

Vibration anharmonicity and fast relaxation in the region of the glass transition

V. N. Novikov*

Universität Bayreuth, Physikalisches Institut, D-95440 Bayreuth, Germany

(Received 11 February 1998)

It is shown that the anharmonicity of vibrations leads to the quasielastic scattering in glasses and supercooled liquids. The vibrational self-energy term which arises due to the anharmonic interaction provides the one-phonon quasielastic response. Estimations show that in the glass transition region the contribution of this mechanism to the quasielastic spectrum is dominant. The underlying fast relaxation process corresponds to the fluctuations of the vibration occupation numbers. For the boson peak vibrations the respective relaxation time is of the order of a picosecond. The spectral shape of this fast relaxation is found. The amplitude of the quasielastic scattering intensity and its temperature dependence is estimated within the framework of the model and compared with experimental data on light scattering for various materials. The strength of the fast relaxation which is the integral ratio of the quasielastic to vibrational contribution was found to be proportional to the squared Grüneisen parameter. It is shown that at high temperatures the quartic anharmonic term suppresses the contribution of the third-order anharmonicity to the quasielastic scattering. As a result, a crossover temperature appears in the model; above this temperature the intensity of the fast relaxation does not increase anymore. This result is in good agreement with the analysis of the Raman scattering data in B_2O_3 [A. Brodin *et al.*, *Phys. Rev. B* **53**, 11 511 (1996)]. Within the framework of the model, the ratio of the crossover temperature to that of the glass transition is proportional to the inverse fourth-order anharmonic coefficient. [S0163-1829(98)03134-8]

I. INTRODUCTION

The relaxation spectra of glass formers have three characteristic contributions that correspond to the primary α - and slow and fast β - relaxation processes.¹⁻⁴ In some materials, e.g., in polymers, the relaxation pattern may be more complicated. On the other hand, there are glass formers where it is impossible to detect the slow or secondary β relaxation. The characteristic relaxation times of these three types of relaxation processes have different temperature dependence. The most dramatic changes shows the α - relaxation time which is of the order of a laboratory time, i.e., of one to one thousand seconds, at the glass transition temperature T_g . It changes by many orders of magnitude in the vicinity of T_g where its temperature dependence normally can be approximated by the Vogel-Fulcher-Tamman law $\tau_\alpha \propto \exp[B/(T - T_0)]$ with $T_0 < T_g$. The slow β - relaxation time is of the order of $10^{-7} - 10^{-9}$ sec at T_g and has an activation temperature dependence with the activation energy of some thousands degrees K.⁵ The fast relaxation process, the main subject of the present paper, is a universal feature of glass formers. It has a characteristic relaxation time of the order of a picosecond which is practically temperature independent in a broad interval including T_g (see, e.g., Refs. 1,2,4). Contrary to the α relaxation, the fast relaxation is observed both at very low temperatures, deep in the glassy state, and at high temperatures—even above the melting point.⁶ It was found that the susceptibility spectrum of the fast relaxation has a low-frequency power-law wing with an exponent of less than 1 and a high frequency Debye-like part.⁷⁻⁹ The intensity of the fast relaxation at some reference temperature, e.g., at T_g , as compared with the intensity of the microscopic vibrational band is higher in fragile glass formers and lower in strong ones.¹⁰ Above the glass transition temperature the intensity

of the fast relaxation strongly increases; here the interest in the fast relaxation was stimulated by the predictions of mode-coupling theory³ on the scenario of the glass transition.

The nature of the fast relaxation is still not quite clear. Various mechanisms that can lead to the quasielastic scattering in glasses and liquids are suggested. At temperatures deep in the glassy state the thermally activated relaxation in the asymmetric double-well potentials^{9,11-13} may give the main contribution to the fast relaxation spectrum, a mechanism which is the same as that for the acoustic attenuation in glasses at temperatures 10–300 K.¹⁴ The soft potential model (SPM),¹⁵ in principle, is quite suitable for the phenomenological description of such a mechanism of the relaxation. However, in its present formulation it fails to describe the details of the spectral shape and temperature dependence of the fast relaxation.⁹ It can be easily improved by a more accurate choice of the distribution functions of the soft potential's parameters.¹⁶ Another recent phenomenological model for polymeric glasses connects the quasielastic scattering (QES) both in glassy and supercooled liquid states with the fast fluctuations of the dynamical free volume holes.¹⁷⁻¹⁹ However, the microscopic mechanism of the relaxation is not clear in the model.

Experimentally, the fast relaxation process is intensively investigated using inelastic light and neutron scattering both in glassy and supercooled liquid states. By Raman (see., e.g., Refs. 6,17,18,20–28,39,40) and inelastic neutron scattering (Ref. 29) the high-frequency part of the fast relaxation spectrum can be measured; it reveals itself as a quasielastic component which dominates the spectra at frequencies below $5-15 \text{ cm}^{-1}$ and has anharmonic temperature dependence. Using a tandem Fabry-Perot interferometer, much broader spectra of the fast relaxation (typically, 1–600 GHz) were obtained.⁷⁻⁹ The fast relaxation process may give a contribu-

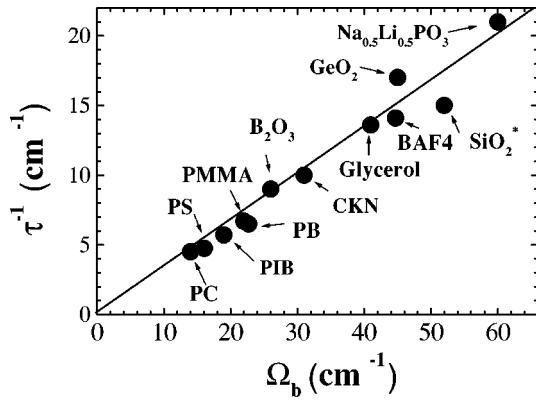


FIG. 1. Correlation between the inverse relaxation time τ^{-1} and the boson peak frequency Ω_b . Data from: $\text{Na}_{0.5}\text{Li}_{0.5}\text{PO}_3$ (Ref. 28), polymers (Ref. 18), glycerol (Ref. 25), GeO_2 (Ref. 40), BAF4 (Ref. 39), CKN (Ref. 9), B_2O_3 (Ref. 6). In SiO_2 τ^{-1} is at 600 K (Ref. 63).

tion to the QES in two different ways. First, light or neutrons can be scattered directly by relaxational modes. This is the case, e.g., of the Theodorakopoulos and Jäckle,¹¹ Gilroy and Phillips,¹² and soft potential¹⁵ models in which the relaxation mode corresponds to thermally activated jumps of some entity in an effective double well potential. The second contribution comes from light or neutron scattering by vibrations which are damped by the same relaxation process.^{22,23,25} Both contributions have the same spectral shape (except at high temperatures, see below) but are controlled by different coupling constants and obviously have different relations to the vibrational properties.

In Refs. 22,25,30–33 it was argued that the second contribution dominates the QES. The argumentation was based on the experimental evidence of some nontrivial similarities between the spectra of the QES and that of the one-phonon scattering on vibrations in the spectral region of the boson peak. The latter is a universal feature of the low-frequency (maximum at $\Omega_b \sim 15\text{--}80\text{ cm}^{-1}$) vibrational spectra of glasses (see, e.g., Refs. 22,34,35). These similarities were discussed in detail e.g., in Refs. 30,32,33 and are briefly discussed in the following. In Raman spectra, the quasielastic line and the boson peak have the same depolarization ratio²² and the same value of the light to vibration coupling coefficient $C(\omega)$, $C_{\text{QES}} \approx \text{const} = C(\Omega_b)$.³⁶ In neutron scattering, QES and the boson peak have the same q dependence of the dynamic structure factor $S(q, \omega)$ (in silica³⁷ and polybutadiene³⁸). Finally, there is an empirical correlation between the value of the inverse fast relaxation time τ^{-1} and the frequency of the boson peak maximum Ω_b : $\tau^{-1} \approx \Omega_b/3$, Fig. 1 (here Ω_b is taken from low-temperature Raman spectra and for τ^{-1} some characteristic value is assumed from a broad interval where it is practically constant, specifically, near T_g). It is difficult to explain these similarities without additional assumptions if the QES is direct light or neutron scattering on the relaxation modes independent of the low-frequency vibrations.

A phenomenological model of QES which accounts for these similarities was proposed in Refs. 22,25: it was assumed that the quasielastic line corresponds to a low-frequency relaxationlike part of the one-phonon response function which arises due to coupling of vibrations to an

unspecified relaxation mode. This phenomenological model in the single relaxation time approximation has been applied by various authors to describe the quasielastic light scattering spectra in a broad temperature interval both in glasses and supercooled liquids^{6,17–19,25–28,30,39} and a reasonable fit of the spectra has been obtained. However, the microscopic mechanism of the relaxation was not considered within the framework of this model.

