

# Dielectric study of supercooled triphenylphosphite and butyronitrile: Comparison with a mesoscopic model

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Dielectric relaxation has been studied in the supercooled liquids triphenylphosphite (TPP) and butyronitrile (BN). BN is relatively strong according to Angell's classification and can be characterized by a fragility index  $m = 47$ . TPP, on the other hand, appears to be the most fragile non-polymeric liquid studied so far ( $m = 160$ ). The dielectric response of the two glass-formers exhibits different degrees of non-exponentiality which is analyzed in terms of a mesoscopic model of dynamically correlated domains. The relation of this model to the strong versus fragile liquid classification scheme is discussed.

## 1. Introduction

The strong versus fragile classification of supercooled liquids has proven to be very useful in rationalizing various properties of glass-forming materials.<sup>1</sup> For instance it has been possible to relate, in a quantitative fashion, the departures from thermally activated behavior as described by the fragility index  $m$ , with the step in the specific heat capacity in the glass transformation range.<sup>2</sup> Furthermore, the fragility index has been shown to be related with the structural state dependence,<sup>3</sup> with the low-temperature heat capacity,<sup>4</sup> and with the non-exponentiality of the linear primary response subsequent to external perturbations produced e.g. by time dependent electric fields. The correlation of non-exponentiality and fragility has been investigated theoretically<sup>5,6</sup> and experimentally in many different types of glass-formers, like for instance polymers, covalently bonded networks, ionic melts, and supercooled liquids.<sup>7</sup> From the latter study it became obvious that few data are available for very fragile supercooled liquids, like e.g. triphenylphosphite<sup>8</sup> as well as for short-chain aliphatic, "simple" glass-formers. The latter ones, such as 3-bromopentane,<sup>9</sup> 1-butene,<sup>10</sup> butyronitrile,<sup>11</sup> and others, are particularly attractive, since their relatively simple molecular structure makes them ideal objects for computer simulation studies.

However since the salient dynamical features in the glass transformation range are quite universal in character, i.e. largely independent of microscopic details, a mesoscopic treatment of the relaxation processes may be adequate. Therefore, in the following, we explore the relationship of a mesoscopic model of dynamically correlated domains<sup>12,13</sup> with the strong and fragile classification. The frequency dependent susceptibility derived from the mesoscopic model is then compared with results obtained for two supercooled liquids, triphenylphosphite,  $(C_6H_5O)_3P$ , and butyronitrile,  $CH_3-CH_2-CH_2-CN$ . The experimental technique employed in this study is dielectric spectroscopy which, as detailed e.g. in the book by Scaife,<sup>14</sup> can yield important information about dynamical processes in condensed matter.

## 2. The mesoscopic model

There exist a large number of theoretical approaches that deal with the glass transition, but relatively few of them are able to provide quantitative predictions concerning the dynamical properties of amorphous materials near the laboratory glass transition.<sup>15</sup> One of the models which however is quite appealing in this respect, is the thermodynamic model of dynamically correlated domains.<sup>13</sup> It is based on the assumption, that glass-forming materials contain regions that relax independently. These regions exhibit features of cooperativity, since they are envisaged as domains containing  $s$  cooperatively rearranging subunits. Accordingly the response function may be written as

$$\Phi(t) = \sum_s A(s)n(s)e^{-tw(s)}. \quad (1)$$

The amplitude of the response is an extensive quantity, therefore  $A(s) \propto s$ . Using the central limit theorem, the distribution of cluster sizes ought to be a Gaussian distribution  $n(s) \propto \exp[-(s - \langle s \rangle)^2/\sigma^2]$ . Obviously, this argument holds only if chemical bonding specifics do not alter the global randomness (implicit in the normal distribution) on the length scale set by the size variance  $\sigma$ . The exponential term in Eq. (1) implies that the domains relax independently from one another, but the crucial input into the model is the size dependence of the rate  $w(s)$ .

This size dependence can be obtained from the consideration, that within one domain  $s$  particles exhibit rotational or vibrational excitations within a band  $\Delta$  of energies. In a given glass-former the energy level spacing for these dispersive excitations goes inversely proportional to size  $s$ . In a typical linear response experiment, the external perturbation modifies the occupation of the energy levels. If the return to the equilibrium occupation, as given by the Boltzmann distribution, couples to a change in an externally observable quantity, like e.g. polarization, then from linear response experiments insight should be gained into the problem how energy is redistributed in the level scheme.

