

## Anharmonic potentials and vibrational localization in glasses

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The soft-potential model (an extension of the well-known tunneling model for two-level states in glasses) has been formulated in terms of soft-mode eigenvectors in order to characterize the localization of these modes. The interaction with high-frequency modes explains the absence of very small restoring-force constants. A quantitative comparison to specific-heat and neutron-scattering data from vitreous silica, amorphous selenium, and vitreous boron trioxide shows that both the two-level systems and the low-energy vibrational states can be explained by the same distribution of localized modes.

### I. INTRODUCTION

The thermal properties of glasses below 1 K differ drastically from those of crystals.<sup>1,2</sup> They are dominated by two-level states which seem to be well described by the tunneling model.<sup>3-5</sup> The model assumes double-well potentials for some unspecified motion of one or several atoms. This description, however, fails to account for the glassy anomalies above 1 K, between 1 and 10 K, where again one finds clear evidence for additional states coexisting with the sound waves.<sup>1,2</sup> Recent neutron measurements<sup>6</sup> have shown these to be soft harmonic vibrations with a crossover to anharmonicity at the low-frequency end (at frequencies corresponding to several degrees Kelvin). This evidence supports the theoretical model of Karpov, Klinger, and Ignatiev,<sup>7</sup> and others,<sup>8-14</sup> which describes both the tunneling and the soft vibrational motion in terms of soft anharmonic potentials with locally varying parameters.

The present paper intends to put the soft-potential model on a more quantitative basis by considering the localization of these modes in detail and by adapting the model to measured specific-heat and neutron-scattering data of three different glasses, namely silica, amorphous selenium, and vitreous B<sub>2</sub>O<sub>3</sub>. This quantitative comparison does not only give information about the form of the distribution of the soft-potential parameters, but also on the number of atoms participating in the tunneling or soft vibrational motion.

The paper proceeds as follows: after this introduction, the soft-potential model is formulated in terms of extended soft modes in Sec. II. The same section contains a crude estimate of the interaction of the soft mode with higher-frequency modes. Section III discusses the predictions of the soft-potential model for the specific heat in the crossover region between harmonic and anharmonic states around 1 K. The application of the results to the three aforementioned glasses is given in Sec. IV. Section V gives a summary and some conclusions.

### II. NORMAL-MODE FORMULATION OF THE SOFT-POTENTIAL MODEL

#### A. Localization of the soft mode

In what follows we assume an amorphous solid with only one mode of exceptionally soft potential, thus disregarding the interactions between different soft modes. Let us denote the eigenvector of the soft mode for atom  $i$  with mass  $M_i$  by  $\mathbf{e}_i$ . Then

$$\sum_{i=1}^N \mathbf{e}_i^2 = 1 \quad (1)$$

and the motion of the atoms in the soft mode is described by

$$\mathbf{u}_i(t) = f(t)\mathbf{e}_i / M_i^{1/2}, \quad (2)$$

where  $f(t)$  is the same for all atoms and may be a tunneling or a soft vibrational motion according to circumstances.

Without loss of generality, we can assume atom 1 to have the biggest displacement in the soft mode. We define  $x$  as the amplitude of this displacement of atom 1 in the soft mode. Then the kinetic energy of the mode

$$\begin{aligned} E_{\text{kin}} &= \sum_{i=1}^N \frac{1}{2} M_i \dot{\mathbf{u}}_i^2 = \frac{1}{2} [\dot{f}(t)]^2 = \frac{1}{2} (M_1 / \mathbf{e}_1^2) \dot{\mathbf{u}}_1^2 \\ &= \frac{1}{2} (M_1 / e_1^2) \dot{x}^2. \end{aligned} \quad (3)$$

This relation defines the effective mass  $M_s$  of the soft mode

$$M_s = M_1 / \mathbf{e}_1^2 \quad (4)$$

and this in turn defines  $N_s$ , the effective number of atoms in the mode

$$N_s = M_s / \bar{M}, \quad (5)$$

where  $\bar{M}$  is the average mass of the participating atoms.

This definition of the participation number is slightly different from that used in computer simulations on localization problems,<sup>15,16</sup>

$$N_s^* = \frac{1}{\sum_{i=1}^N (e_i^2)^2}, \quad (6)$$

but in the general case both definitions will tend to give similar numbers.

