

Connection between fragility, mean-squared displacement and shear modulus in two van der Waals bonded glass-forming liquids

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The temperature dependence of the high-frequency shear modulus measured in the kHz range is compared to the mean-squared displacement measured in the nanosecond range for the two van der Waals bonded glass-forming liquids cumene and 5PPE. This provides an experimental test for the assumption connecting two versions of the shoving model for the non-Arrhenius temperature dependence of the relaxation time in glass formers. The two versions of the model are also tested directly and both are shown to work well for these liquids.

Keywords: Elastic models, shoving model, glass transition, viscous liquids, neutron scattering, mean-squared displacement, shear modulus

I. INTRODUCTION

The glass transition happens when a supercooled liquid falls out of equilibrium, i.e., when the structural relaxation time is so long that the liquid cannot equilibrate within a given experimental time. The temperature dependence of the relaxation time in the liquid just above the glass transition is in most cases super-Arrhenius. Liquids with a strongly super-Arrhenius behaviour are traditionally referred to as “fragile” liquids following the convention of Angell¹ as opposed to “strong” liquids with a close to Arrhenius behaviour. It is generally assumed that the relaxation dynamics are governed by energy barriers to be overcome by thermal activation, similar to an activation energy for a chemical reaction². In order to obtain super-Arrhenius behaviour in this view, the activation energy, ΔE needs to be a decreasing function of the temperature, T , and the relaxation time, τ is given by

$$\tau(T) = \tau_0 \exp\left(\frac{\Delta E(T)}{k_B T}\right), \quad (1)$$

where $\tau_0 \sim 10^{-14}$ s is a typical microscopic time and k_B is the Boltzmann constant. The fundamental question is then; what causes the temperature dependence of the activation energy that almost always increases upon cooling with only a few exceptions, causing the super-Arrhenius behaviour.

In the viscous liquid just above the glass transition there is a separation of time scales between the fast thermal vibrations taking place on the order of picoseconds, and the relaxation time which has a time scale of the order of hundreds of seconds. The separation of time scales has the consequence that the liquid will appear solid-like on time scales much shorter than the relaxation time, τ , and it will show liquid behaviour on time scales much longer than τ . In the energy landscape picture³, this corresponds to a separation between fast vibrations around the energy minima on short time scales and the inherent dynamics on longer time scales, due to jumps between potential energy minima.

There is no consensus on what governs the super-Arrhenius temperature dependence of the relaxation time in liquids, though numerous models and theo-

ries have been developed in trying to encompass the phenomenon^{2,4,5}. The shoving model which is the focus of this paper belongs to a class of models referred to as elastic models^{6,7}.

The starting point of elastic models is that a flow event, a molecular rearrangement, takes place on very short time scales by barrier transition. The transition itself is a fast process, but in the viscous liquid it is rare, which leads to slow relaxation. Since the transition is fast, it is governed by properties of the liquid at short time scales where it appears as a solid. This gives a link between the vibrational, short-time elastic properties of the liquid and the relaxation on long time scales. As the liquid is cooled, the liquid hardens, the mechanical moduli increase and the vibrational amplitudes decrease. This leads to an increase in the barrier height which in turn leads to the super-Arrhenius behaviour of the liquid’s relaxation time. The details of the argument vary for the different versions of the elastic models.

There is a series of more phenomenological results, which are not directly related to elastic models, but which support the notion that there is a connection between fast and slow dynamics. One of the first was the observation in 1992 by Buchenau and Zorn of a relation between fast and slow dynamics in selenium⁸. They found a relation between the temperature dependence of the slow structural relaxation, the viscosity, and the fast mean-squared displacement (MSD) studied with neutron time-of-flight. A connection between fast vibrational and slow structural dynamics was also suggested in several other works (see, e.g., the references of Ref. 2). Some of these suggest a connection between the vibrational and elastic properties of the glass and the fragility of the corresponding liquid⁹⁻¹¹, others suggest a connection between the temperature dependence of the vibrations in the liquid and the temperature dependence of the structural relaxation time, the alpha relaxation,¹²⁻¹⁴ closer to the original result from Buchenau⁸ and the predictions of the shoving model discussed in Sec. II.

