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2007 J. Phys.: Condens. Matter 19 196101

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# Interrelation between fast relaxation and mode-coupling theory temperature in glass formers

N V Surovtsev

Institute of Automation and Electrometry, Russian Academy of Sciences, Novosibirsk, 630090, Russia

Received 12 February 2007, in final form 7 March 2007

Published 17 April 2007

Online at [stacks.iop.org/JPhysCM/19/196101](http://stacks.iop.org/JPhysCM/19/196101)

## Abstract

The damping parameter, describing the contribution of fast relaxation to the low-frequency Raman spectrum, versus temperature is considered for a wide set of glass formers. It is found that at the critical temperature  $T_c$ , within the framework of the mode-coupling theory, the damping parameter takes the same value of 0.3 for all glass formers. The correlation between the damping parameter at the glass transition temperature and the fragility, proposed in Novikov *et al* (2005 *Phys. Rev. E* **71** 061501), is considered for a wider set of data and discussed. A possible interpretation of the findings is suggested.

## 1. Introduction

Fast relaxation is the relaxation response of glassy and liquid substances manifesting in the GHz–THz spectral range. Fast relaxation can be studied by inelastic light scattering down to temperatures much below the glass transition temperature  $T_g$  [1]. In the glassy state the fast relaxation is usually described as a manifestation of an anharmonic response due to defects (for example [2]). Interest in the features of fast relaxation in supercooled liquids was stimulated by mode-coupling theory (MCT) [3, 4], predicting a two-step response for glass former substances near the glass transition. A number of studies have been carried out for different glass formers, including a description of fast relaxation in the framework of MCT (see references in a recent review [5]). Usually, the fast relaxation response is associated with a fast response in the framework of MCT. So one could expect that the fast relaxation characteristic should correlate with other properties of glass formers. One of the interesting attempts to search for such a correlation is work in which the relative intensity of the fast relaxation was correlated with the fragility [6]. This result was refined recently in the work [7], where the authors used the damping parameter to describe the fast relaxation intensity. This parameter arises in the model of a damped oscillator, in the framework of which the low-frequency Raman spectrum is written as [8]

$$I_n(T, \omega) = \frac{2}{\pi} \int_0^\infty \frac{I_n^0(T, \Omega) \Omega^4 \delta_0^2 \gamma / (\omega^2 + \gamma^2) d\Omega}{(\Omega^2 - \omega^2 - \delta_0^2 \gamma^2 \Omega^2 / (\omega^2 + \gamma^2))^2 + (\delta_0^2 \gamma \Omega^2 \omega / (\omega^2 + \gamma^2))^2}. \quad (1)$$

**Table 1.** The value of parameters used in the paper:  $T_g$ ,  $m$  and the  $T_c/T_g$  ratio for different materials and corresponding references. Also references for light scattering data, from which  $\delta_0^2$  was taken, are indicated, the asterisk indicating those where  $\delta_0^2$  was calculated in the referenced works.

	Glass former	$T_g$ (K), ref.	$m$ , ref.	$T_c/T_g$ , ref.	Light scattering, ref.
1	B <sub>2</sub> O <sub>3</sub>	525 [9]	32 [30]	1.6 [9]	[9, 34]*
2	As <sub>2</sub> S <sub>3</sub>	461 [29]	37 [14]	1.3 [13]	[13]*
3	Propylene glycol	167 [30]	52 [30]	1.5 [31]	[35]*
4	Polybutadiene (PB)	180 [31]	59 [31]	1.2 [31]	[8]*
5	Salol	218 [32]	73 [30]	1.17 [32]	[32]
6	Poly(propylene-glycol)	200 [15]	75 [30]	1.25 [15]	[15]
7	Selenium	308 [30]	87 [30]	1.1 [14]	[14]*
8	Ca <sub>0.4</sub> K <sub>0.6</sub> (NO <sub>3</sub> ) <sub>1.4</sub> (CKN)	333 [31]	93 [31]	1.12 [31]	[36, 1]
9	Toluene	117 [11]	107 [30]	1.3 [11]	[11]
10	Polystyrene (PS)	375 [30]	139 [30]	1.15 [33]	[8]*