The next step is to characterize the anharmonicity. Since neutron experiments<sup>6,17</sup> show a similarity between soft-mode eigenvectors and those at the first maximum of the vibrational density of states at a crystal-like frequency  $\omega_c$  that frequency can be used to set the energy scale for the soft mode. Then one can define a displacement  $a$  at which the fourth-order term of the soft mode equals the harmonic term of the unaffected crystal-like mode:

$$\frac{1}{2}M_s\omega_c^2a^2 = \frac{1}{24}\frac{\partial^4V}{\partial x^4}a^4 = \epsilon. \quad (7)$$

We insert these definitions into the well-investigated soft-potential expression<sup>7-14</sup>

$$V(x) = \epsilon[\eta(x/a)^2 + t(x/a)^3 + (x/a)^4] \quad (8a)$$

or, alternately

$$V(x) = \epsilon[h'(x/a) + \eta'(x/a)^2 + (x/a)^4], \quad (8b)$$

where the soft mode is characterized by parameters  $\eta$  and  $t$  (or  $h'$  and  $\eta'$ ) much smaller than unity. These two parameters decide whether one deals with a tunneling mode or a soft quasiharmonic vibration or something in between. The two expressions (8a) and (8b) are equivalent in the sense that they transform into each other by an appropriate shift of the origin of  $x$ . What is not equivalent, however, is a situation with a constant distribution of  $\eta$  and  $t$  around zero on the one hand and a situation with a constant distribution of  $h'$  and  $\eta'$  around zero on the other. It has been shown<sup>9</sup> that the latter leads to a distribution function

$$P(\eta, t) = P_0|\eta| \quad (9)$$

around zero  $\eta$  and  $t$  in the former, the so-called ‘‘seagull’’ singularity (see Fig. 1). This suppresses states with very small restoring force constants. Later on, we will discuss a possible physical reason for the origin of such a singularity.

In principle, given distribution functions for  $\eta$  and  $t$ , the resulting states are characterized by the three parameters  $\epsilon$ ,  $a$ , and  $M_s$ . It is useful, however, to introduce a shorthand notation for two combinations of them,

$$\eta_L = (\hbar^2/2M_s a^2 \epsilon)^{1/3}, \quad (10)$$

and

$$W = \epsilon \eta_L^2. \quad (11)$$

Later, we will extract  $\omega_c$  and  $W$  from experimental data. From these two, one calculates the others via the relations

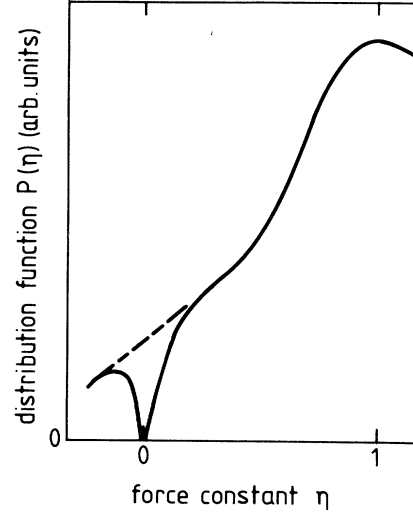


FIG. 1. Distribution function for the restoring force constant  $\eta$  with (solid line) and without (dashed line) the seagull singularity.

$$\hbar^2/2M_s a^2 = 4W^3/(\hbar\omega_c)^2, \quad (12)$$

$$\epsilon = (\hbar\omega_c/W)^3 \hbar\omega_c/16, \quad (13)$$

and

$$\eta_L = 4(W/\hbar\omega_c)^2. \quad (14)$$

## B. Order of magnitude estimates

Since our definitions put  $x$  on the scale of single-atom displacements, one expects  $a$  to be about half a nearest-neighbor distance  $d$ ,

$$a \approx d/2. \quad (15)$$

So  $a$  does not scale with  $N_s$ . Whereas from Eq. (7) follows

$$\epsilon \approx \epsilon_a N_s, \quad (16)$$

where  $\epsilon_a$  is the value characteristic for one-atom motion.