The shoving model and related elastic models have recently been discussed in the context of several theoretical developments. In 2013 Yan, Düring, and Wyart discussed from a general point of view the connection between glass elasticity and fragility in a model that connects the two properties such that elasticity is a good pre-

dictor of fragility¹⁵. Mirigian and Schweizer proposed a unified model for the viscosity of simple liquids going from the less-viscous regime of “ordinary” liquids to the highly viscous supercooled regime, in which the deviation from Arrhenius temperature dependence in the high-viscosity regime is dominated by the elastic “shoving” work done on the surroundings to locally lower the density¹⁶. In 2015 Schirmacher, Ruocco, and Mazzone proposed a unified theory for the viscosity, the low-temperature alpha relaxation and the high-frequency vibrational anomalies. The basic idea was to regard the system as a spatial mixture of different Maxwell viscoelastic elements characterized by a distribution of activation energies, each proportional to the local high-frequency shear modulus¹⁷. Also in 2015 Betancourt, Hanakata, Starr, and Douglas connected the short-time vibrational MSD to free volume and cooperativity, arguing that several apparently different models for the viscous slowing down are, in fact, different aspects of the same mechanism¹⁸. The shoving model and related elastic models have also been used recently for interpreting experimental findings, e.g., in Ref. 19–27.

The shoving model exists in two different formulations, one which connects the relaxation time to the high-frequency shear modulus, G_∞ , and one which relates the relaxation time to short-time MSD. The two versions of the model are equivalent under a few simple approximations. One of these assumptions is somewhat implicit, namely that the two properties are measured at the same time scale – or that they are measured in a range where there is no time scale dependence of the properties. However, as the alpha relaxation time becomes longer, i.e., beyond the millisecond range, many liquids exhibit one or more beta relaxation processes at shorter time scales than the alpha relaxation time. The beta relaxation can have a quite large amplitude in the shear modulus²⁸ and the elastic properties and the temperature dependencies of these will therefore be different when probed at different time scales. Many of the tests of the G_∞ version of the shoving model are made based on measurements made on the kHz range, whereas the MSD version has been tested primarily based on neutron scattering data performed on the pico- or nanosecond time scale.

The issue of which time scale to use in elastic models has been discussed previously^{29,30}. Since the thermal motion that gives rise to the transition is dominated by phonons, it is argued that the relevant time scale should be the picosecond time scale. However, for some liquids elastic models appear to work better when tested at longer time scales where the properties are more temperature dependent than at the phonon-times^{29,30}. In other words, the temperature dependence of the vibration on the phonon time scale is not always large enough to account for the super-Arrhenius temperature dependence of the relaxation time. Based on these types of observations, Buchenau³⁰ argues that the elastic models need to be combined with an Adam-Gibbs model, and that both the hardening of the liquid and the decrease of entropy are to be included to properly explain the temperature dependence of the relaxation time. However, there is also a paper where the G_∞ version of the model is supported by G_∞ data determined from a range of techniques using different time scales in order to establish the plateau value

correctly³¹. In a recent review on experimental tests³² of both versions of the shoving model, it was found that the shoving model works in many cases, but in other cases not, yet there is no apparent system in when it works and when it does not work.

In this paper we present an experimental test of the main approximation connecting the G_∞ and the MSD version of the shoving model. This is done by measuring G_∞ at the kHz range and the MSD at the nanosecond range. Moreover, we directly compare the performance of the two versions of the shoving model. To the best of our knowledge, this is the first time the connection between G_∞ and the MSD is directly established experimentally, as well as being the first paper to include data to test different versions of the shoving model on the same systems.