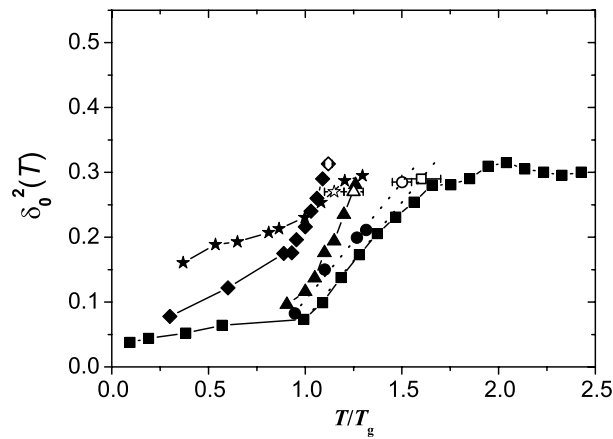
Here  $I_n(\omega) = I(\omega)/[(n+1)\omega]$  is the spectral density presentation for the Raman spectrum and  $n = (\exp(\hbar\omega/k_B T) - 1)^{-1}$  is the Bose factor.  $I_n^0(T, \Omega)$  is the vibrational Raman spectrum at temperature  $T$ , in the absence of fast relaxation. This vibrational spectrum can be found from a very low-temperature spectrum taking into account its quasi-harmonic shift with temperature. Equation (1) assumes the one-relaxation time for the relaxation response, the parameter  $\delta_0^2(T)$  describes the strength of the relaxation process and a coupling between the vibration and relaxation modes, being equal to the ratio of the integral over the fast relaxation spectral density to that of the boson peak [8]. In [7] it was found that at the glass transition temperature  $T_g$  the magnitude of the damping parameter  $\delta_0^2(T_g)$  is proportional to the fragility index.

Another important feature predicted by MCT is that at  $T > T_c$ , where  $T_c$  is the critical temperature in the framework of MCT, the fast relaxation spectrum is temperature independent. This prediction was proved in the case of a strong glass former B<sub>2</sub>O<sub>3</sub> [9]. In fragile glass formers this prediction cannot be seen directly in the spectra, since  $\alpha$  relaxation provides a significant contribution to the experimental Raman spectrum at  $T > T_c$ . Indeed, the prediction was proved for a number of fragile glass formers in [10–12], in which the fast relaxation spectrum above  $T_c$  was found by subtraction of the contribution of the  $\alpha$  relaxation. In addition, in [13] it was noted that the parameter  $\delta_0^2(T_c) \approx 0.3$  is the same for two different glass formers, B<sub>2</sub>O<sub>3</sub> and As<sub>2</sub>S<sub>3</sub>. This result was extended in our recent work [14] to selenium, toluene and propylene glycol glass formers.

The present work extends the analysis of the behaviour of  $\delta_0^2(T_c)$  and  $\delta_0^2(T_g)$  for a wide range of materials and is addressed to the question of how these results should be rationalized. Both published data for  $\delta_0^2$  and our analysis by equation (1) of the published light scattering spectra are used in the present work. Table 1 provides information about the data used.

## 2. Fast relaxation intensity at specific temperatures of vitrification

The procedure for the subtraction of the contribution of  $\alpha$  relaxation, which is needed for fragile materials at and above  $T_c$ , is a delicate point, as it can cast doubts on the results of analysis. That is why in [14] an alternative method was suggested, which takes into account that the fast relaxation increases approximately as a linear function in the range  $T_g < T < T_c$ . Figure 1 illustrates this for a number of glass formers. Data are taken from the literature as indicated in table 1. The parameter  $\delta_0^2$  was either taken directly from the literature (if the reference in the table is marked with an asterisk) or was found by fitting the original light scattering spectra. In



**Figure 1.** Temperature dependence of the  $\delta_0^2$  parameter for different glass formers scaled by glass transition temperature:  $B_2O_3$  (squares), propylene glycol (circles), poly(propylene-glycol) (triangles), CKN (diamonds), polystyrene (stars). Open symbols correspond to  $\delta_0^2(T_c)$  estimation by interpolation or extrapolation (extrapolations are shown by dotted lines).

cases when the literature data were fitted by equation (1), the low-frequency cut-off  $\sim 100$  GHz was used in order to be able to fit the data within the one relaxation time approximation, which is suggested in equation (1). For poly(propylene-glycol) we used an average value  $T_c = 250$  K between  $T_c = 265$  K found in [15] by scaling Brillouin–Raman data and  $T_c = 236$  K, found in this work from photon-correlation spectroscopy data. Dielectric relaxation time data from figure 4 of [15] were fitted by MCT expression, and  $T_c \sim 250$  K was found from this fit. In figure 1 the temperature was scaled by  $T_g$  in order to compare different glass formers.