Consider the expansion of the energy of the amorphous solid in terms of atomic displacements  $R_s$ ,

$$\begin{aligned} V &= \frac{1}{2} \sum_{s,t=1}^{3N} A_{st} R_s R_t + \frac{1}{6} \sum_{s,t,u=1}^{3N} B_{stu} R_s R_t R_u + \dots \\ &= U_2 + U_3 + \dots \end{aligned} \quad (17)$$

( $s$  indicates the number of the atom as well as its displacement direction). In Eq. (17), again the third-order term  $U_3$  will become comparable to the harmonic term  $U_2$  as the displacements approach the size of  $a$ . If we assume a pairwise interaction between the atoms the sums in Eq. (17) are reduced to sums over the bonds connecting the atoms participating in the soft mode to the rest of the glass. There will then be approximately  $zN_s$  such terms

for each order, where  $z$  is the coordination number. We have absorbed the factor  $z$  in our definition of  $\epsilon_a$ . Since, however, the contributions to the third-order term vary in sign on average only a contribution  $\sim\sqrt{z}$  remains. Together with the factor  $z$  included in  $\epsilon_a$  this gives a factor  $z^{-1/2}$ . For a rough order-of-magnitude estimate we write

$$U_3 \approx z^{(-1/2)} \sum_s (\epsilon_a / a^3) R_s^3. \quad (18)$$

$R_s$  is decomposed into a part due to the soft mode and a second part due to all other modes,

$$R_s = \beta_s x + r_s. \quad (19)$$

Then

$$R_s^3 = \beta_s^3 x^3 + 3\beta_s^2 x^2 r_s + 3\beta_s x r_s^2 + r_s^3. \quad (20)$$

The coefficients  $\beta_s$  will be of order unity for  $N_s$  displacements, but, in general, with varying signs. Thus the first term of Eq. (20) yields the cubic term in Eq. (8a) with

$$t^2 \approx 1/zN_s. \quad (21)$$

The second term in Eq. (20) gives a phonon dressing to the potential. It effects a large reduction of the individual tunnel splittings. Commonly this dressing is included by using an effective tunneling mass, larger than the mass  $M_s$  of the mode.<sup>18</sup> We will see that this effect influences our results on the distribution functions only weakly.

After averaging over the high-frequency vibrations the third term in Eq. (20) gives a finite linear term in  $x$ , which is proportional to the mean-square displacement of the atoms. This term is in principle able to explain the singularity, i.e., the linear term in Eq. (8b). Here we want to point out that, even if such a term does not exist at the

glass temperature where the soft modes are formed and frozen in, it will appear on cooling down to low temperatures. In order to estimate its magnitude, we note that the mean-square displacement at the glass temperature in a glass is approximately the same as the mean square displacement in a crystal near melting, so we can use the empirical Lindemann criterion of melting<sup>19</sup>

$$\langle R_s^2 \rangle \approx 0.01 d^2 \approx 0.04 a^2 \quad (22)$$

to estimate a linear term

$$\overline{h'^2} \approx 0.01/zN_s. \quad (23)$$

The original model of soft atomic potentials<sup>7,8</sup> is applicable provided the characteristic scatter of the random quantities  $t$  and  $h$  are bigger than  $\eta_L^{1/2}$  and  $\eta_L^{3/2}$ , respectively. If this is the case one can assume the distribution function  $P_0$  to be constant. In our case (see Table I below) these conditions are satisfied. Thus we conclude that the distribution function, Eq. (9), and the results following from this form are applicable for the substances in Table I.

### III. THE DENSITIES OF QUASIHARMONIC AND TUNNELING STATES

In the following we derive expressions for the densities of states in the limiting cases where either harmonic motion or the strongly anharmonic tunneling motion prevails. These expressions will be used to extract the crossover energy  $W$  given by Eq. (11) from specific-heat data.

We begin with the quasiharmonic states which behave as harmonic ones at  $E \gg W$ . In this case we can assume

$$\eta_L \ll \eta \ll 1 \quad (24)$$

TABLE I. Parameters of the soft-potential model and derived quantities for three different glasses.