In order to facilitate identifying the dominant transition mechanism it is noted, that the excitation bandwidth will be of the order of the Debye-temperature  $\Theta_D$  of the corresponding crystal. Assuming a typical cluster size of the order of one nanometer, it is seen that the typical level spacing  $\delta E = \Delta/s$  is much smaller than the energy available near  $T_g$  ( $\approx \Theta_D$ ). Therefore, at these relatively high temperatures, redistribution of energy within the domain can be anticipated to be due to direct overlap of the levels, which in turn goes like the square of the fluctuation probability,  $P(\delta E)$ , of the level energy. In the vicinity of the minimum of the free energy density  $f$  one has<sup>16</sup>

$$P_e(\delta E) \propto \exp\left[-\alpha f''(E_e) s(\delta E)^2 / k_B T\right]. \quad (2)$$

Here  $\alpha$  is a constant and  $f''$  denotes the curvature of  $f$  with respect to energy. From Eq. (2), the size-dependent rate can be obtained by weighting the overlap with the Boltzmann factor and integrating over  $\delta E$ . One obtains

$$w(s) \propto w_\infty \exp\left(\frac{1}{4sf''k_B T}\right). \quad (3)$$

Usually the relatively weak  $(\pi k_B T / 4sf'')^{0.5}$ -dependence of  $w_\infty$  is neglected and  $w_\infty$  is identified with the relaxation rate of an (asymptotically) large cluster. Inserting Eq. (3) and the expressions for  $A(s)$  and  $n(s)$  into Eq. (1) yields for quasi-continuous cluster size distributions

$$\Phi(t) \propto \int_0^\infty x \exp[-(x - \langle x \rangle)^2] \exp[-tw_\infty e^{-C/x}] dx. \quad (4)$$

Here the rescaled average domain size is given by  $\langle x \rangle = \langle s \rangle / \sigma$  and  $C$  denotes the so called correlation coefficient with  $1/C = -4\sigma f''(E_e) k_B T$ . The assignment of  $C$  stems from the fact that for  $C \rightarrow 0$ , Eq. (4) is a simple exponential. For  $C < 0$  a steepest descend analysis shows that in the vicinity of the average rate Eq. (4) can be approximated by a stretched exponential

$$\Phi(t) \propto \exp[-(t / \tau_K)^\beta]. \quad (5)$$

Here  $\beta$  is called the stretching exponent.<sup>17</sup> From Eq. (4) the dynamic susceptibility can be obtained by Fourier transforming the time derivative of  $-\Phi(t)$ , yielding

$$\chi(\omega) \propto \int_0^\infty \frac{x \exp[-(x - \langle x \rangle)^2]}{1 + i\omega / [w_\infty \exp(-C/x)]} dx. \quad (6)$$

In addition to an amplitude prefactor this equation contains three adjustable parameters. The time scale of the relaxation process is described by  $w_\infty$ , while the spectral form of  $\chi(\omega)$  is governed by  $C$  and  $\langle x \rangle$ .

### 3. Relation to the strong versus fragile pattern

The temperature dependence of the mean relaxation time  $\langle \tau \rangle = \langle w^{-1} \rangle$  in supercooled liquids usually shows pronounced deviations from the simple Arrhenius law

$$\langle w^{-1} \rangle \propto \exp(E_a / k_B T), \quad (7)$$

where  $E_a$  is an activation energy. The deviations from Eq. (7) have been quantified using the fragility index<sup>18</sup>

$$m \equiv \left. \frac{d \log_{10} \langle w^{-1} \rangle}{d(T_g / T)} \right|_{T=T_g} \quad (8)$$

Typically network melts are characterized by a small fragility index, they are strong against structural degradation in the supercooled regime. The medium range order of ionic or metallic melts, on the other hand, can undergo major changes in the vicinity of the glass transition. These materials are fragile.

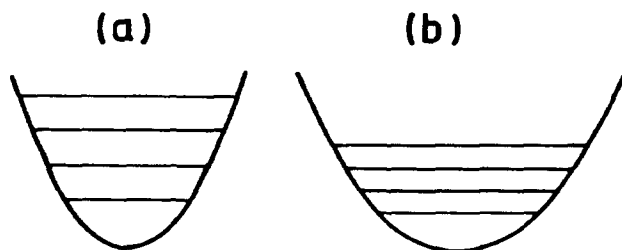
Various arguments have been put forward in order to relate the fragility index with other material characteristics including explanations in terms of rugged and smooth potential energy hypersurfaces<sup>1</sup> and coupling parameters.<sup>19</sup> Thus it may be worthwhile to exploit the mesoscopic model discussed here, in order to find out whether it is able to provide useful insights into the nature of fragility and whether these insights lead to specific consequences.