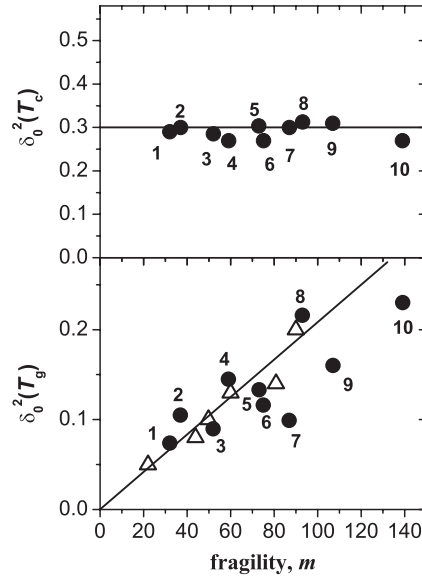
Interpolation or extrapolation of data presented in figure 1 provide the estimation for the damping parameter  $\delta_0^2$  at  $T_c$ . Open symbols in figure 1 correspond to the  $\delta_0^2(T_c)$  estimation. In the case of the glass former  $B_2O_3$  the high-temperature limit can be obtained directly from the experiment and it is seen that the extrapolated value is in good agreement with  $\delta_0^2(T \rightarrow \infty)$ . In figure 1 a few typical examples are shown ( $B_2O_3$ , propylene glycol, poly(propylene-glycol), CKN, polystyrene), covering the different types of glass formers: strong and fragile ones, covalent and ionic ones, monomers and polymers.

The common feature of the temperature dependences of the damping parameter is a change of the behaviour at  $T = T_g$ , marking the sensitivity of the fast relaxation to this specific point of vitrification. The magnitude of  $\delta_0^2(T_g)$  is different for different glass formers.

Figure 2 presents the magnitudes of the parameter  $\delta_0^2$  at two specific temperatures  $T_g$  and  $T_c$  versus fragility,  $m$ . The bottom part of the figure checks the correlation

$$\delta_0^2(T_g) \propto m, \quad (2)$$

proposed in [7]. It is seen that in general this correlation is supported by the present data, but for three materials—selenium, toluene and polystyrene—one finds a significant deviation from the linear law suggested in [7]. It looks as these substances would have a fragility higher than expected from equation (2). It is interesting to note that in recent work [16] it was found that selenium and toluene show disagreement between their kinetic and thermodynamic fragilities, while over 50 nonpolymeric glass-forming materials provide good agreement between their kinetic fragility and thermodynamic variables. So it looks like the deviation of selenium and toluene from equation (2) is not random, but reflects a peculiarity of these materials. If one takes



**Figure 2.** Value of  $\delta_0^2$  parameter at  $T = T_c$  (top figure) and  $T = T_g$  (bottom figure) versus fragility of glass formers. Numbers correspond to table 1. Triangles in the bottom figure are from [7].

the thermodynamic fragility for selenium ( $m_{\text{calc}} = 40$ ) and toluene ( $m_{\text{calc}} = 63$ ) from [16], than the correlation with equation (2) is restored for these substances.

The top part of figure 1 demonstrates that all studied substances follow the rule

$$\delta_0^2(T_c) \approx 0.3. \quad (3)$$

The high precision with which equation (3) is obeyed and the absence of exceptions are astonishing and provide a challenge for theories of vitrification. It is not clear how this result should be rationalized. The main questions are why is there universality for different glass formers and why this value?

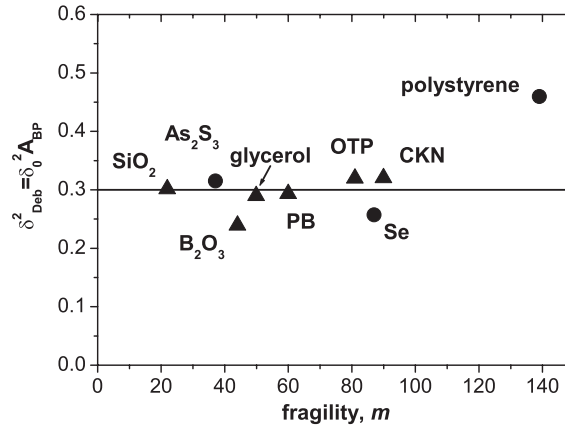
In [7] a Debye-scaled damping parameter  $\delta_{\text{Deb}}^2$  at the glass transition temperature was calculated,