Substance	<i>a</i> -SiO <sub>2</sub>	<i>a</i> -Se	<i>a</i> -B <sub>2</sub> O <sub>3</sub>
From neutron-scattering data:			
$\hbar\omega_c$ (meV)	12.4±1 <sup>a</sup>	5.2±0.5 <sup>b</sup>	7.7±1 <sup>c</sup>
From specific-heat data:			
$T^*$ (K)	2.1±0.4 <sup>d</sup>	0.6±0.1 <sup>e</sup>	1.2±0.2 <sup>f</sup>
$n_{\text{TLS}}$ (10 <sup>45</sup> J <sup>-1</sup> m <sup>-3</sup> )	6.6 <sup>g</sup>	4.1 <sup>g</sup>	6.3 <sup>g</sup>
	8.42 <sup>h</sup>	4.5 <sup>h</sup>	9.05 <sup>h</sup>
Derived quantities:			
$W$ (meV)	0.3±0.05	0.08+ 0.02	0.17±0.03
$10^3\eta_L$	2.3±1	1±0.5	2±1
$\hbar^2/2M_s a^2$ (μeV)	0.7±0.4	0.08±0.05	0.3±0.2
$\epsilon$ (eV)	55±30	90±60	45±30
$x_{0.1}/a$	0.07	0.04	0.06
Estimate of the number of atoms $N_s$ participating in the soft modes:			
$\overline{M}$ (a.u.)	16	79	16
$d$ (nm)	0.26	0.38	0.24
$M_s a^2 / \overline{M} d^2$ ( $\approx N_s$ )	24	20	68

<sup>a</sup>Reference 17.

<sup>b</sup>Reference 28.

<sup>c</sup>Reference 29.

<sup>d</sup>See references in Fig. 2.

<sup>e</sup>See references in Fig. 3.

<sup>f</sup>Reference 26.

<sup>g</sup>This work at  $T^*$ .

<sup>h</sup>Reference 31.

(typical estimates for  $\eta_L$  are  $10^{-3}-10^{-4}$ ) and neglect the fourth-order term in Eq. (8). There is another condition for the potential to be one-well,<sup>8,11</sup>

$$9t^2/32 < \eta. \quad (25)$$

If  $t \ll 4\sqrt{2\eta}/3$  we can also neglect the cubic term in Eq. (8a) and the potential becomes harmonic. The second simplification is that we are interested in low frequencies:  $\omega < \omega_c \sqrt{\delta\eta}$  (rough estimates for  $\delta\eta$  and  $\delta t$  are  $\delta\eta \simeq 0.1$ ,  $\delta t \simeq 0.3$ ).

The density of quasiharmonic states is given by

$$n(\hbar\omega) = \langle \delta[\hbar\omega - E(\eta, t)] \rangle_{\eta, t}, \quad (26)$$

where  $E(\eta, t)$  gives the level spacing in the potential characterized by  $\eta$  and  $t$  and the angular brackets denote an average over  $\eta$  and  $t$ . A straightforward calculation<sup>13</sup> assuming the validity of Eq. (9) yields

$$n_{\text{TLS}}(\hbar\omega) = \frac{2\sqrt{2}\eta_L^2}{W} \int_{\eta_{\min}}^0 \frac{d\eta}{\sqrt{|\eta|}} P_0(\eta) \frac{\hbar\omega}{\left[ (\hbar\omega)^2 - W^2 \exp\left[ -\frac{2\sqrt{2}}{3} \frac{|\eta|^{3/2}}{\eta_L^{3/2}} \right] \right]^{1/2}}. \quad (31)$$

Changing the variable from  $\eta$  to  $p = (\Delta_0/\hbar\omega)^2$  we get

$$n_{\text{TLS}} = \frac{2^{1/3}}{3^{1/3}} \frac{\eta_L^{5/2}}{W} \int_{p_{\min}}^1 \frac{dp}{p\sqrt{1-p}} \frac{P_0[\eta(p)]}{\log^{2/3}(W/\hbar\omega\sqrt{p})},$$

where  $p_{\min} = [\Delta_0(\eta_{\min})/\hbar\omega]^2$ .