In strong systems which are typically characterized by directional, often covalent, bonds it may be expected that the energetic minima in configuration space are relatively well defined, i.e. that the free energy curvature is relatively large. In fragile glass-formers on the other hand  $f''$  may be comparably small, see Fig. 1. This situation leads to several interesting conclusions:

i) Jump in the heat capacity near  $T_g$ : It can be shown quite easily that the free energy curvature is given by  $|f''| = 1/(TC_p)$ . This means that for strong glass-formers a small contribution to the heat capacity can be expected, as is observed experimentally. It has to be noted that although the heat capacity jump near  $T_g$  is often ascribed to a changes in *configurational* entropy, it may contain appreciable contributions from vibrational excitations,<sup>20</sup> which play a key role in the mesoscopic model.

ii) Non-exponentiality: From Eq. (4) it is seen that the correlation coefficient  $C$ , which in the case of single exponential response tends to zero, is given by  $|C| \sim 1/f''$ . This prediction is also in qualitative accord with the experimental situation.

iii) Cooperativity: There are indications that in supercooled liquids cooperative regions exist and that their spatial extent is the larger the more fragile the glass-former is.<sup>21</sup> It has to be cautioned however that the experimental situation is still not entirely settled. The rescaled mean cluster sizes has been found for several glass-formers to exhibit a quasi-universal value of  $\langle x \rangle / |C| \approx 0.19$ . Then also  $\langle x \rangle$  is inversely proportional to the free energy curvature, i.e. in strong glass-formers the typical domain size is small.



**Figure 1** Schematic representation of the free energy curvature for strong (a) and fragile (b) amorphous systems. Case (b) may in fact be more complicated since the thermal fluctuations can mix nearly degenerate levels into a "superlevel".<sup>13</sup>

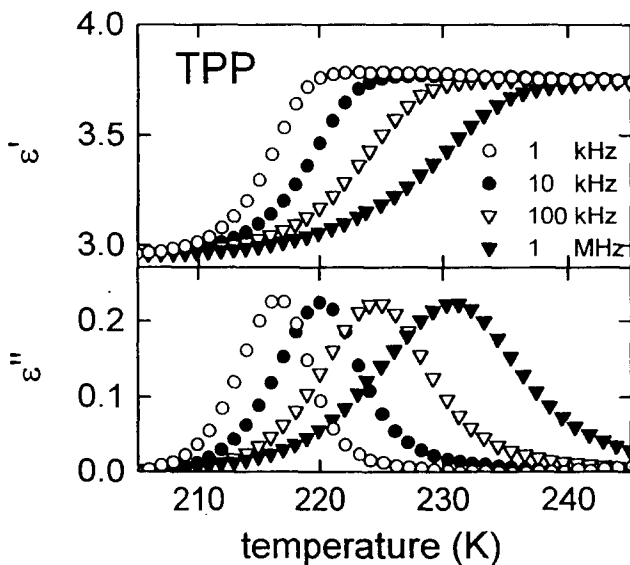
iv) Deviations from the Arrhenius law, Eq. (7): It is difficult to draw quantitative conclusions in this respect, since the mean relaxation time  $\int \Phi(t)dt$  cannot be evaluated from Eq. (4) in an analytical fashion.

#### 4. Experimental details

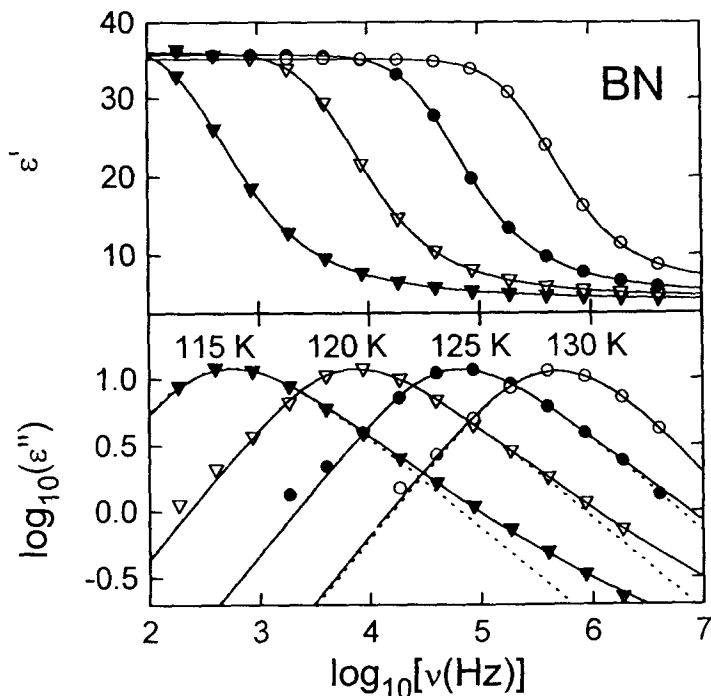
Triphenylphosphite (TPP) and butyronitrile (BN), with stated purities of 97% and 99%, respectively, were obtained from Merck Co. and were used without further purification. Both liquids studied in this work exhibited a pronounced tendency to crystallize when cooled with rates smaller than 1 K/min. Therefore the dielectric measurements were carried out during cooling with rates of typically 1.5 - 2.0 K/min. Acquisition of a frequency scan, using the impedance analyzers HP 4192 A and 4284 A, took about 12 seconds. In order to obtain quasi-isothermal spectra for analysis in the frequency domain, parabolic interpolation of the temperature dependent data was employed.