In the present paper it is shown that the lattice anharmonicity produces a quasielastic part in the one-phonon scattering in glass formers. The QES caused by this mechanism is inevitable (since anharmonicity is inevitable in any glass) and is independent of whether direct light scattering by some relaxational modes in the glass exists or not. Such modes, if they exist and influence the scattering, will give rise to an additional quasielastic spectrum. However, the estimations of the present work show that the QES caused by anharmonicity is sufficient to explain the total amplitude of the quasielastic scattering at the glass transition temperature in all materials for which we are able to find the needed data. Moreover, it is shown that the width of the quasielastic line correlates with the position of the low-frequency vibrational peak (the boson peak) in accordance with predictions of the model and is determined by the relaxation time of the phonon density fluctuations. It is shown that in the third-order anharmonic approximation the integral ratio of the quasielastic to vibration spectrum is determined by the squared Grüneisen parameter. When the fourth-order anharmonic term is taken into account, a crossover temperature T_c appears in the model. Above this temperature the fast relaxation does not increase anymore. In particular, the temperature dependence of the fast relaxation in B_2O_3 (Ref. 6) including a crossover at 800–900 K is well described. Within the frames of the model the relative interval $(T_c - T_g)/T_g$ (which correlates with the degree of fragility) is determined by the magnitude of the fourth-order anharmonic coefficient. The spectral shape of the fast relaxation predicted by the model is in agreement with experimental data. In a simplified version the anharmonic theory of the QES can be also formulated in terms of the Gochijaev *et al.* model²⁵ where a coupling between vibrational and unspecified relaxational modes is introduced; in the anharmonic mechanism all parameters of the model are specified, in particular, the vibration-relaxation coupling constant is the Grüneisen coefficient and the relaxation mode corresponds to the phonon density fluctuation.

This paper is organized as follows. In Sec. II the contribution to QES caused by the third-order anharmonicity is estimated through the vibration self-energy and general expressions for the intensity and the spectrum of the QES are obtained. A simplified derivation of these results is also given in order to explain the physical sense of the model. In Sec. II F the fourth-order term is incorporated in the model and the crossover behavior due to damping of the fast relaxation at high temperatures is described. In Sec. III quantitative estimates of the quasielastic intensity and spectral shape in some glass formers are obtained within the framework of the model and the approximations used are discussed. Comparison with the experimental data on light scattering both in fragile and strong glass formers is performed and the relation between anharmonicity and fragility is discussed. Finally, in Sec. IV the results are summarized.

II. THEORY

A. One-phonon light scattering and vibration self-energy

We consider one-phonon light scattering in a glass taking into account the anharmonicity of vibrations. The anharmonic interaction produces a self-energy term in the phonon response function which modifies the spectral shape and temperature dependence of the light scattering intensity in comparison with the case of harmonic vibrations; in particular, it leads to a quasielastic line. The intensity of the one-phonon Raman scattering by vibrations with a frequency Ω , $I_\Omega(\omega)$, is determined by the imaginary part of their response function $\chi(\omega, \Omega)$,

$$I_\Omega(\omega) \propto [n(\omega) + 1] [C(\Omega)/\Omega] \chi''_\Omega(\omega), \quad (2.1)$$

$$\chi_\Omega(\omega) = -[\omega^2 - \Omega^2 + \Sigma_\Omega(\omega)]^{-1}, \quad (2.2)$$

where $\Sigma_\Omega(\omega) = \Sigma'_\Omega(\omega) + i\Sigma''_\Omega(\omega)$ is the self-energy of the mode which has both real and imaginary parts and $C(\Omega)$ is the light to vibrations coupling constant; the extra Ω in the denominator in Eq. (2.1) is a standard factor that corresponds to the squared matrix element of a harmonic oscillator. In the simplest case $\Sigma_\Omega(\omega)$ can be approximated by the Debye relaxation function

$$\Sigma_\Omega(\omega) = \frac{\delta^2(\Omega)}{1 - i\omega\tau} \quad (2.3)$$

with a single relaxation time τ and relaxation strength parameter $\delta^2(\Omega)$. This approximation was used, e.g., in Refs. 6,17–19,25–28,30,39,41. The imaginary part of the vibrational susceptibility is equal to

$$\chi''_\Omega(\omega) = \frac{\Sigma''_\Omega(\omega)}{[\omega^2 - \Omega^2 + \Sigma'_\Omega(\omega)]^2 + [\Sigma''_\Omega(\omega)]^2}. \quad (2.4)$$

To obtain the total Raman scattering intensity $I(\omega)$ one needs to integrate over the vibrational spectrum

$$I_r(\omega) = \int \chi''_\Omega(\omega) C(\Omega) g(\Omega) d\Omega / \Omega, \quad (2.5)$$

where

$$I_r(\omega) = I(\omega) / [n(\omega) + 1] \quad (2.6)$$

is the reduced scattering intensity and $g(\Omega)$ is the density of the vibrational states. At moderate temperatures, when $\Sigma_\Omega(\omega)$ is small [$\Sigma_\Omega(\omega) \ll \Omega^2$] the vibrational susceptibility at low frequencies $\omega \ll \Omega$ is determined only by the imaginary part of the self-energy

$$\chi''_\Omega(\omega) \approx \Sigma''_\Omega(\omega) / \Omega^4 \quad (2.7)$$

in first order on the relaxation strength parameter. With these conditions the reduced quasielastic light scattering intensity can be written in the form

$$I_r^{\text{QES}}(\omega) = \int \Sigma''_\Omega(\omega) C(\Omega) g(\Omega) d\Omega / \Omega^5. \quad (2.8)$$

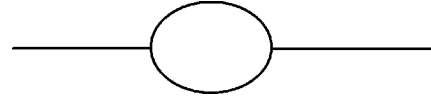


FIG. 2. Self-energy bubble diagram.

Below it will be shown that the cubic anharmonic interaction of vibrational modes leads to the self-energy $\Sigma(\omega)$ that describes QES in quantitative agreement with experimental data.

B. Third-order anharmonic self-energy

The calculation of the vibration self-energy has been discussed in many papers, in particular, in connection with the central mode in the structural phase transitions (see, e.g., Refs. 42,43). The Hamiltonian of vibrations with the third-order anharmonic term has the form

$$H = H_0 + V, \quad (2.9)$$

where

$$H_0 = \sum_\alpha \hbar \omega_\alpha a_\alpha^\dagger a_\alpha, \quad (2.10)$$

$$V = \sum_{\alpha, \beta, \gamma} V_{\alpha\beta\gamma} A_\alpha A_\beta A_\gamma. \quad (2.11)$$

Here a_α^\dagger and a_α are the operators of creation and annihilation of a phonon in mode α ,

$$A_\alpha = a_\alpha^\dagger + a_\alpha. \quad (2.12)$$

Due to the structural disorder the modes can be labeled by their frequency. Since in the spectral region of the boson peak and QES the depolarization ratio of the scattered light is typically high, the vibrations responsible for the boson peak are of transverse or rotation-libration type (see, e.g., Ref. 44). The self-energy of such vibrations corresponds to the bubble diagram of Fig. 2 and in the relaxation time approximation is given by (see, e.g., Refs. 42,43)

$$\Sigma_\Omega(\omega) = \frac{72\Omega}{T} \sum_\alpha \frac{V_\alpha^2 n_\alpha (n_\alpha + 1)}{1 - i\omega\tau_\alpha}, \quad (2.13)$$

where the third-order anharmonic coefficient V_α couples a mode of the frequency Ω with two modes of the frequency Ω_α , $n_\alpha \equiv n(\Omega_\alpha) \approx T/\Omega_\alpha$ is the phonon occupation number, M is the molecular mass, v is the transverse sound velocity, and τ_α is the relaxation time of the phonon occupation number of the mode α . It is convenient to express the cubic anharmonic coupling coefficient via the mode Grüneisen parameter γ_α (Ref. 42)

$$V_\alpha(\Omega) = \gamma_\alpha \frac{\Omega_\alpha}{6v} \left(\frac{\Omega}{2M} \right)^{1/2}. \quad (2.14)$$

In terms of this parameter

$$\Sigma_\Omega(\omega) \approx \frac{\Omega^2 T}{M v^2} \sum_\alpha \frac{\gamma_\alpha^2}{1 - i\omega\tau_\alpha}. \quad (2.15)$$

C. Spectrum of fast relaxation

From Eq. (2.13) the frequency dependence of the susceptibility function of the fast relaxation can be found if one knows the frequency dependence of the relaxation time $\tau(\Omega)$ and that of the density of vibrational states $g(\Omega)$. Assuming for γ_α^2 some average value in the region of the boson peak one has for the fast relaxation

$$\Sigma''_{\Omega}(\omega) \approx \frac{\omega \Omega^2 T \gamma^2}{M v^2} \int_0^{\Omega_m} \frac{\tau(\Omega_\alpha) g(\Omega_\alpha) d\Omega_\alpha}{1 + \omega^2 \tau^2(\Omega_\alpha)}, \quad (2.16)$$

where Ω_m is the frequency near the end of the acoustical spectrum. To obtain a rough estimate of the integral (2.16) we suppose the simplest power-law frequency dependence for the density of states and the relaxation time $g(\Omega) = A \Omega^\nu$ and $\tau^{-1}(\Omega) = B \Omega^{2\beta}$, where A and B are some frequency-independent parameters. Then, using also Eq. (2.8) one has

$$\Sigma''_{\Omega}(\omega) \approx \frac{\omega \Omega^2 T \gamma^2 A}{M v^2 B} \int_0^{\Omega_m} \frac{\Omega_\alpha^{\nu-2\beta} d\Omega_\alpha}{1 + \omega^2 \tau^2(\Omega_\alpha)}. \quad (2.17)$$

