

## Dynamics of glass-forming liquids at high temperatures: a general scenario

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys.: Condens. Matter 8 9587

(<http://iopscience.iop.org/0953-8984/8/47/067>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.207

The article was downloaded on 14/05/2010 at 05:39

Please note that [terms and conditions apply](#).

## Dynamics of glass-forming liquids at high temperatures: a general scenario

A P Sokolov<sup>†</sup>, W Steffen<sup>†</sup> and E Rössler<sup>‡</sup>

<sup>†</sup> Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021, Mainz, Germany

<sup>‡</sup> Physikalisches Institut, Universität Bayreuth, D-95440, Germany

Received 15 July 1996, in final form 10 September 1996

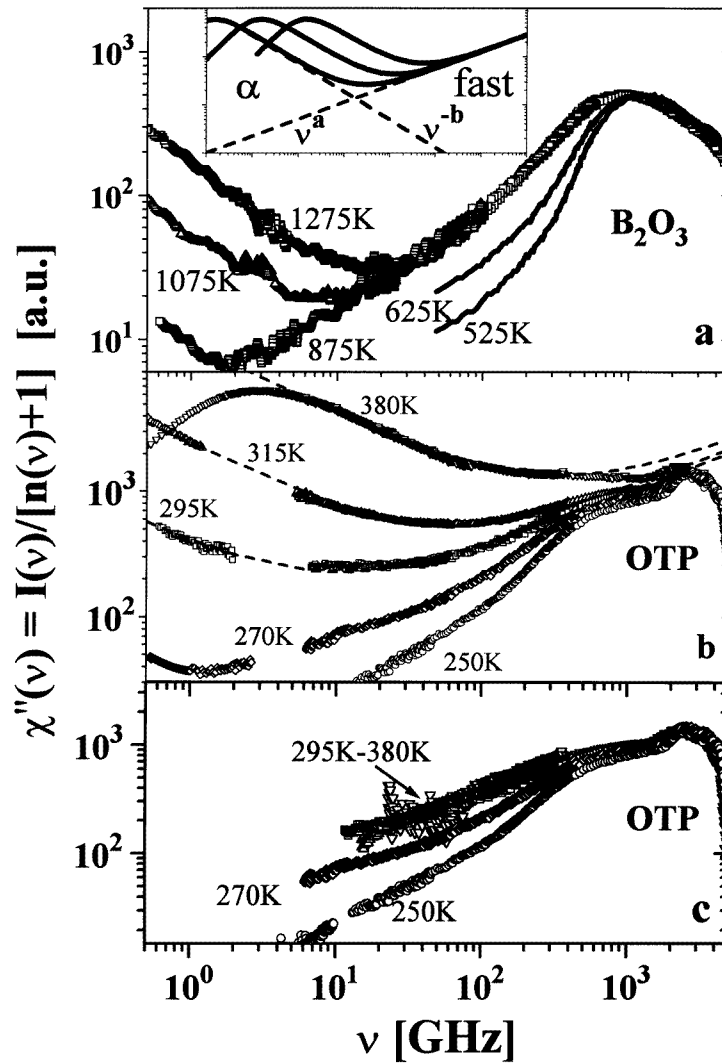
**Abstract.** An analysis of light scattering spectra of different glass-forming liquids is presented. It is shown that at high temperatures one finds a scenario for the temperature variations of dynamic spectra at high frequencies which is common for strong and fragile liquids. This scenario breaks down at some crossover temperature  $T_x$ . One conclusion is that the difference between strong and fragile glass-forming liquids is the temperature range between  $T_x$  and  $T_g$ : it is small for fragile and large for strong glass-forming systems.

Many liquids of quite different molecular origin can be supercooled down to the glassy state. However, the nature of the liquid-to-glass transition is still not understood, even on a qualitative level. Different materials show different temperature behaviours of viscosity e.g. near-Arrhenius for covalently bonded structures and strongly non-Arrhenius for van der Waals liquids. According to a classification introduced by Angell [1] the former are called *strong* and the latter *fragile* liquids. Recent achievements of the mode-coupling theory of the glass transition (MCT) [2] strongly stimulated new experimental investigations. MCT predicts the existence of some critical temperature  $T_c$  where the dynamics of the supercooled liquid should change significantly. MCT was rather successfully used for the analysis of fragile systems and  $T_c$  was identified to be  $\simeq 15$ – $25\%$  higher than the calorimetric glass transition temperature  $T_g$  [3]. However, the analysis of the non-fragile glass formers  $B_2O_3$  [4] and glycerol [5–7] revealed deviations from the leading-order asymptotic MCT predictions.