$$\delta_{\text{Deb}}^2(T_g) = \delta_0^2(T_g) A_{\text{BP}}, \quad (4)$$

where  $A_{\text{BP}}$  is the maximum of the ratio of the boson peak amplitude to the Debye level. It was found that  $\delta_{\text{Deb}}^2(T_g) \approx 0.3$  for different glass formers and does not depend on fragility. It is interesting to note the appearance again of the value 0.3. Figure 3 presents  $\delta_{\text{Deb}}^2$  versus fragility both for data from [7] and for new data from the present work. For selenium  $A_{\text{BP}} = 2.6$  was taken from [7], for  $\text{As}_2\text{S}_3$  it was assumed that  $A_{\text{BP}} = 3$  is the same as for  $\text{B}_2\text{O}_3$ , since their experimental low-temperature specific heat and Debye level are very close (see, for example, [17]). For polystyrene the density of states was found by solving the integral equation for low-temperature specific heat (in the way described in [18]). Low-temperature specific heat was taken from [19, 20] and the Debye level from [21]. The value of  $A_{\text{BP}} = 2$  was found for polystyrene.

From figure 3 it is seen that the data for  $\text{As}_2\text{S}_3$  and selenium support the finding of [7], while those for polystyrene do not. The disagreement for polystyrene is mainly due to too the ‘high’ value of  $A_{\text{BP}}$ . Indeed, it can be checked that this value is in disagreement with the correlation

$$A_{\text{BP}} \propto m^{-1}, \quad (5)$$



**Figure 3.** The parameter  $\delta_0^2(T_g)A_{\text{BP}}$  versus fragility. Triangles are data from [7], circles from the present work.

found in [7], if one compares the polystyrene value with figure 8 of [7]. It is interesting to note that the fit of the correlation of figure 8 in [7] provides a dependence,

$$m = 160 * A_{\text{BP}}, \quad (6)$$

corresponding to the maximum fragility of 160, since the extreme case corresponds to  $A_{\text{BP}} = 1$ . (For fitting, data from the present work, except for the case of polystyrene, were added to data from [7].) This estimation is close to those made in [16], where it is predicted that fragility cannot exceed  $m = 170$ .

The example of polystyrene underlines that the complexity of the molecular structure could cause the violation of the rules of equations (2), (4) and (5). Probably, this signals that these correlations are only correlations, and not ‘cause’ and ‘consequence’. In contrast to this, the rule of  $\delta_0^2(T_c) = 0.3$  has no exceptions (to our knowledge).

### 3. Discussion

In previous work [13] the rule of  $\delta_0^2(T_c) = 0.3$  was suggested on the basis of only two glass formers; in the present work the validity of it is shown for a set of glass formers with different properties. It seems from figure 2 that this rule is more general than equation (2) and to our present knowledge there are no exceptions to this rule.

The magnitude of  $\delta_0^2$  is usually attributed to the ratio of the integral over fast relaxation spectral density to that of the boson peak [8], but this is true only for the approximation of one relaxation time. It is known now that this approximation is not true for the consideration of the fast relaxation spectrum in a wide relaxation range down, say, to  $\sim 1$  GHz [1]. The very low-frequency part of the fast relaxation susceptibility can be described by an expression like  $\chi''(\omega) \propto \omega^\beta$ , where  $\beta$  can be lower than 1 in contrast to the one relaxation time approximation [1]. It can be checked that value of  $\beta$  is different for the different materials presented in figures 2 and 3. This means that the total integral over the fast relaxation spectral density is very different for the different materials, and for this integral rules like equations (2)–(4) are not valid. Thus, we conclude that it is not the integral intensity of the fast relaxation that provides the regularities like equations (2)–(4).

In [13] it was suggested that the relaxation broadening of the boson peak vibrations is the key parameter which makes the rule  $\delta_0^2(T_c) = 0.3$ . This suggestion clarifies the situation.

Indeed, the susceptibility  $\chi''(\omega)$  of a damped oscillator with frequency  $\Omega$  can be written as

$$\chi''(\omega) = \frac{-1}{\omega^2 - \Omega^2 + \Omega^2 M(\omega)}. \quad (7)$$

Here the hydrodynamic attenuation term is neglected and omitted,  $\Omega^2 M(\omega)$  is memory function, describing the coupling between the oscillator and relaxation, with the frequency squared coupling term (hydrodynamic-like) picked out [8], and

$$M(\omega) = \sum_j \frac{\delta_0^2(\tau_j)}{1 - i\omega\tau_j}. \quad (8)$$

For relatively weak attenuation of the vibration the relaxation width (FWHM)  $\Gamma$  is estimated as  $\Gamma \cong \Omega M''(\Omega)$ , or