Let us introduce a new variable $x = 1/\omega \tau(\Omega_\alpha) = \Omega_\alpha^{2\beta}/\omega B$. Then $\Omega_\alpha = (\omega B x)^{1/2\beta}$, and Eq. (2.17) can be expressed via the dimensionless integral

$$\Sigma''_{\Omega}(\omega) \approx \frac{\omega^\alpha \Omega^2 T \gamma^2 A}{M v^2 B^{2-\alpha}} \int_0^{x_m} \frac{x^\alpha dx}{1+x^2}, \quad (2.18)$$

where

$$\alpha = (\nu + 1)/2\beta \quad (2.19)$$

and $x_m = 1/\omega \tau_0$. Here τ_0 is the minimum relaxation time which provides the cutoff of the relaxation time distribution. Now, to obtain the total scattering spectrum one should integrate $\Sigma''_{\Omega}(\omega)$ over contributions of vibrations of different frequencies Ω , as in Eq. (2.8):

$$\begin{aligned} I_r^{\text{QES}}(\omega) &= \int \Sigma''_{\Omega}(\omega) C(\Omega) g(\Omega) d\Omega / \Omega^5 \\ &= S \omega^\alpha \int_0^{x_m} \frac{x^\alpha dx}{x^2 + 1}, \end{aligned} \quad (2.20)$$

where S is a constant:

$$S = \frac{T \gamma^2 A}{M v^2 B^{2-\alpha}} \int C(\Omega) g(\Omega) d\Omega / \Omega^4. \quad (2.21)$$

At high frequencies, $\omega \gg \tau_0^{-1}$, one has $x_m \ll 1$, so the denominator in the integral in Eq. (2.20) can be put equal to 1. As a result, one obtains the Debye-like behavior for the high-frequency tail of the fast relaxation

$$\chi''(\omega) \propto I_r^{\text{QES}}(\omega) \approx (\omega \tau_0)^{-1} \frac{S}{(\alpha + 1) \tau_0^\alpha}. \quad (2.22)$$

At frequencies $\omega \ll \tau_0^{-1}$, since $x_m \gg 1$, the upper limit in the integral in Eq. (2.20) can be replaced by ∞ . In this case the integral is a constant equal to $\pi/[2\cos(\pi\alpha/2)]$, so

$$\chi''(\omega) \propto I_r^{\text{QES}}(\omega) \approx \omega^\alpha \frac{\pi S}{2 \cos(\pi\alpha/2)}. \quad (2.23)$$

This power-law dependence describes the low-frequency tail of the fast relaxation.

D. Single relaxation time approximation

Equation (2.13) includes many relaxation processes, each characterized by its own coupling strength and relaxation time. However, the Debye relaxation function (2.3) is a reasonable approximation of Eq. (2.13) with parameters γ^2 and τ chosen as appropriate average values and

$$\delta(\Omega) \approx \delta_0 \Omega, \quad (2.24)$$

$$\delta_0^2 = \gamma^2 \frac{T}{M v^2}. \quad (2.25)$$

The parameter δ_0 characterizes the strength of the relaxation. According to Eq. (2.7) the imaginary part of Eq. (2.3) describes the quasielastic line in the Raman spectra in the single time approximation

$$I_r^{\text{QES}}(\omega) \approx \frac{2}{\pi} \frac{\delta_0^2 \omega \tau}{1 + \omega^2 \tau^2} \int I_r^{\text{vib}}(\Omega) d\Omega / \Omega, \quad (2.26)$$

where

$$I_r^{\text{QES}}(\omega) = I^{\text{QES}}(\omega) / [n(\omega) + 1] \quad (2.27)$$

is reduced QES intensity and

$$I_r^{\text{vib}}(\Omega) \equiv C(\Omega) g(\Omega) / \Omega \quad (2.28)$$

is the reduced intensity of the Raman scattering by vibrations in the absence of the relaxation. Equation (2.26) can be used only when the quasielastic line and the boson peak are clearly separated; at higher temperatures when there is a significant overlapping of the quasielastic line and the boson peak the exact expression (2.2) of $\chi(\omega)$ via $\Sigma(\omega)$ must be used (see, e.g., Refs. 18,25). From Eq. (2.26) it is clear that the relaxation strength parameter δ_0^2 is equal to the ratio of the integrated quasielastic and vibrational spectra

$$\delta_0^2 \approx \frac{\int I_r^{\text{QES}}(\Omega) d\Omega / \Omega}{\int I_r^{\text{vib}}(\Omega) d\Omega / \Omega}. \quad (2.29)$$

Using δ_0 and τ as phenomenological fitting parameters one can fit the low-frequency Raman and neutron spectra well (see, e.g., Refs. 18,26,28,30, where one can find a more detailed discussion of the procedure and results of the fit).

E. Simplified derivation in single relaxation time approximation

In order to have a simple interpretation of the presented mechanism of relaxation it is useful to give a simplified derivation of Eq. (2.25). As is well known from the theory of light and neutron scattering near the structural phase transitions (see, e.g., Refs. 43,45), a vibration response with the

Debye self-energy function can result from the linear coupling of a bare vibration to any fluctuations in the solid that have a Debye relaxation spectrum. It is easy to see that the cubic anharmonic term produces such linear coupling of vibrational and relaxational modes. Let the effective potential energy for a vibration mode η of a frequency Ω be

$$U(x) = M\Omega^2 \eta^2/2 + B_3 \eta^3, \quad (2.30)$$

where Ω and M are the mode frequency and effective mass, respectively. In order to remove the apparent dependence of the parameters of the model on the frequency and mass it is convenient to use the normalized mode

$$x = M^{1/2} \Omega \eta. \quad (2.31)$$

In terms of x , $U = x^2/2 + b_3 x^3$, where

$$b_3 = B_3 / M^{3/2} \Omega^3. \quad (2.32)$$

The anharmonic term $b_3 x^3$ can be represented as $b_3 x(\overline{x^2} + \Delta x^2)$ where $\overline{x^2}$ means the square amplitude averaged over a time interval of the order of the period of the vibration and Δx^2 is a fluctuation of this mean square vibration amplitude. Such a representation makes sense if the respective relaxation time is larger than the period of the vibration. The fluctuation Δx^2 just plays the role of the relaxation mode ξ of the problem

$$\xi(t) = \Delta \overline{x^2}(t). \quad (2.33)$$

After a trivial shift of x by a constant factor $2b_3 \overline{x^2}$ in order to eliminate the linear term $x \overline{x^2}$ one has

$$U(x) = x^2/2 + b_3 x \xi + a \xi^2/2, \quad (2.34)$$

where the term $a \xi^2/2$ is added to U in order to take into account the minimum work needed to create a given thermal fluctuation ξ . For the Gaussian fluctuations the constant a is proportional to the inverse mean square value of ξ^2 , $a = T/\langle \xi^2 \rangle$.

The standard methods of fluctuation theory can be applied now to obtain the susceptibility function of the vibration $\chi_\Omega(\omega)$ using the equations of motion for the variables x and ξ . Introducing a dissipation function for the relaxation variable ξ , $F(\xi) = h \dot{\xi}^2/2$, where h is a dissipation constant⁴⁶ and neglecting the contribution γ_0 to the width of the vibrational mode due to processes other than the relaxational process under consideration, we obtain the following equations of motion:

$$\ddot{x}/\Omega^2 + x + b_3 \xi = f(t), \quad (2.35)$$

$$h \dot{\xi} + a \xi + b_3 x = 0, \quad (2.36)$$

where $f(t)$ is a random force term. For the Fourier transform of ξ one has from Eq. (2.36)

$$\xi(\omega) = \frac{-x b_3/a}{1 - i \omega \tau}, \quad (2.37)$$

where

$$\tau = h/a \quad (2.38)$$

is the relaxation time of ξ . Using expression (2.37) for $\xi(\omega)$ in the Fourier transform of Eq. (2.35), one obtains

$$\chi_\Omega(\omega) = -[\omega^2 - \Omega^2 + \Omega^2 \delta_0^2 / (1 - i \omega \tau)]^{-1}, \quad (2.39)$$

i.e., the vibration susceptibility $\chi_\Omega(\omega)$ associated with the mode x has a Debye self-energy (2.24) with the relaxation strength parameter δ_0^2 equal to