#### 5. Results and Discussion

The temperature dependence of the complex dielectric constant  $\epsilon = \epsilon' - i\epsilon''$  of TPP is shown in Fig. 2 for several frequencies. Dispersion steps and dielectric loss peaks associated with a freezing of the orientations of the molecular dipole moments are clearly seen. The effects are relatively weak, indicating that the dipole moment of TPP is rather small, as expected for a molecule which is close to threefold axially symmetric.



**Figure 2** Temperature dependence of real part (upper frame) and imaginary part (lower frame) of the dielectric constant of triphenylphosphite as measured at several frequencies.

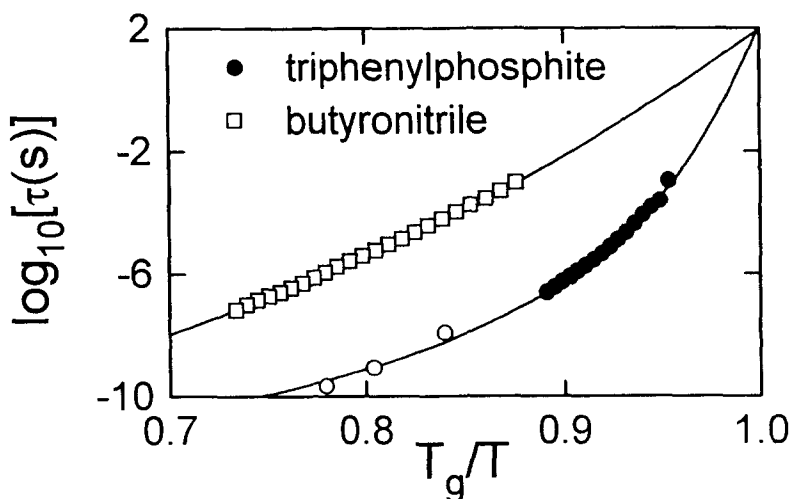


**Figure 3** Frequency dependence of the dielectric constant of butyronitrile. The upper panel shows the real part; the lower panel shows the dielectric loss in a double logarithmic representation. Solid lines are calculated using the model of dynamically correlated domains, Eq. (6). Dashed lines represent fits using the Fourier transform of the Kohlrausch function, Eq. (5), which does not give a proper description of the data at the highest frequencies.

The dipole moment of BN is considerably larger than that of TPP, and therefore also are the dispersion steps and the dielectric loss peaks. Real and imaginary parts of  $\epsilon(\nu)$  are shown in Fig. 3 for several temperatures. The solid lines are least square fits using the mesoscopic model and are seen to give very good descriptions of the experimental data. Fits of similar quality were also obtained for TPP (not shown). The data of both liquids were also fitted using the Fourier transform of the empirical Kohlrausch function, Eq. (5), with slightly less satisfactory results, see Fig. 3b. It has to be stressed however, that it is well known for many liquids that the deviations from Eq. (5) are quite substantial if data covering a range of more than 6 - 7 decades can be obtained.<sup>13</sup>

Using the model function we find a ratio of  $\langle x \rangle / |C| = 0.30 \pm 0.03$  (and  $C \approx -3$ ) for BN, while for TPP a considerably smaller ratio  $\langle x \rangle / |C| = 0.14 \pm 0.02$  (and  $C \approx -7$ ) is

obtained. Both values are found to be independent of temperature but are different from the ratio of  $\langle x \rangle / |C| \approx 0.19$  reported for a number of other amorphous materials.<sup>13</sup>



**Figure 4** Angell plot of the average relaxation time  $\langle \tau \rangle$ . The open circles are from a stimulated Brillouin scattering study of TPP.<sup>8</sup> The solid lines have been calculated with the Vogel-Fulcher equation, given in the text, using the following parameters: BN:  $A = 1 \times 10^{-16}$  s,  $B = 1850$  K, and  $T_0 = 58$  K; TPP:  $A = 5 \times 10^{-14}$  s,  $B = 691$  K, and  $T_0 = 186$  K. The scaling temperatures used for this plot were  $T_g = 99$  K (BN) and  $205$  K (TPP). The calorimetric glass transition temperatures are  $97$  K for BN<sup>11</sup> and  $204$  K for TPP.