The quantity  $p_{\min}$  is small and we can omit  $p$  in the expression  $\sqrt{1-p}$ . Thus the quantity we have to estimate is

$$I = \int_{\eta_{\min}}^0 \frac{d\eta}{\sqrt{|\eta|}} P_0(\eta). \quad (32)$$

We have introduced  $\eta_{\min}$  because if  $p(\eta) = \text{const}$  this integral diverges at the lowest limit. Actually the quantity  $\eta_{\min}$  is determined by the duration time of the experiment,  $t_{\text{expt}}$ . Indeed, if we want to extract  $n(\hbar\omega)$  from the specific-heat experiments, the only TLS that contribute to the specific heat are those which have made a transition during  $t_{\text{expt}}$ . On the other hand, the characteristic transition rate is given by the relation<sup>20</sup>

$$\frac{1}{\tau} = \frac{1}{\tau_0(\omega)} \left[ \frac{\Delta_0}{\hbar\omega} \right]^2 = \frac{1}{\tau_0(\omega)} \left[ \frac{W}{\hbar\omega} \right]^2 \exp\left[ -\frac{2\sqrt{2}}{3} \frac{|\eta|^{3/2}}{\eta_L^{3/2}} \right]. \quad (33)$$

Here  $\tau_0(\omega)$  can be expressed in the form

$$\tau_0(\omega) = \omega_0^2/\omega^3, \quad (34)$$

where  $\omega_0 = (\rho\hbar s^5)^{1/2}/\gamma$ ,  $\rho$  is the density of the glass,  $\gamma$  is the characteristic value of deformation potential, and  $s$  is the sound velocity. Making use of Eq. (33) we get

$$n_H(\hbar\omega_c) = \frac{16\sqrt{2}}{3} \frac{P_0}{\hbar\omega_c} \left[ \frac{\omega}{\omega_c} \right]^4, \quad \omega \gg W/\hbar. \quad (27)$$

To calculate the density of tunneling states one should take into account

$$\hbar\omega = (\Delta^2 + \Delta_0^2)^{1/2}, \quad (28)$$

where asymmetry  $\Delta$  and tunnel contribution  $\Delta_0$  are connected with  $\eta, t$  via relations<sup>7</sup>

$$\Delta = \frac{\epsilon}{\sqrt{2}} |t| |\eta|^{3/2} = \frac{W}{\eta_L^2 \sqrt{2}} |t| |\eta|^{3/2}, \quad (29)$$

$$\Delta_0 \simeq W \exp\left[ -\frac{\sqrt{2}}{3} \frac{|\eta|^{3/2}}{\eta_L^{3/2}} \right], \quad (30)$$

and the preexponential factor in Eq. (30) has been neglected. As in the previous case we can assume the function  $P(\eta, t)$  to be independent of  $t$ . It is convenient to change the variable  $t$  to  $\Delta$  and to use  $\delta[\hbar\omega - (\Delta^2 + \Delta_0^2)^{1/2}]$ . As a result we get

$$\eta_{\min} = \eta_L \mathcal{L}^{2/3}, \quad (35)$$

where

$$\mathcal{L} = \frac{3}{\sqrt{2}} \ln \left[ \frac{W}{\hbar\omega} \left[ \frac{t_{\text{expt}}}{\tau_0(\omega)} \right]^{1/2} \right].$$

Here  $\hbar\omega$  is of the order of  $k_B T_{\text{expt}}$  where  $T_{\text{expt}}$  is the temperature of the experiment in low-temperature specific heat. In a reasonable approximation

$$\mathcal{L} = \frac{3}{2\sqrt{2}} \ln [t_{\text{expt}}/\tau_0(k_B T_{\text{expt}})]. \quad (36)$$

The estimate of the integral (32) depends on the ratio between  $\eta_{\min}$  and  $\delta\eta$ , the characteristic scale of the function  $P(\eta)$ . If  $\eta_{\min} \ll \delta\eta$  we can assume Eq. (9) to be valid and

$$I = 2\sqrt{\eta_{\min}} P_0 = 2P_0 \eta_L^{1/2} \mathcal{L}^{1/3}. \quad (37)$$

Assuming  $W/\hbar\omega \simeq 10$ ,  $\tau_0 \simeq 10^{-6}$  s,  $t_{\text{expt}} = 10^2$  s, we get  $\mathcal{L} \simeq 20$ ; if  $\eta_L = 3 \times 10^{-3}$  we get  $\eta_{\min} \simeq 0.02$ . If  $\eta_{\min} > \delta\eta$  we can give only an order-of-magnitude estimate of the integral (32):  $I \simeq 2/\sqrt{\delta\eta} P_0$ .