$$\delta_0^2 = b_3^2/a = b_3^2 \langle \xi^2 \rangle / T. \quad (2.40)$$

Since, according to definition, ξ is the fluctuation of $\overline{x^2}$, then using for the latter the harmonic oscillator value $\overline{x^2} = \Omega(n + 1/2)$ we see that the relaxation mode ξ is determined by the fluctuation of the phonon occupation number δn

$$\xi = \Omega \delta n, \quad (2.41)$$

respectively, $\langle \xi^2 \rangle = \Omega^2 \langle \delta n^2 \rangle$. It is known (see, e.g., Ref. 46) that the mean square fluctuation of the occupation number for the noninteracting bosons is equal to

$$\langle \delta n^2 \rangle = n(n+1). \quad (2.42)$$

Since the anharmonicity is already taken into account in Eq. (2.40) by the factor b_3^2 we can use in other terms the expressions for harmonic excitations. Then one finds

$$\delta_0^2 \approx b_3^2 \Omega^2 n(n+1)/T \approx b_3^2 T, \quad (2.43)$$

where we took into account that at high temperatures $n(\Omega) \approx T/\Omega$. The cubic anharmonic coefficient b_3 can be expressed via the mode Grüneisen parameter $\gamma_\Omega = -(\partial \ln \Omega / \partial \ln V)_T$; a simple estimation gives $\gamma_\Omega = b_3 L M^{1/2} \Omega$, where L is a characteristic length of the vibration with frequency Ω . For the quasilocalized vibrations that form the boson peak, the acousticlike relation $\Omega \sim v/L$ holds;^{22,34,35,47} hence,

$$b_3 = \gamma_\Omega / v M^{1/2}. \quad (2.44)$$

Using this expression for b_3 in Eq. (2.43) one obtains again the result of Eq. (2.25). This simple derivation has the purpose of clearing up the physical sense of the relaxation process to obtain estimates of the relevant parameters and provide a basis to deal with the more complicated anharmonic potentials which are difficult to handle using regular perturbation theory.

F. High-temperature damping of the fast relaxation by fourth-order anharmonicity

The fourth-order anharmonic term can be neglected at low enough temperatures, when the relaxation strength parameter δ_0^2 from Eq. (2.43) is small (as all anharmonic effects are). However, with increasing temperature the influence of the fourth-order anharmonic term may be significant and should be taken into account. We use here the simple approach presented in the previous section to find the respective corrections to Eq. (2.43). With the fourth-order anharmonic term the effective potential energy can be written in the form

$$\begin{aligned} U(x) &= M\Omega^2 \eta^2/2 + B_3 \eta^3 + B_4 \eta^4 \\ &= x^2/2 + b_3 x^3 + b_4 x^4, \end{aligned} \quad (2.45)$$

where $b_4 = B_4/M^2\Omega^4$. Using again the decomposition $x^2 = \bar{x}^2 + \xi$ with $\xi \equiv \Delta\bar{x}^2$ one can find an approximate expression of the potential $U(x)$ via the coupled vibration and relaxation modes

$$U(x) \approx x^2(1 + 2b_4\bar{x}^2)/2 + b_3x\xi + b_4\xi\bar{x}^2 + b_4\xi^2 + a\xi^2. \quad (2.46)$$

Here the term $1 + 2b_4\bar{x}^2$ renormalizes the frequency and the term $b_4\xi\bar{x}^2$ is unimportant for what follows since it does not influence the susceptibility. The equations of motion in this case can be found in the same way Eqs. (2.35),(2.36) were found and are the following:

$$\ddot{x}/\Omega^2 + (1 + 2b_4\bar{x}^2)x + b_3\xi = f(t), \quad (2.47)$$

$$h\dot{\xi} + (a + 2b_4)\xi + b_3x = 0. \quad (2.48)$$

The respective susceptibility is equal to

$$\chi_\Omega(\omega) = -[\omega^2 - \bar{\Omega}^2 + \bar{\Omega}^2\bar{\delta}_0^2/(1 - i\omega\bar{\tau})]^{-1}, \quad (2.49)$$

where

$$\bar{\Omega}^2 = \Omega^2(1 + 2b_4\bar{x}^2) \approx \Omega^2(1 + 2b_4T) \quad (2.50)$$

is the renormalized frequency,

$$\bar{\tau} = \tau/(1 + 2b_4T) \quad (2.51)$$

is the renormalized relaxation time and the modified expression for the relaxation strength parameter is

$$\bar{\delta}_0^2 \approx \frac{b_3^2 T}{(1 + 2b_4T)^2} = \frac{\gamma^2 T/Mv^2}{(1 + 2b_4T)^2}. \quad (2.52)$$

As the most important consequence, Eq. (2.52) predicts that at high enough temperatures the fast relaxation will no longer increase as temperature increases, providing the sound velocity does not decrease faster than $T^{1/2}$. The characteristic temperature T_a at which the fast relaxation strength parameter $\bar{\delta}_0^2$ stops increasing is determined by the condition $2b_4T_a \sim 1$, so

$$T_a \sim 1/2b_4. \quad (2.53)$$

In the next section this point will be discussed in more detail. Let us note that the term $2b_4T$ in the denominator of Eq. (2.52) can be written in the form

$$2b_4T \approx U_4/U_0, \quad (2.54)$$

where $U_0 = \bar{x}^2/2 \approx T/2$ and $U_4 = b_4\bar{x}^4 \sim b_4T^2$ are the average values of the harmonic and fourth-order anharmonic parts of the vibration potential energy, respectively. This means that within the framework of the model the fast relaxation saturates at a temperature when, roughly, the contribution of the fourth-order anharmonic term to the energy becomes comparable with that of the main harmonic term

$$\bar{U}_4(T_a)/\bar{U}_0(T_a) \sim 1. \quad (2.55)$$

Comparison of Eqs. (2.25) and (2.52) shows that the latter equation can be obtained from the first one by the renormalization of the Grüneisen parameter

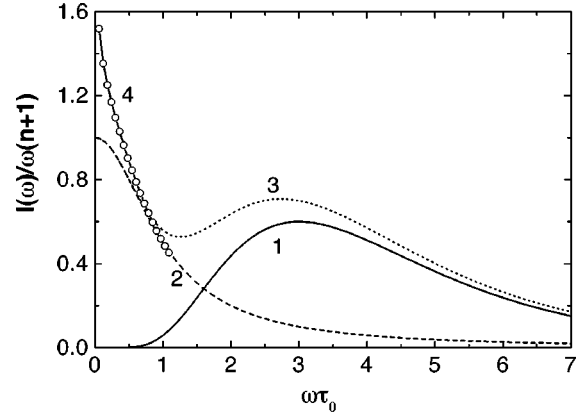


FIG. 3. Schematic presentation of a typical low-frequency Raman spectrum in a glass. (1) The boson peak, (2) the quasielastic line in the Debye approximation, (3) the sum of curves 1 and 2, (4) low-frequency wing of the quasielastic line when there is a distribution of the fast relaxation times at $\tau < \tau_0$.

$$\bar{\delta}_0^2 \approx \gamma_T^2 T/Mv^2, \quad (2.56)$$

where

$$\gamma_T = \frac{\gamma}{1 + 2b_4T}. \quad (2.57)$$

Indeed, it is known that the fourth-order anharmonicity leads to such a renormalization of the Grüneisen parameter in the isothermal conditions.⁴⁸

III. DISCUSSION

A. Schematic presentation of light scattering spectrum

For what follows, it is useful to present schematically the quasielastic and vibration contributions to the scattering spectrum. This is done in Figs. 3, 4. In Fig. 3 the spectral density normalization $I(\omega)/\omega(n+1)$ is used which corresponds to the direct light scattering intensity at high T . In these coordinates the boson peak can be observed most easily; in Fig. 3 this is a peak (solid line, curve 1) with a maximum at $\omega \sim 3$ (the quasielastic line width τ_0^{-1} is chosen as unity). The short dashed line (curve 2) represents the quasielastic spectrum in the single relaxation time approximation,

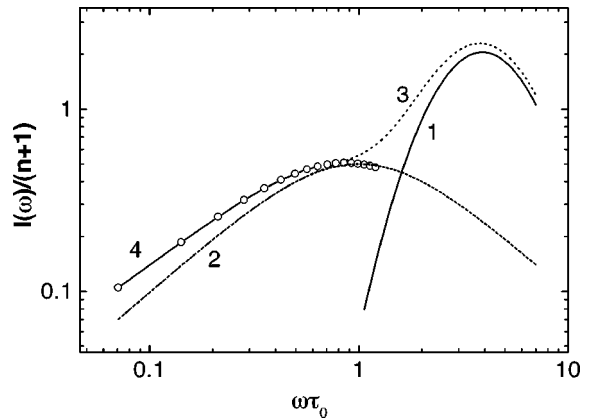


FIG. 4. The same curves as in Fig. 3 in susceptibility representation and log-log coordinates.