For BN the temperature dependence of  $w_\infty$  can be fitted either with an Arrhenius law,  $\ln w_\infty = 72.5 - 79.8T_g/T$  or by the relationship,  $\ln w_\infty = 23.6 - 36.3(T_g/T)^4$ , which was used earlier. In order to distinguish between the two laws, the asymptotic relaxation rate needs to be determined over an extended temperature range.

The average relaxation times  $\langle \tau \rangle$  deduced from fits using the Kohlrausch function are plotted in Fig. 4. Their temperature dependence shows characteristic deviations from the behavior implied by Eq. (5). The solid lines in Fig. 4 have been calculated using the Vogel-Fulcher expression,  $\langle \tau \rangle = A \exp[B/(T - T_0)]$ , from which, in turn, the fragility index  $m$  has been estimated using Eq. (8). For BN we obtain  $m = 47$ ; for TPP a fragility  $m = 160$  is found, in accord with what can be calculated from published data<sup>8</sup> obtained by stimulated Brillouin-scattering in the MHz to GHz range. The Kohlrausch exponents for TPP is  $\beta = 0.51 \pm 0.02$ , independent of temperature. For BN, the exponent increases from  $0.7$  to  $0.8$  as  $T$  increases from  $110$  K to  $130$  K.

## 6. Discussion

The two glass-formers chosen for this study exhibit quite different correlation coefficients  $C$  and in fact mark opposite behaviors in Angell's liquid classification scheme. BN is relatively strong; TPP on the other hand is the most fragile non-polymeric liquid studied to date.<sup>22</sup> Consequently it may be expected that TPP will show a particularly large step  $\Delta C_p$  of the specific heat capacity in the glass transformation range. At present no  $C_p$  data seem to have been published for this compound. Although calorimetric information is available on BN, it has been obtained on vapor-deposited samples.<sup>11</sup> The enthalpy relaxation detected by Oguni *et al.*<sup>11</sup> was found to be considerably more non-exponential than the dielectric relaxation reported in the present work. This observation suggests that vapor-deposition leads to an amorphous state which is characterized by an increased heterogeneity.

Furthermore the average relaxation times reported in the calorimetric study are longer than those extrapolated from our dielectric data. This observation can be related to the well known fact that after a temperature jump to  $T = T_f$  from below, in the course of structural equilibration, relaxation times can be obtained that are longer than the equilibrium relaxation time at  $T_f$ .<sup>23</sup>

Interestingly the parameters  $m$  and  $\beta$ , obtained on our conventionally cooled BN liquids, are almost identical to those found for supercooled 3-bromopentane.<sup>9</sup> Both glass-formers exhibit a similar short-chain aliphatic molecular (*simple liquid*) structure.

## 7. Summary

By associating the free energy curvature  $f''$  with the shape of the intermolecular interaction potential we have related the model of dynamically correlated domains with the strong versus fragile classification scheme. The comparison is quite fruitful since the mesoscopic model allows a unified view on various salient properties of the supercooled liquid state, like the magnitude of the heat capacity step near  $T_g$ , the non-exponentiality of relaxation in the linear response regime, and aspects of cooperativity.

The frequency dependent susceptibility derived in the framework of the model compares favorably with the dielectric constant  $\epsilon(\nu)$  of triphenylphosphite and butyronitrile that we have investigated in the audio-frequency range. The rescaled cluster sizes  $\langle x \rangle / |C|$  were found to be 0.14 and 0.30, respectively. Consequently an analysis in terms of the Kohlrausch formalism revealed rather different stretching exponents. The result for TPP is particularly remarkable, since from its large fragility index ( $m = 160$ ) a higher degree of non-exponentiality would have been anticipated.<sup>7</sup> Although no temperature dependence of  $\beta$  could be detected in the range studied, it cannot be ruled out that the Kohlrausch exponent decreases on further approaching the glass transition. In order to answer this question, low frequency measurements need to be carried out.

## Acknowledgment

This project was supported by the Deutsche Forschungsgemeinschaft within the Sonderforschungsbereich 262. We thank one of the referees for stimulating comments on taking measurements "on the fly".



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