As a result we have<sup>9</sup>

$$n_{\text{TLS}} = \frac{4\sqrt{2}\eta_L^2 \sqrt{\bar{\eta}} P_0}{W}, \quad (38)$$

where  $\bar{\eta} = \min(\eta_{\min}, \delta\eta)$ . It should be stressed that this expression is valid at  $\omega \ll W/\hbar$ . Making use of Eqs. (27) and (38) we can relate the density of quasiharmonic states at  $\omega \gg W/\hbar$  to the density of tunneling states at

$\omega \ll W/\hbar$ . We have<sup>9</sup>

$$n_H(\hbar\omega) = \frac{1}{24} n_{\text{TLS}} \left( \frac{\eta_L}{\bar{\eta}} \right)^{1/2} \left( \frac{\hbar\omega}{W} \right)^4 \quad (39)$$

or

$$\frac{n_H(\hbar\omega)}{n_{\text{TLS}}} = \frac{1}{\eta_L^2} \left( \frac{4\eta_L}{9\bar{\eta}} \right)^{1/2} \left( \frac{\omega}{\omega_c} \right)^4. \quad (40)$$

This equality can serve as a basis to determine  $W$  from specific-heat data. The contribution of TLS to the low-temperature specific heat is

$$c_V^{\text{TLS}} = \frac{\pi^2}{6} n_{\text{TLS}} k_B^2 T, \quad (41)$$

while the contribution of harmonic states is

$$c_V^H = 30 n_{\text{TLS}} \left[ \frac{\bar{\eta}_L}{\bar{\eta}} \frac{k_B^6 T^5}{W} \right]^{1/2}. \quad (42)$$

The temperature  $T^*$  at which these two contributions become equal is given by the equality

$$\begin{aligned} kT^* &= W \left( \frac{\pi^2}{180} \right)^{1/4} \left( \frac{\bar{\eta}}{\eta_L} \right)^{1/8} \\ &= W \left( \frac{\pi^2}{180} \right)^{1/4} \left( \frac{3}{2\sqrt{2}} \ln \frac{t_{\text{expt}}}{\tau_0} \right)^{1/12}. \end{aligned} \quad (43)$$

With  $t_{\text{expt}} = 10$  s and  $\tau_0 = 1$   $\mu$ s we get

$$W = 1.6 k_B T^*. \quad (44)$$

In the derivation of Eq. (43) we have neglected phonon dressing effects on the tunneling element  $\Delta_0$ . These effects are additional to the ones on the soft vibration where they cause an effective mass. In general, transitions between the two minimum configurations of the tunneling entity do not only involve the soft mode but also other modes since their equilibrium positions are changed. These additional transitions can be described by their overlap integrals which are of order  $(1-1/N)$  but contribute due to their multitude. (Here  $N$  is the number of atoms in the glass.) Since we consider slow tunneling processes, most of these additional relaxations will follow the tunneling particles asymptotically, i.e., the particles get dressed. This dressing effect has been studied in another context, e.g., for the quantum diffusion of hydrogen where it mediates the activation.<sup>21</sup> The exact size of the dressing effect in the glassy situation is not known so far. Calculations on tunneling of interstitial atoms in a crystal give about the same order of magnitude as the exponential part of the naked  $\Delta_0$ , Eq. (30).<sup>22</sup> This would add a factor of two to the logarithmic term in (43). Due to the exponent  $\frac{1}{12}$  this has only a very small effect on  $T^*$ , and we conclude that phonon dressing and therefore also the effective tunneling mass as distinct from the localized mode mass cannot be determined from  $T^*$ .

#### IV. PARAMETER DETERMINATION FOR THREE DIFFERENT GLASSES

In order to determine the crossover energy  $W$  between harmonic and anharmonic states we take the corresponding crossover temperature  $T^*$  from log-log plots of the specific heat over  $T$  cubed versus temperature  $T$  and use Eq. (44) of the preceding section. In this way, one uses the limiting forms [Eq. (38) and Eq. (27)] at low and (comparatively) high frequencies to determine the crossover. For vitreous silica, one can use results of many authors, some of which are plotted in Fig. 2 (the anomaly in the data for suprasil  $W$  has been discussed by v. Löhneysen and Platte<sup>24</sup>). For amorphous selenium, the results in the crossover region are plotted in Fig. 3. In the case of vitreous boron trioxide, one can benefit from earlier fits<sup>26</sup> of linear, third- and fifth-order terms of the specific heat to determine  $T^*$ . The resulting  $W$  values are tabulated in Table I.