TABLE I. The values of parameters used in the model (at $T=T_g$). γ_{th} is found from Eq. (2.25). δ_0^2 and v_t are taken from Ref. 18 for polymers, from Ref. 6 for B_2O_3 , from Ref. 25 for glycerol, and from Ref. 63 for SiO_2 . γ for polymers is from Ref. 52, for SiO_2 from Ref. 64. Molecular mass M is in atomic units.

	$\delta_0^2(T_g)$	γ	$(T_g/Mv_t^2)^{1/2}$	γ_{th}	T_g (K)	v_t (10^5 cm/s)	M
PC	0.31	4.5	0.11	4.0	418	1.08	270
PS	0.21	3.2	0.16	3.3	373	1.12	111
PMMA	0.16	2.5	0.16	2.5	370	1.1	100
PB	0.13	2.4	0.16	2.3	175	1.1	54
Glycerol	0.1				186		92
B_2O_3	0.07		0.14	2.7	526	1.91	70
SiO_2	0.05	1.8	0.14	1.8	1480	3.8	60

so it is described by a Lorentzian. The dotted line (curve 3) is the sum of both contributions. The solid line with the open circles (curve 4) describes the quasielastic spectrum when there is a distribution of the relaxation times at $\tau \geq \tau_0$; it corresponds to a realistic Raman spectrum. Typically, the low-frequency Raman data are presented and analyzed in the coordinates of Fig. 3. The tandem Fabry-Perot light scattering data are normally presented as a log-log plot in a normalization that corresponds to the susceptibility $\chi'' \propto I(\omega)/(n+1)$. This case is illustrated by Fig. 4 with the same curves as in Fig. 3. Curve 4 clearly shows here the stretched low-frequency wing of the fast relaxation.

B. Relaxation strength parameter

The low-frequency Raman and neutron spectra of some glasses and supercooled liquids were fitted earlier using Eq. (2.5) and the Debye self-energy (2.3) with δ_0 and τ as phenomenological fitting parameters (see, e.g., Refs. 17–19, 25–28, 30, 39). In some cases the authors used δ ($\delta \equiv \delta_0 \Omega$) for fitting the parameter supposing that it is frequency independent; one should note, however, that both in the hydrodynamic approximation^{23,30,49} and in the case of the quasilocalized vibrations with the acousticlike relation $\Omega \propto L^{-1}$, Eq. (2.24) with a frequency-independent δ_0 holds. So, for a number of materials the temperature dependence and numerical values of δ_0 and τ are known. Typically, $\delta_0^2(T)$ is in the interval 0.05–0.3 and it is a monotonously increasing function of temperature with a more or less sharp jump of the slope at the glass transition temperature T_g (see, e.g., Ref. 18). The relaxation time τ is essentially temperature independent below T_g and has a tendency to slightly decrease above T_g . At $T \sim T_g$ the coefficient between δ_0^2 and γ^2 , T/Mv^2 [Eq. (2.25)], is more or less the same constant for various glass formers since T_g linearly correlates with Mv^2 . It is easy to show that this is a consequence of the Lindemann criterion of melting⁵⁰ and of the relation $T_g \approx 2T_m/3$ where T_m is the melting temperature. The relation $T_g \propto Mv^2$ was also confirmed by a direct comparison of both parameters for a lot of materials in Ref. 51. A good approximation of Eq. (2.25) at $T \leq T_g$ is

$$\delta_0^2 \approx \alpha_L^2 \gamma^2 T/T_g, \quad (3.1)$$

where $\alpha_L = 0.12$ – 0.16 is the Lindemann ratio that is a more or less universal parameter for various materials. From the

latter equation it follows that the strength of the fast relaxation at T_g is determined only by the Grüneisen parameter

$$\delta_0(T_g) \approx \alpha_L |\gamma| \approx 0.14 |\gamma|. \quad (3.2)$$

A direct estimate of Eq. (2.25) at $T=T_g$ gives $\delta_0^2 \sim 2 \times 10^{-2} \gamma^2$ (see Table I), in agreement with the estimate that uses the Lindeman ratio.

With a typical value of the Grüneisen parameter for polymers, $\gamma = 2$ – 4 (Ref. 52) one has $\delta_0^2 = 0.1$ – 0.3 at $T=T_g$ in good agreement with the results of the fit of the QES spectra which was performed in Ref. 18 for polycarbonate (PC), polystyrene (PS), polymethylmethacrylate (PMMA), and polybutadiene (PB), see Table I. In strong glass formers such as B_2O_3 and SiO_2 , the relaxation strength is lower than in polymers, see Table I. Let us note that there is a correlation between the strength of the fast relaxation δ_0 and the fragility of the system: the higher the fragility, the larger δ_0 (see Table I). This is of course in agreement with the observation of Sokolov *et al.*¹⁰ on the correlation between the fragility and a parameter which characterizes the relative strength of the QES in comparison with the boson peak intensity. According to the present model, this means that in fragile glass formers the anharmonicity is higher than in strong ones, see Eq. (3.2). Such a correlation was discussed by Angell¹ and was also obtained in the coupling model of Ngai (see, e.g., Ref. 53).

In Fig. 5 the temperature dependence of the relaxation strength parameter δ_0^2 as found from the fit of QES spectra in B_2O_3 (Ref. 6) is compared to the predictions of the model, Eq. (2.25), with $\gamma = 2.7$. The temperature dependence of the sound velocity was taken from the above cited paper. The comparison shows that Eq. (2.25) reasonably describes both the magnitude and temperature dependence of the fast relaxation strength δ_0 in B_2O_3 in some vicinity of T_g . Table I also shows good agreement between the predictions of the anharmonic model and the results of the free fit of the light scattering data by the Gochijaev *et al.* phenomenological model for other materials for which we were able to find the respective data. This means that the anharmonic mechanism of the quasielastic scattering is predominant at temperatures in the vicinity of and above T_g . The situation may be different at lower temperatures deep in the glassy state, where anharmonic effects decrease. In this case, the thermally activated jumps in the asymmetric double well potentials may be the dominant mechanism of the fast relaxation,⁹ which is the

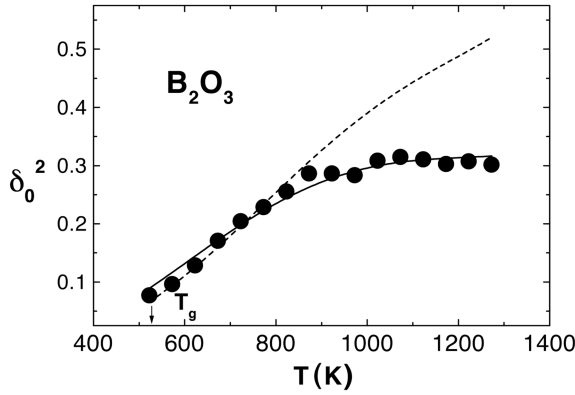


FIG. 5. Comparison of theory and experiment for the temperature dependence of the relaxation strength parameter δ_0^2 in B_2O_3 . Solid circles are data from light scattering, dash lines are the fit using Eq. (2.25), the solid line is the fit Eq. (2.52). Data for δ_0^2 and sound velocity from Ref. 6.

very subject of the Gilroy and Phillips¹² and the soft potential¹⁵ models. However, in the present paper we consider only the high-temperature regime.

C. Saturation of fast relaxation

The light scattering data of Ref. 6 show that in B_2O_3 the fast relaxation strength no longer increases with temperature at $T \geq T_a \approx 900$ K (Fig. 5), so Eq. (2.25) ceases to describe the $\delta_0^2(T)$ behavior at $T > T_a$. This may be explained by the influence of the quartic anharmonic term: according to Eq. (2.52) its contribution increases with temperature and may be important at high enough temperatures in B_2O_3 . In this case instead of Eq. (2.25) one should use the more complicated Eq. (2.52) which predicts saturation and an even decrease of $\delta_0^2(T)$ at high temperatures. In the majority of glass formers this effect is hidden by the α relaxation that comes into the spectral region of the fast relaxation at high temperatures; in B_2O_3 α relaxation is still far away from this region at temperatures around 1000 K which gives the possibility to observe here the fast relaxation saturation. The fit of $\delta_0^2(T)$ by Eq. (2.52) describes the crossover behavior of the fast relaxation strength parameter in B_2O_3 with $b_3 = 2 \times 10^{-2} \text{ K}^{-1/2}$ and $b_4 = 0.9 \times 10^{-3} \text{ K}^{-1}$ well. According to the general properties of the anharmonic coefficients, normally b_3^2 and b_4 should be of the same order of magnitude (see, e.g., Ref. 54). In our case $b_4 \sim 2b_3^2$, so the parameter b_4 which is responsible for the saturation of the fast relaxation in B_2O_3 has a quite reasonable value by the order of magnitude.

From Eq. (2.51) it follows that the inverse relaxation time should linearly increase with temperature with a slope determined by b_4 (if one neglects other possible contributions to the temperature dependence of τ). This prediction is checked in Fig. 6 where experimental points are found from the data of Ref. 6, b_4 is taken from the fit of $\delta_0^2(T)$ as described above, and $\tau(T \rightarrow 0) = 4.6 \text{ cm}^{-1}$. As follows from this figure, the temperature dependence of the relaxation time in B_2O_3 can be well described by the fourth-order anharmonic term.