Until now it has not been clear whether the dynamics of the glass transition exhibits the same scenario for both strong and fragile liquids. It is the aim of the present communication to show that at temperatures higher than some crossover temperature,  $T_x$  one can find a common behaviour in light scattering spectra of different glass formers.

To compare our result, let us recall the main asymptotic predictions of idealized MCT for a susceptibility spectrum [2]. At high temperatures,  $T > T_c$ , the spectrum of the fast dynamics should be essentially temperature-independent; only  $\alpha$ -relaxation shifts with temperature without changing its spectral shape and intensity (inset figure 1(a)). Power-law dependencies as asymptotes for the low-frequency tail of the fast dynamics spectrum,  $\chi''(\nu) \propto \nu^a$ , and for the high-frequency tail of the  $\alpha$ -relaxation,  $\chi''(\nu) \propto \nu^{-b}$  ( $0 < a < 0.395$ ,  $0 < b < 1$ ) are predicted. As a result, a minimum in  $\chi''(\nu)$  appears with a universal form:

$$\chi''(\nu) = \chi_{min} \frac{(b(\nu/\nu_{min})^a + a(\nu/\nu_{min})^{-b})}{(a+b)} \quad (1)$$



**Figure 1.** Depolarized light scattering spectra at different temperatures. (a) Strong glass former  $B_2O_3$  ( $T_g = 525$  K) [4]; the inset shows a qualitative scenario suggested by MCT. (b) Fragile glass former OTP ( $T_g = 243$  K) [9]; dashed lines show master curves (equation 1) with the exponents  $a = 0.45$  and  $b = 0.55$ . (c) The same OTP spectra after subtraction of the  $\alpha$ -relaxation contribution.

where  $\chi_{min}$  and  $\nu_{min}$  are the amplitude and position of this minimum. They are related to each other and to the maximum in frequency of the  $\alpha$ -relaxation  $\nu_\alpha$  [2, 8]:

$$\chi_{min} \propto (\nu_{min})^a \quad \chi_{min} \propto (\nu_\alpha)^{ab/(a+b)} \quad \nu_{min} \propto (\nu_\alpha)^{b/(a+b)}. \quad (2)$$

It is important to note that all these predictions (1), (2) are simple consequences of this qualitative scenario which is sketched in the inset of figure 1(a). According to MCT this scenario should break down at  $T_c$ .

Let us turn to a phenomenological analysis of experimental data. Figure 1(a) shows the light scattering susceptibility spectra  $I/(n+1)$  (here  $I$  is a measured intensity and

$n + 1 = [1 - \exp(-h\nu/kT)]^{-1}$  is a temperature Bose factor) of the strong glass former  $B_2O_3$  [4]. One can see in the temperature range between  $T_g \simeq 525$  K and  $T \simeq 800$  K a strong variation of the spectrum of the fast dynamics ( $\nu > 50$  GHz). However, above  $T \simeq 800$ – $900$  K the spectrum of the fast dynamics is nearly temperature-independent (figure 1(a)). The only temperature variation is a shift of the  $\alpha$ -relaxation contribution to higher frequency with increase of  $T$ .

