therefore grounds for assuming that random soft potentials in glasses correspond to the probability density of Eq. (2), which depends linearly on the absolute local quasielastic constant. This behavior is responsible for the very fast rise in the density of quasilocal vibrations with energy and for the possibility of the collectivization of these vibrations. This accounts for the experimental data on the excess specific heat of glasses at moderately low temperatures ($T \gtrsim 10$ K).

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¹⁾In the preceding investigations the assumption $\delta\eta, \delta t \gg \eta_L$ has been made for the scale of the decrease in the distribution $P(\eta, t)$ (Refs. 4 and 6–8).

²⁾This is true if fluctuations of the coefficient in front of the linear term in Eq. (3) relative to the average value $\langle h' \rangle = 0$ are sufficiently large: $\delta h' \gg \eta_L^{3/2}$.

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