Mode coupling theory predicts a temperature-independent fast relaxation in the liquid state above the so-called critical

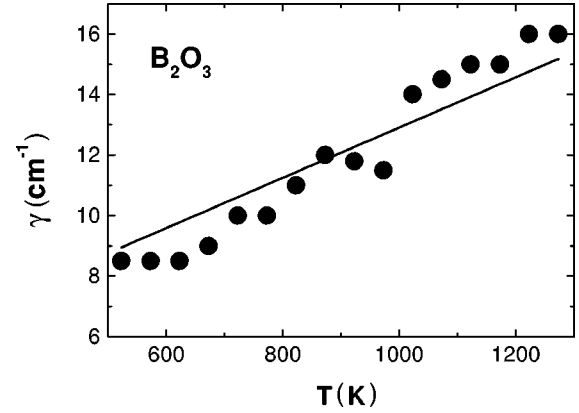


FIG. 6. Temperature dependence of the inverse relaxation time in B_2O_3 . Solid line: Eq. (2.51), solid circles: data from Ref. 63.

temperature T_c^3 . On the other hand, in the present anharmonic model of fast relaxation we are going from temperatures below T_c , beginning even in the glassy state, and also obtain a crossover behavior of the fast relaxation at some temperature T_a . This is in qualitative agreement with the predictions of the MCT and even quantitative (for the case of B_2O_3) with the phenomenological analysis of the high-temperature behavior of the fast relaxation performed in Ref. 55, where the authors found a crossover temperature both in strong and fragile glass formers and showed that in the latter case it is equal to the critical temperature of the MCT.

D. Relation between the anharmonicity and the ratio T_c/T_g

As it was shown in Sec. II. F in the anharmonic model the crossover temperature T_a is determined by Eq. (2.53) and corresponds to a temperature when the fourth-order anharmonic term U_4 becomes comparable to the main harmonic contribution U_0 to the vibration Hamiltonian. One of the consequences of this prediction explains the relation between the degree of fragility and the ratio T_c/T_g . It is known that in fragile glass formers this ratio is typically 1.2 while in strong glass formers it is higher (e.g., 1.6 in B_2O_3). If one takes for the crossover temperature the estimate (2.53) of the present work then

$$T_g/T_c = 2b_4T_g. \quad (3.3)$$

This means that at fixed T_g the ratio T_g/T_c decreases with decreasing anharmonic coefficient b_4 . However, in many cases, T_g is higher in materials with lower anharmonicity, so from Eq. (3.3) it is difficult to make a conclusion about the relation between T_g/T_c and anharmonicity itself. On the other hand, if the effective anharmonic potential for a mode η , Eq. (2.45) is written in dimensionless coordinates,

$$U(x) = (ka^2/2)[(\eta/a)^2 + f_3(\eta/a)^3 + f_4(\eta/a)^4], \quad (3.4)$$

where $k \equiv M\Omega^2$ is a fourth constant and a is an average interatomic distance, then the relative strength of the fourth-order anharmonic term may be characterized by a parameter f_4 which is the ratio of the coefficients at $(\eta/a)^4$ and $(\eta/a)^2$,

$$f_4 \equiv \frac{B_4 a^4}{ka^2/2}. \quad (3.5)$$

According to the definition, Eq. (2.45), $B_4 = b_4 k^2$ so one has $f_4 = 2b_4 k a^2$. As was mentioned above, the parameter $ka^2 = M\Omega^2 a^2 \propto Mv^2$ scales as T_g . In the Einstein oscillator model the coefficient can easily be found using the Lindemann criterion of melting: if one supposes that at $T = T_g$ the mean square atomic displacement is a universal part α_L of the average interatomic distance, $\eta \approx \alpha_L a$, then $k\eta^2(T_g) \approx k\alpha_L^2 a^2 \approx T_g$. As a result, $ka^2 \approx T_g/\alpha_L^2$ and

$$f_4 \approx 2b_4 T_g / \alpha_L^2. \quad (3.6)$$

A comparison with Eq. (2.45) gives

$$T_g/T_c \approx \alpha_L^2 f_4. \quad (3.7)$$

This result showed that the ratio T_g/T_c is proportional to the relative magnitude f_4 of the fourth-order anharmonicity. Qualitatively, this conclusion is in agreement with the results of the preceding subsections: the stronger the glass former the lower the anharmonicity.

E. Spectral shape of the fast relaxation

The spectral shape of the anharmonic contribution to fast relaxation is given by Eq. (2.20). This expression predicts the asymmetric susceptibility function with the high- and low-frequency tails described by Eqs. (2.22) and (2.23), respectively. The high-frequency tail is Debye-like, $\chi'' \propto \omega^{-1}$; this is a consequence of the existence of a minimum relaxation time τ_0 . The Raman data for the quasielastic line in glasses (typically, $\omega \geq 1 \text{ cm}^{-1}$) which represent mainly the high-frequency part of the fast relaxation are in agreement with this prediction: normally, they can be well fitted by a simple Lorentzian after properly accounting for the vibration contribution.^{18,22,25} At low frequencies, $\omega \ll \tau_0^{-1}$, a power-law spectrum of the fast relaxation is predicted, $\chi'' \propto \omega^\alpha$ with the exponent α defined by Eq. (2.19). The difference in the Debye-like behavior at these frequencies $\chi'' \propto \omega$ is due to existence of some distribution of the relaxation times at $\tau \geq \tau_0$. It is easy to find from Eq. (2.16) that in the present model the relaxation time distribution function $G(\tau)$ is determined by the equation

$$G(\tau) = g(\Omega) |\partial\Omega/\partial\tau| \quad (3.8)$$

with Ω found as a function of τ from the equation $\tau = \tau(\Omega)$. For the same power-law ansatz as in Sec. II, $g(\Omega) = A\Omega^\nu$ and $\tau^{-1}(\Omega) = B\Omega^{2\beta}$, one has

$$G(\tau) = (1 + \alpha)\tau_0^\alpha / \tau^{\alpha+1} \quad \text{for } \tau \geq \tau_0, \quad (3.9)$$

$$G(\tau) = 0 \quad \text{for } \tau < \tau_0. \quad (3.10)$$

In Eqs. (3.9), (3.10) τ_0 provides a cutoff of $G(\tau)$ at small τ which leads to a Debye behavior at $\omega \geq \tau_0^{-1}$. We note that in this respect the characteristic time t_c found previously in neutron scattering experiments⁵⁶ can be viewed as τ_0 .

Typically, for polymers in the region of the boson peak the density of vibrational states is practically linear in frequency, $\nu = 0.9-1$ (see, e.g., data for PS, PC, and PMMA in Refs. 18,36,58,57). According to sound absorption data in PS, some other polymers and $a\text{-SiO}_2$ at frequencies up to 440 GHz $l^{-1} \propto \omega^2$ (see Ref. 59); if one suppose that the diffusion coefficient D is frequency independent in the region

of the boson peak, so $\tau^{-1}(\Omega) \sim D l^{-2}(\Omega)$, then $\beta \approx 2$. With these values of the parameters ν and β one obtains $\alpha \approx 0.5$. For the Debye vibrational density of states ($\nu = 2$) and Rayleigh phonon scattering ($\beta = 4$) one has $\alpha \approx 3/8$. The vibrations in the THz region in glasses have not been studied enough to make reliable conclusions about the frequency behavior of the diffusion constant D . Our suggestion is based on the results of the computer simulation of a model glass,⁶⁰ where essentially the frequency-independent diffusion coefficient that describes the evolution of the vibration density fluctuation was found at frequencies corresponding to the boson peak. However, the alternative relation $\tau^{-1}(\Omega) \sim \nu/l(\Omega)$ with frequency-independent sound velocity can also be considered. In this case all the differences in the preceding results come from changing $\beta \rightarrow \beta/2$ in the expression for the exponent α (2.23). In particular, for the typical value of α in polymers one obtains 1 instead of 0.5; for the case of the Debye vibrations one obtains $\alpha \approx 3/4$ instead of $3/8$.

Light scattering spectra of the picosecond relaxation in a broad frequency range (typically, 1–600 GHz) can be measured using a tandem Fabry-Perot interferometer. Such data have been obtained up to now for temperatures around and above T_g in some glass formers and are in agreement with the predictions of the model, exhibiting a Debye high-frequency behavior and a stretched low-frequency wing with the slope α in the interval from 0.3 to 0.8 in various materials.⁸ Recently, spectra of the fast relaxation were measured by light scattering in a broad frequency and temperature range in the glassy state of polymers of CKN and silica.⁹ The value of the exponent α at room temperature in most cases was found to be equal to 0.5–0.6, in agreement with the anharmonic model of relaxation.