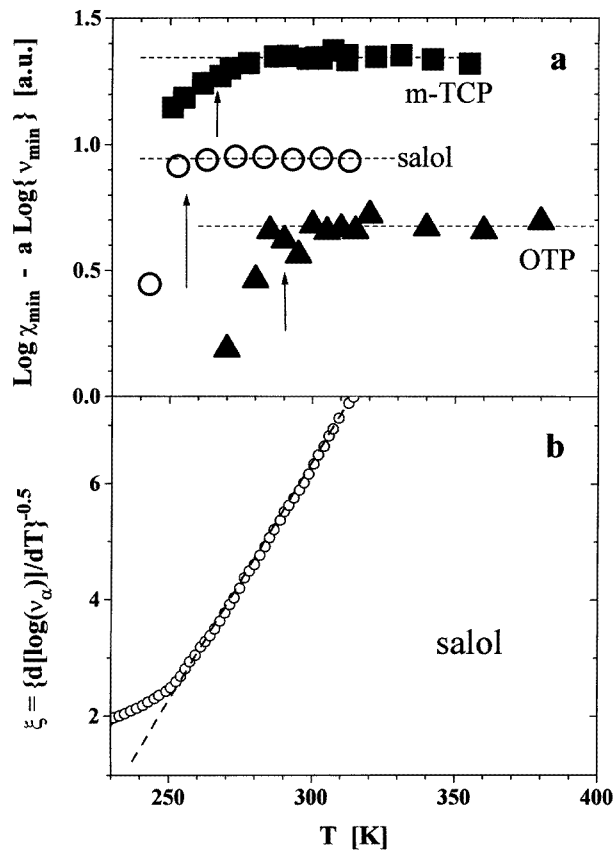
This temperature dependence of the spectrum of the fast dynamics has not been seen as clearly for other glass formers. Figure 1(b) shows an example of a fragile system, *ortho*-terphenyl (OTP) [9] where one can see the variations of the intensity in the frequency range of fast dynamics at all temperatures. It was shown in [7] that at temperatures above  $\simeq 290$  K the spectra around the susceptibility minimum can be approximately described by a single master curve (1) with exponents  $b \approx 0.55$  and  $a \approx 0.45$  (figure 1(b)). Moreover, it was shown that all relations (2) hold for this temperature range and give the same exponents  $a$  and  $b$  [7]. This indicates that the same qualitative scenario (inset figure 1(a)), which was clearly observed in  $B_2O_3$ , holds also for OTP.

The advantage of a strong glass former such as  $B_2O_3$  is that even at high  $T$ , the  $\alpha$ -relaxation is still far away in frequency from the fast dynamics. As a result, one can easily follow the temperature evolution of the fast dynamics contributions [4]. In contrast, for most of the fragile and intermediate liquids the  $\alpha$ -relaxation contribution overlaps strongly with the spectrum of the fast dynamics at  $T > T_x$  and a shift of the  $\alpha$ -relaxation peak with temperature produces variations of the spectrum even in the frequency range of the fast dynamics (figure 1(b)). However, if one subtracts the contribution  $\chi''(\nu) \propto \nu^{-b}$  described approximately by the parameters of the master curve on the low-frequency side of the minimum, the same scenario for the temperature evolution of the fast dynamics spectrum is revealed for OTP (figure 1(c)): the spectrum of the fast dynamics varies strongly below  $\simeq 290$  K and then becomes essentially temperature-independent. The analysis of different glass formers showed [7] that the same scenario (equations (1) and (2)) also holds for CKN, salol, m-TCP and glycerol. It was shown [10] that it holds also for the spectra of water in the temperature range 255–353 K. Thus very different liquids such as  $B_2O_3$  (covalent bonds), glycerol and water (hydrogen bonds), OTP, salol and m-TCP (van der Waals liquids), and CKN (ionic system) show similar behaviours in the dynamics at high temperatures.

However, this scenario breaks down at a certain crossover temperature. One can clearly see the break at  $T_x \simeq 800$ – $900$  K for the case of  $B_2O_3$  (figure 1(a)). One can also find the break as a deviation from the predictions (equations (1) and (2)), for example, as a deviation from a single power-law relation between  $\chi_{min}$  and  $\nu_{min}$ . This analysis has been carried out [7] and allows us to identify  $T_x$  (figure 2(a)). One can see that the single power-law relation with the same exponent  $a$ , as it was found from the master curve, holds at higher  $T$  and then breaks down at some temperature  $T_x$ .