The possibility to fit specific-heat data in this way supports the interpretation of the rise above  $T^*$  in terms of a fourth-order quasiharmonic density of states, though it cannot be considered as a final proof of the whole picture. A more stringent test could be done by inelastic neutron-scattering measurements at low temperatures and frequencies, where the temperature dependence of the signals should enable a separation of harmonic and anharmonic contributions. Some indication of an onset of anharmonicity at a frequency corresponding to about twice the  $W$  calculated from the specific heat has been seen in vitreous silica,<sup>6</sup> but this originated from classical

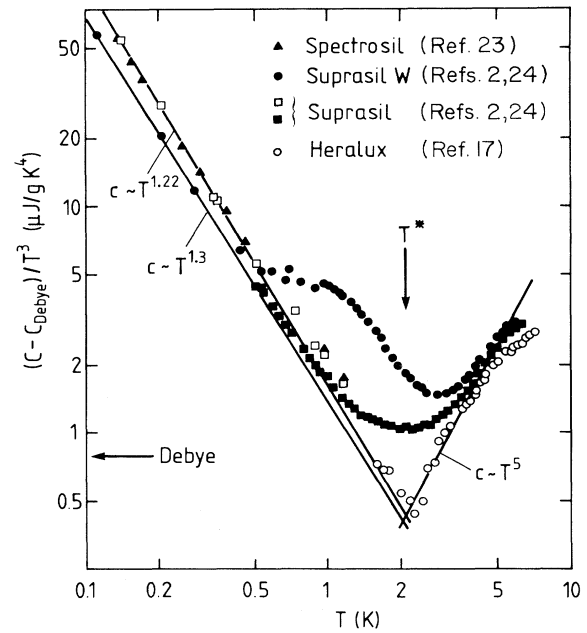


FIG. 2. Specific heat (Debye contribution subtracted) over temperature cubed vs temperature in a log-log plot for different vitreous silica samples after Zeller and Pohl (Ref. 23), Hunklinger and Raychaudhuri (Ref. 2), v. Löhneysen, Rüsing, and Sander (Ref. 24), and Buchenau *et al.* (Ref. 17).

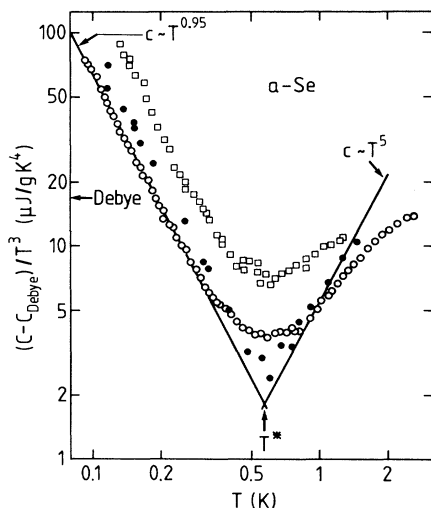


FIG. 3. Specific heat (Debye contribution subtracted) over temperature cubed vs temperature in a log-log plot for amorphous selenium after Zeller and Pohl (Ref. 23) (solid circles); Lasjaunias, Maynard, and Thoulouze [Ref. 25(a)] (open squares); and Brand and v. Löhneysen [Ref. 25(b)] (open circles).

relaxation over the barriers at higher temperatures. Thus an experimental proof of a fourth-power quasiharmonic vibrational density of states in glasses is still missing, though existing data<sup>6,27</sup> show harmonic behavior down to relatively low frequencies.