The estimations performed in this subsection use some approximations. First, the Grüneisen constant was assumed to be frequency independent in the region of the boson peak; second, the density of vibrational states $g(\Omega)$ can only roughly be approximated by some power law in the region of the boson peak (especially in strong glass formers). Additionally, according to Ref. 61, the frequency dependence of the sound absorption in the region of the boson peak may change its behavior from ω^2 to ω^4 law, as was shown in Ref. 61 for longitudinal vibrations in amorphous silica where a crossover was found at 210 GHz. Therefore, for a more accurate estimation of the spectral shape of the fast relaxation additional experimental data on $\tau(\Omega)$ and $\gamma(\Omega)$ and a numerical evaluation of the integral (2.16) are needed.

Let us note that the soft potential model in its standard formulation predicts the logarithmic frequency dependence of the thermally activated fast relaxation in double well potentials.¹⁵ Therefore, it fails to correctly describe the low-frequency power-law tail of the fast relaxation in glassy state in the regime of the thermal activation. Thus, the SPM needs some further development, e.g., an improvement of the distribution function of the soft potential parameters.

F. Relaxation time

As was shown above the relaxation time τ in the self-energy function (2.16) is that of the fluctuations of the phonon occupation number. Here we make a rough estimate of

this relaxation time τ chosen as an appropriate average value, i.e., for the Debye relaxation approximation. For propagating phonons, the relaxation time of the occupation number fluctuations can be expressed through the phonon diffusion coefficient D and the phonon mean free path length l : $\tau^{-1} \sim D/l^2$. On the other hand, a simple estimate of the diffusion coefficient is $D \approx vl/3$ (v is the sound velocity of the appropriate phonon branch). As a result, a rough estimate of the relaxation time is

$$\tau^{-1} \sim (1/3)v/l. \quad (3.11)$$

Now we intend to use this formula for the vibrations near the maximum of the boson peak. Although there are controversial opinions on the propagating, localized, or diffusive nature of these vibrations, one can safely suppose that vibrations with a frequency near the maximum of the boson peak Ω_b satisfy the Ioffe-Regel criterion in the sense that their characteristic length L_b is of the order of the mean free path length l at Ω_b . Taking into account the relation $\Omega_b \sim v/L_b$ commonly used for the boson peak frequency, one can conclude that the characteristic fast relaxation time correlates with Ω_b :

$$\tau^{-1} \sim \Omega_b/3. \quad (3.12)$$

Although the exact value of the coefficient in this formula is of course out of the framework of the accuracy of this simple estimate, it corresponds to the experimental data obtained by Raman scattering surprisingly well. In Fig. 1 the correlation between Ω_b and τ^{-1} is shown for various glass formers, both fragile and strong. Here Ω_b is taken as the position of the boson peak at low temperatures and τ^{-1} as the width of the quasielastic line at temperatures where it is almost temperature independent, i.e., near T_g . In Fig. 1 values of τ^{-1} are used which were found by fitting the low-frequency Raman spectra using Eqs. (2.3)–(2.5) (which is essentially the Gochijaev *et al.* phenomenological model, Refs. 18,25) with τ as a free parameter. We also note that, in fact, in most cases τ^{-1} can be found precisely enough when the low-frequency Raman spectrum is fitted by a sum of a Lorentzian from Eq. (2.26), which represents the QES spectrum and the boson peak with temperature-dependent position and amplitude, as described in detail in Ref. 18.

It is useful to also make an estimate of the relaxation time using the relation $\tau^{-1} \sim D/l^2$ and known values of the thermal diffusion coefficient D . For example, in amorphous silica $D = 0.007\text{--}0.008$ cm²/s in the temperature range 300–1000 K.⁶² Taking $D = 0.007$ cm²/s and $l = 1$ nm we have $\tau^{-1} = 0.7$ THz. From Raman measurements, $\tau^{-1} \approx 0.5$ THz (see Fig. 1), so this estimate also gives a reasonable value of the fast relaxation time.

G. Direct light scattering on the relaxation mode

In the Introduction it was pointed out that QES and the boson peak have some similar properties, e.g., the value of the depolarization ratio. In the present paper, as also in Refs. 22,23,25, this similarity was explained using the assumption that the quasielastic line is a low-frequency relaxationlike

response of the vibration susceptibility function while the direct coupling of light to relaxation modes which damp the vibrations is small. In the anharmonic model of the present paper the nature of the relaxation mode ξ that damps the vibrations and leads to the central line is specified: at temperatures near T_g this is the phonon density fluctuation $\xi \propto \delta n$. The mode is quadratic in the vibration amplitude η . The same operator determines the two-phonon scattering.⁴² Hence, a direct coupling of light or neutrons to the relaxation mode in the present model corresponds to the two-phonon scattering and is small until the latter is smaller than the one-phonon contribution to the scattering. Typically, this is so at moderate temperatures but well above T_g both contributions may be comparable and direct coupling to the relaxation mode has to be taken into account. At these temperatures the above listed similarities between the central line and the boson peak may be violated. However, it is difficult to observe this experimentally since α relaxation usually comes at these temperatures to the region of quasielastic scattering making it impossible to separate the fast relaxation contribution.

IV. CONCLUSION

It was shown that anharmonicity of vibrations is one of the mechanisms of the fast relaxation in glasses and supercooled liquids. At temperatures near and above T_g its contribution to the quasielastic scattering is dominant and well describes both the intensity and the spectral shape of the latter. At lower temperatures, deep in the glassy state, the contribution of the vibration anharmonic terms decreases; one can suppose that here other mechanisms such as thermal activation in the double well potentials may be dominant and such models as the Gilroy-Phillips¹² and SPM (Ref. 15) are relevant. In comparison with these models an advantage of the anharmonic mechanism is that it is based on the well-established Hamiltonian of anharmonic vibrations. According to this mechanism, the quasielastic line is determined by the low-frequency relaxationlike part (the self-energy) of the vibration susceptibility function. This naturally explains the nontrivial similarities between the quasielastic scattering spectra and the boson peak found previously in light and neutron scattering experiments. In the present paper the self-energy part of the vibration susceptibility function was estimated for anharmonic vibrations taking into account both third- and fourth-order anharmonic terms. The strength of the fast relaxation δ_0^2 which is the integral ratio of the quasielastic to vibrational contribution was found to be proportional to the squared Grüneisen parameter γ ; in particular, at T_g this is a universal function of γ^2 , Eq. (3.2). Both fast relaxation strength and Grüneisen parameter increase when one moves in direction from strong to fragile glass formers.

It is shown that at high temperatures the quartic anharmonic term suppresses the contribution of the third-order anharmonicity to the quasielastic scattering. As a result, a crossover temperature T_a appears in the model; above T_a the intensity of the fast relaxation does not increase anymore, Eq. (2.52). At this temperature the mean value of the quartic anharmonic term in the vibrational Hamiltonian is of the order of the main harmonic one. This is in agreement with the Raman scattering data in B_2O_3 ,⁶ which is to our knowl-

edge the only known experimental result where the fast relaxation spectrum is not masked by α relaxation even at the crossover temperature. The width of the quasielastic line is determined by the relaxation time of the phonon occupation number. The high-frequency tail of the fast relaxation is Debye-like while the low-frequency one is described by a power law with the exponent less than unity which is determined by the frequency dependence of the density of vibrational states and that of the relaxation time of the phonon

density fluctuations. This exponent was estimated and compared with the light scattering experimental data.

ACKNOWLEDGMENTS

The author thanks H. Cummins, E. Duval, A. Sokolov, E. Rössler, and N. Surovtsev for useful discussions. This work was partially supported by INTAS Grant No. 93-2185ext and RFFI Grant No. 96-02-16202a. The support of Sonderforschungsbereich 279 is also acknowledged.