The question arises whether one can identify this crossover temperature from the analysis of other properties? Recently, a model-independent method for the analysis of the temperature variation of  $\nu_\alpha$  was suggested by Stickel *et al* [11]. In particular, the analysis of  $\xi = \{d[\log(\nu_\alpha)]/dT\}^{-0.5}$  was suggested, which for the case of the Vogel–Fulcher–Tammann behaviour  $\nu_\alpha \propto \exp[-B/(T - T_0)]$  varies linearly with temperature  $\xi = (T - T_0)/B$ . The analysis of  $\xi$  for salol [11] is presented in figure 2(b). It shows clearly a change in temperature variation of  $\nu_\alpha$  at  $T_x$  where the parameters of the susceptibility minimum deviate from a single power-law relation (figure 2(a)). Thus this crossover temperature where the observed high-temperature scenario for the dynamics breaks down also shows up in the temperature dependence of  $\nu_\alpha$ .

Our analysis shows that a general scenario for the high-temperature dynamics of strong



**Figure 2.** (a) Temperature dependence of the relation between the minimum parameters (equation (2)) for different systems [7]; arrows show  $T_c$  estimated within MCT analysis. (b) Temperature dependence of the  $\alpha$ -relaxation parameter  $\xi$  for salol [11].

and fragile-glass forming liquids exists: the spectrum of fast dynamics is essentially temperature independent and only the  $\alpha$ -relaxation contribution shifts with temperature. At some crossover temperature  $T_x$  this scenario breaks down. The spectrum of the fast dynamics becomes temperature dependent at  $T < T_x$ : the low-frequency vibrational contribution (the so-called boson peak) becomes more pronounced and the intensity of the fast relaxation decreases strongly with decreasing temperature below  $T_x$  [4, 5]. We note that the extracted crossover temperature  $T_x$  is close to the critical temperature  $T_c$  reported within MCT analysis. Another important conclusion is that the ratio  $T_x/T_g$  correlates with the degree of fragility: it is  $\simeq 1.15$  for CKN (extremely fragile),  $\simeq 1.2$  for OTP and salol (fragile), but  $\simeq 1.55$ – $1.7$  for  $B_2O_3$  (strong). Thus one difference between strong and fragile glass formers is the temperature range between  $T_x$  and  $T_g$ . Whether one can find also a general scenario for the dynamics in this temperature range is open to question, although there is one suggestion in this direction [12].

## References

- [1] Angell C A 1984 *Relaxation in Complex Systems* ed K L Ngai and G B Wright (Washington: Office of Naval

Research) p 3

- [2] Götze W and Sjögren L 1992 *Rep. Progr. Phys.* **55** 241
- [3] 1989 *Dynamics of Disordered Materials* ed D Richter, A J Dianoux, W Petry and D Teixeira (Berlin: Springer)  
1995 Relaxation kinetics in supercooled liquids—mode coupling theory and its experimental tests, ed S Yip  
*Trans. Theory Stat. Phys.* **24**
- [4] Brodin A, Börjesson L, Engberg D, Torell L M and Sokolov A P 1996 *Phys. Rev. B* **53** 11 511
- [5] Rössler E, Sokolov A P, Kisliuk A and Quitmann D 1994 *Phys. Rev. B* **49** 14 967  
Sokolov A P, Kisliuk A, Quitmann D, Kudlik A and Rössler E 1994 *J. Non-Cryst. Solids* **172-174** 138
- [6] Wuttke J, Hernandez J, Li G, Coddens G, Cummins H Z, Fujara F, Petry W and Sillescu H 1994 *Phys. Rev. Lett.* **72** 3052
- [7] Sokolov A P, Steffen W and Rössler E 1995 *Phys. Rev. E* **52** 5105
- [8] Li G, Du W M, Chen X K, Cummins H Z and Tao N J 1992 *Phys. Rev. A* **45** 3867
- [9] Steffen W, Patkowski A, Gläser H, Meier G and Fischer E W 1994 *Phys. Rev. E* **49** 2992
- [10] Sokolov A P, Hurst J and Quitmann D 1995 *Phys. Rev. B* **51** 12 865
- [11] Stickel F, Fischer E W and Richert R 1995 *J. Chem. Phys.* **102** 6251; 1996 *J. Chem. Phys.* **104** 2043
- [12] Novikov V N, Rössler E, Malinovsky V K and Surovtsev N V 1996 *Europhys. Lett.* **35** 289