The quantity  $\omega_c$  can be taken from neutron measurements of the vibrational density of states as that frequency where the density of states exhibits the first maximum. This maximum has been measured for vitreous silica,<sup>17</sup> for amorphous selenium,<sup>28</sup> and for vitreous boron trioxide.<sup>29</sup>

Having  $W$  and  $\omega_c$ , the quantities  $\eta_L$ ,  $\epsilon$ , and  $M_s a^2$  can be calculated from Eqs. (12) or (14). Inserting these values into Eq. (30), one can calculate the negative  $\eta$  and from this, the displacement  $x_{0.1}$  of a tunneling state with a tunnel-splitting temperature of 0.1 K ( $\Delta_0 = 0.1 k_B$ ) but neglecting phonon-dressing effects. The number of atoms participating in a single localized vibrational or tunneling mode is not obtained directly. For an order of magnitude estimate of  $N_s$  we calculate the ratio  $M_s a^2 / \bar{M} d^2 \approx N_s$ , where  $\bar{M}$  is the atomic mass and  $d$  the interatomic distance which were introduced in Sec. III A. For a rough estimate, it seemed reasonable to choose oxygen masses and oxygen distances in vitreous silica, because the bond-stretching frequency of the Si—O bond is much higher than the bond bending one which determines  $\omega_c$ . For the same reason we chose the oxygen masses and distances in boron trioxide. In the case of selenium, the van der Waals distance of 0.38 nm was chosen rather than the short covalent bonding distance. The results of the estimate are also given in Table I, and show participation numbers of between 10 and 100 atoms.

## V. SUMMARY AND CONCLUSION

To summarize, the soft-potential model<sup>7–14</sup> which extends the well-known tunneling model<sup>3,4</sup> to include soft vibrations in glasses, has been put on a more quantitative

basis by comparison to specific-heat and neutron-scattering data. As compared to the standard tunneling model the soft potential has three additional parameters; two of these, however, enter only as a product, so that one has effectively three parameters. The first of the additional parameters is the frequency  $\omega_c$  of the soft mode in ordered surroundings. We assign to  $\omega_c$  the frequency of the lowest maximum in the vibrational density of states of the glass, a procedure suggested by neutron results.<sup>17</sup> Thus  $\omega_c$  can be obtained directly from experiment. The other two parameters are the effective mass  $M_s$ , which characterizes the number of atoms participating in the mode, and the atomic displacement  $a$  at which the anharmonic part of the potentials begins to prevail. These latter two parameters enter only in the combination  $M_s a^2$ . Thus only two parameters are in fact added to the original tunneling model. One of these ( $\omega_c$ ) is directly accessible to experiment while the second one ( $M_s a^2$ ) describes combined effects of vibrational localization and anharmonicity and is obtained from the temperature  $T^*$  where the specific heat changes from  $c_V \sim T$  to  $c_V \sim T^5$ .

Since the comparison indicated from the very beginning a relatively high number of atoms partaking in a single soft mode, it seemed reasonable to define the localization of the soft mode in terms of its eigenvector [Eqs. (4) and (5)]. The final result of a reasonably localized mode is based on a comparison of densities of quasiharmonic soft vibrations on one hand and tunneling states on the other. Since the latter have larger atomic displacements than the former, the question arose whether the anharmonic interaction with high-frequency modes might invalidate the comparison. Our results show, however, this influence to be weak.

The comparison does not give directly the number of partaking atoms, but rather the product of the effective mass with the square of a displacement  $a$  at which anharmonic terms of the potential become dominant. This quantity characterizes the behavior of the mode at higher displacements and will thus be useful for the description of these modes at higher temperatures, possibly even in the undercooled limit. The number of 10–100 partaking atoms is obtained via a crude estimate of the length  $a$ .

The resulting picture of a tunneling mode of a 10–100 atoms with tunneling distances of less than one-tenth of atomic distances is not what is often found in translational tunneling in crystalline solids. In those cases, the motion is localized to one atom and its immediate neighborhood. Nevertheless, the picture of many atoms receives some support from computer simulation studies,<sup>15,16</sup> where all vibrational excitations of disordered solids at lower frequencies were found to be extended modes. Since localization in a computer simulation becomes visible only if the number of partaking atoms is smaller than the square root of the total number of atoms of the simulated system, and since the number of particles in these simulations never exceeded 4096 atoms, the numerical work so far does not contradict a localization to hundred atoms. Preliminary results of a computer simulation show localized modes with localization to about 20 atoms.<sup>30</sup>

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