- *On leave from Institute of Automation & Electrometry, Russian Academy of Sciences, Novosibirsk, 630090, Russia.
- ¹C. A. Angell, *Science* **267**, 1924 (1995).
 - ²B. Frick and D. Richter, *Science* **267**, 1939 (1995).
 - ³W. Götzke and L. Sjögren, *Rep. Prog. Phys.* **55**, 241 (1992).
 - ⁴E. Rössler, V. N. Novikov, and A. P. Sokolov, *Phase Transit.* **63**, 201 (1997).
 - ⁵A. Kudlik, C. Tschirwitz, S. Benkhof, T. Blochowicz, and E. Rössler, *Europhys. Lett.* **40**, 579 (1997).
 - ⁶A. Brodin, D. Engberg, L. M. Torell, L. Börjesson, and A. P. Sokolov, *Phys. Rev. B* **53**, 11 511 (1996).
 - ⁷G. Li, W. M. Wu, X. K. Chen, H. Z. Cummins, and N. J. Tao, *Phys. Rev. A* **45**, 3867 (1992).
 - ⁸H. Z. Cummins, G. Li, W. M. Du, and J. Hernandez, *Physica A* **204**, 169 (1994); R. M. Pick, A. Aouadi, C. Dreyfus, R. Torre, and P. Bartolini, *J. Phys.: Condens. Matter* **8**, 9593 (1996); H. Z. Cummins, G. Li, W. Du, Y. H. Hwang, and G. Q. Shen, *Prog. Theor. Phys. Suppl.* **N126**, 21 (1997).
 - ⁹N. V. Surovtsev, J. Wiedersich, V. N. Novikov, A. P. Sokolov, and E. Rössler (unpublished).
 - ¹⁰A. P. Sokolov, E. Rössler, A. Kisliuk, and D. Quitmann, *Phys. Rev. Lett.* **71**, 2062 (1994).
 - ¹¹N. Theodorakopoulos and J. Jäckle, *Phys. Rev. B* **14**, 2637 (1976).
 - ¹²K. S. Gilroy and W. A. Phillips, *Philos. Mag. B* **43**, 735 (1981).
 - ¹³A. P. Sokolov, V. N. Novikov, and B. Strube, *Europhys. Lett.* **38**, 49 (1997).
 - ¹⁴D. Tielbürger, R. Merz, R. Ehrenfels, and S. Hunklinger, *Phys. Rev. B* **45**, 2750 (1992).
 - ¹⁵V. G. Karpov, M. I. Klinger, and F. M. Ignatiev, *Zh. Éksp. Teor. Phys.* **84**, 760 (1983) [*Sov. Phys. JETP* **57**, 439 (1983)]; U. Buchenau, Yu. M. Galperin, V. L. Gurevich, and H. R. Schober, *Phys. Rev. B* **43**, 5039 (1991); V. L. Gurevich, D. A. Parshin, J. Pelous, and H. R. Schober, *ibid.* **48**, 16 318 (1994).
 - ¹⁶J. Wiedersich, N. V. Surovtsev, V. N. Novikov, A. P. Sokolov, and E. Rössler (unpublished).
 - ¹⁷S. Kojima and V. N. Novikov, *Phys. Rev. B* **54**, 222 (1996).
 - ¹⁸V. N. Novikov, A. P. Sokolov, B. Strube, E. Duval, N. V. Surovtsev, and A. Mermet, *J. Chem. Phys.* **107**, 1057 (1997).
 - ¹⁹V. N. Novikov, N. V. Surovtsev, E. Duval, and A. Mermet, *Europhys. Lett.* **40**, 165 (1997).
 - ²⁰R. Nemanich, *Phys. Rev. B* **16**, 1655 (1977).
 - ²¹G. Carini, G. D'Angelo, G. Tripodo, A. Fontana, A. Leonardi, G. A. Saunders, and A. Brodin, *Phys. Rev. B* **52**, 9342 (1995).
 - ²²J. Jäckle, in *Amorphous Solids: Low-Temperature Properties*, edited by W.A. Phillips (Springer, New York, 1981).
 - ²³G. Winterling, *Phys. Rev. B* **12**, 2432 (1975).
 - ²⁴N. V. Surovtsev, E. Duval, A. Mermet, and V. N. Novikov, *J. Phys.: Condens. Matter* **7**, 8077 (1995).
 - ²⁵V. Z. Gochiyaev, V. K. Malinovsky, V. N. Novikov, and A. P. Sokolov, *Philos. Mag. B* **63**, 777 (1991).
 - ²⁶A. P. Sokolov, A. Kisliuk, D. Quitmann, A. Kudlik, and E. Rössler, *J. Non-Cryst. Solids* **172-174**, 1384 (1994).
 - ²⁷M. Krüger, M. Soltwisch, I. Petscherizin, and D. Quitmann, *J. Chem. Phys.* **96**, 7352 (1992).
 - ²⁸B. Rufflé, PhD thesis, Université de Rennes, 1996.
 - ²⁹U. Buchenau, C. Schönfeld, D. Richter, T. Kanaya, K. Kaji, and R. Wehrmann, *Phys. Rev. Lett.* **73**, 2344 (1994); B. Frick, B. Farago, and D. Richter, *ibid.* **64**, 2921 (1990); R. Zorn, A. Arbe, J. Colmenero, B. Frick, D. Richter, and U. Buchenau, *Phys. Rev. E* **52**, 781 (1995); J. Wuttke, W. Petry, G. Coddens, and F. Fujara, *ibid.* **52**, 4026 (1995).
 - ³⁰A. P. Sokolov, V. N. Novkov, and B. Strube, *Phys. Rev. B* **56**, 5042 (1997).
 - ³¹A. P. Sokolov, *Physica B* **219&220**, 251 (1996).
 - ³²V. N. Novikov, *Phys. Rev. B* **55**, R14 685 (1997).
 - ³³V. N. Novikov, *Philos. Mag. B* **77**, 381 (1998).
 - ³⁴V. K. Malinovsky and A. P. Sokolov, *Solid State Commun.* **57**, 757 (1986).
 - ³⁵V. K. Malinovsky, V. N. Novikov, P. P. Parshin, A. P. Sokolov, and M. G. Zemlyanov, *Europhys. Lett.* **11**, 43 (1990).
 - ³⁶A. P. Sokolov, U. Buchenau, W. Steffen, B. Frick, and A. Wischnewski, *Phys. Rev. B* **52**, R9815 (1995).
 - ³⁷U. Buchenau *et al.*, *Phys. Rev. Lett.* **60**, 1318 (1988).
 - ³⁸U. Buchenau, A. Wischnewski, D. Richter, and B. Frick, *Phys. Rev. Lett.* **77**, 4035 (1996).
 - ³⁹F. Terki, C. Levelut, J. L. Prat, M. Boissier, and J. Pelous, *J. Phys.: Condens. Matter* **9**, 3955 (1997).
 - ⁴⁰A. Brodin and L. M. Torell, *MRS Symp. Proc.* **455**, 37 (1997).
 - ⁴¹M. J. Lebon, C. Dreyfus, G. Li, A. Aouadi, H. Z. Cummins, and R. M. Pick, *Phys. Rev. E* **51**, 4537 (1995).
 - ⁴²R. Klein, in *Anharmonic Lattices, Structural Transitions and Melting*, edited by T. Riste (Noordhoff, Leiden, 1974), p. 161.
 - ⁴³A. D. Bruce and R. A. Cowley, *Structural Phase Transitions* (Taylor & Francis, London, 1981).
 - ⁴⁴V. N. Novikov, E. Duval, A. Kisliuk, and A. P. Sokolov, *J. Chem. Phys.* **102**, 4691 (1995).
 - ⁴⁵N. Lagakos and H. Z. Cummins, *Phys. Rev. B* **10**, 1063 (1974).
 - ⁴⁶L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, New York, 1980).
 - ⁴⁷E. Duval, A. Boukenter, and T. Achibat, *J. Phys.: Condens. Matter* **2**, 10 227 (1993).
 - ⁴⁸P. Choquard, *The Anharmonic Crystal* (Benjamin, New York, 1967), p. 268.
 - ⁴⁹J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980).
 - ⁵⁰F. A. Lindemann, *Phys. Z.* **11**, 609 (1911).
 - ⁵¹A. Heuer and H. W. Spiess, *J. Non-Cryst. Solids* **176**, 294 (1994).
 - ⁵²G. Hartwig, *Polymer Properties at Room and Cryogenic Temperatures* (Plenum, New York, 1994).

- ⁵³K. L. Ngai and C. M. Roland, in *Structure and Dynamics of Glasses and Glass Formers*, edited by C. A. Angell *et al.*, MRS Symposia Proceedings No. 455 (Materials Research Society, Pittsburgh, 1997), p. 81.
- ⁵⁴A. Maradudin, *Solid State Phys.* **19**, 1 (1966).
- ⁵⁵A. P. Sokolov, W. Steffen, and E. Rossler, *Phys. Rev. B* **52**, 5105 (1995).
- ⁵⁶J. Colmenero, A. Arbe, and A. Algeria, *J. Non-Cryst. Solids* **172-174**, 126 (1994).
- ⁵⁷N. V. Surovtsev, PhD thesis, Université Lyon-1, 1996.
- ⁵⁸A. Mermet, N. V. Surovtsev, E. Duval, J. F. Jal, J. Dupuy-Philon, and A. J. Dianoux, *Europhys. Lett.* **36**, 277 (1996).
- ⁵⁹C. J. Morath, G. Tas, T.C-D. Zhu, and H. J. Maris, *Physica B* **219**, 296 (1996).
- ⁶⁰P. Sheng and M. Zhou, *Science* **253**, 539 (1991).
- ⁶¹R. Vacher, J. Pelous, and E. Courtens, *Phys. Rev. B* **56**, R481 (1997).
- ⁶²Y. S. Toulounian, R. K. Kirby, R. E. Taylor, and T. Y. R. Lee, *Thermal Properties of Non-Metallic Solids* (IFI/Plenum, New York, 1977).
- ⁶³A. P. Sokolov (unpublished).
- ⁶⁴D. S. Sanditov and B. B. Mantatov, *Phys. Chem. Glasses* **15**, 699 (1989).