$$\Gamma/\Omega \cong M''(\Omega). \quad (9)$$

From equation (9) it is seen that for the relaxation width of a vibration the relaxation magnitude at the vibration frequency is important. It is hard to find  $M''(\Omega_{\text{BP}})$  unambiguously directly from experimental spectrum, since the vibrational spectrum dominates in this frequency range. Usually, the fast relaxation spectrum dominates at  $\omega \leq \Omega_{\text{BP}}/2$ . In this case one needs to find  $M''(\Omega_{\text{BP}})$  from the experimental spectrum in the range  $\omega \leq \Omega_{\text{BP}}/2$ . Near the boson peak maximum  $\Omega_{\text{BP}}$  and down to about  $\sim 0.2\Omega_{\text{BP}}$  the one relaxation time approximation is a rather good approximation for the fast relaxation susceptibility as it can be proved by inspecting the figures, presented in [1, 22]. Thus, when one fits the experimental spectra by equation (1) down to  $\sim (0.1-0.2)\Omega_{\text{BP}}$  one just gets an estimation for  $M''(\omega)$  for relatively high frequency. The assumption, that the ratio  $\Gamma_{\text{BP}}/\Omega_{\text{BP}}$  is the key physical parameter, explains why rules like equations (2)–(4) can exist.

It is interesting to turn to the question of what magnitude of  $\Gamma_{\text{BP}}/\Omega_{\text{BP}}$  corresponds to  $\delta_0^2 = 0.3$ . From equation (1) [13] it follows that

$$\frac{\Gamma_{\text{BP}}}{\Omega_{\text{BP}}} \cong \frac{\delta_0^2 \gamma \Omega_{\text{BP}}}{\Omega_{\text{BP}}^2 + \gamma^2}. \quad (10)$$

We define the boson peak maximum as the maximum of the vibrational density of states divided by squared frequency. In this case the empirical relation between  $\gamma$  and  $\Omega_{\text{BP}}$ , found in [23], is modified to

$$\gamma \approx \Omega_{\text{BP}}/2 \quad (11)$$

(this can be concluded from the comparison of the Raman boson peak maximum of [23] and  $\Omega_{\text{BP}}$  in the work [24]). Thus, from equations (10) and (11),  $\Gamma_{\text{BP}}/\Omega_{\text{BP}} \approx 0.4\delta_0^2$ . For  $\delta_0^2(T_c) \approx 0.3$ ,

$$\frac{\Gamma_{\text{BP}}(T_c)}{\Omega_{\text{BP}}} \approx 0.12. \quad (12)$$

Equation (12) looks like a dynamical analogue of the Lindemann criterion of melting [13]. In a simple model the boson peak can be considered as a consequence of the inhomogeneous structure of the glass at the nanometre level [25, 26]. Then, by speculation from the analogy with the Lindemann criterion, one can interpret the critical temperature  $T_c$  as the temperature of ‘dynamical’ melting of the glassy nanostructure. This corresponds well to the interpretation of  $T_c$  in the framework of the extended MCT version as a crossover temperature between the high-temperature regime dominated by liquid-like cage effects and the low-temperature regime dominated by solid-like activated hopping processes [27].

The existence of alternative approaches for describing the dynamics of supercooled liquids should be noted (for example, [28]). In these approaches the specific temperatures above  $T_g$  could have different meaning. For example, in [28]  $T_c$  serves as a crossover temperature above which a liquid-like dynamics ('high- $T$  physics' in terms of [28]) starts to contribute. It is obvious that this viewpoint is not in contradiction with the present discussion.

The described qualitative approach to rationalization of the result of equation (3) can be considered as a promising one, although detailed theoretical work is needed in this direction. Regardless of explanations, the presented findings indicate that fast relaxation is one of the key parameters of vitrification, responsible for the peculiarities of the microscopic dynamics of material in the glass transition range.

#### 4. Conclusion

The damping parameter  $\delta_0^2$  describing the spectral contribution of the fast relaxation is considered for a wide set of different glass formers. It was found that at the critical temperature  $T_c$ ,  $\delta_0^2(T_c) \approx 0.3$  for all materials analysed. It was argued that this finding has to be rationalized as the existence of a universal value of the relaxation broadening of the boson peak vibrations at  $T = T_c$ . Particular features of the fast relaxation at the glass transition temperature, supposed in [7], are also discussed. The sensitivity of  $\delta_0^2(T)$  to the glass transition temperature and its universal value at  $T_c$  indicate that fast relaxation is one of the key parameters of vitrification, which have to be grounded in the microscopic glass transition theory.

#### Acknowledgments

The author is grateful to V N Novikov and V K Malinovsky for stimulating discussions. This work was supported by RFBR grant no 06-03-32334, by the Interdisciplinary Science Fund of the Siberian Branch of RAS and the Russian Science Support Foundation.

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