Because there seems to be no general trend for when and for which systems elastic models hold³², we will in this paper turn to liquids showing as simple behaviour as possible. Both liquids have been found to obey density scaling, which means that the relaxation time is a unique function of ρ^γ/T , where ρ is density, T is temperature and γ is a material constant^{33–35}. Moreover, they obey time-temperature superposition (TTS), which means that the spectral shape is independent of temperature and time^{36,37}. Shear mechanical and dielectric spectroscopy measured on cumene (see Fig. 1 of this paper and Ref. 35) show a very low amplitude beta relaxation (in the range of percent of the alpha relaxation) whereas 5PPE only exhibits a weak wing³⁶. The absence of a prominent beta relaxation should assure that the elastic shear modulus does not change appreciably in the time scale from milliseconds to seconds.

The paper is structured as follows. Section II introduces the two versions of the shoving model tested in this paper and the underlying assumptions. In Sec. III we present the data of the two van der Waals bonding liquids. In Sec. IV, we test the models and also present our interpretation of the data, before discussing our findings in Sec. V.

II. THE SHOVING MODEL – TWO VERSIONS

In the original G_∞ version of the shoving model^{2,6,32,38}, a local expansion is assumed to take place in order for a flow event to happen. The activation energy is identified as the work done *shoving* aside the surrounding liquid during this local expansion, and the activation energy is associated with the elastic energy located in the surroundings of the flow event. According to the shoving model, because the flow event itself is fast, the surrounding liquid will behave like a solid during the expansion. Assuming the local region that expands is spherical, the relevant elastic constant of the surroundings is the elastic shear modulus, G_∞ . However, even for another geometry where the bulk modulus, K_∞ plays a role, it can be shown that the temperature dependence of the shear modulus, G_∞ by far dominates⁷.

The temperature dependence of the relaxation time according to the shoving model is given by

$$\tau(T) = \tau_0 \exp\left(\frac{V_c G_\infty(T)}{k_B T}\right), \quad (2)$$

where V_c is a characteristic molecular volume which is assumed to be constant.

In the MSD version of the shoving model⁷, the activation energy is related to the MSD associated with molecular vibrations taking place on time scales where the glass-forming liquid acts like a solid. The idea is that larger vibrations are connected to a softer potential, which leads to a smaller energy barrier. The MSD version of the shoving model is given by

$$\tau(T) = \tau_0 \exp\left(\frac{a^2}{\langle u^2 \rangle(T)}\right), \quad (3)$$

where $\langle u^2 \rangle(T)$ is the vibrational MSD, and a is a characteristic molecular length assumed to be constant.

The approximate equivalence between the two versions of the shoving model is derived by modelling the vibrations harmonically and averaging over the two types of phonons, yielding⁷

$$\langle u^2 \rangle(T) \propto T \left(\frac{2}{G_\infty(T)} + \frac{1}{M_\infty(T)} \right). \quad (4)$$

where G_∞ and M_∞ are the transverse and longitudinal moduli, respectively. It can be shown that the temperature dependence of the shear modulus dominates⁷, leading to

$$\langle u^2 \rangle(T) \propto \frac{T}{G_\infty(T)}. \quad (5)$$

Combining Eq. (5) with Eq. (3) gives the equivalence of the two versions of the shoving model and one ends up with three proportional terms:

$$\frac{\Delta E(T)}{k_B T} \propto \frac{V_c G_\infty(T)}{k_B T} \propto \frac{a^2}{\langle u^2 \rangle(T)}. \quad (6)$$

III. THE EXPERIMENTS AND DATA

We present new MSD and inelastic fixed window scans³⁹ measured with neutron backscattering as well as new data on the shear modulus measured by broadband shear-mechanical spectroscopy on the liquid cumene (isopropyl benzene). Cumene has been studied for many years with other techniques, for example in Refs.^{29,40–43}. Cumene is a fragile liquid ($m \approx 70$) with only a very small beta relaxation.

In Sec. IV C we also test the elastic models for another van der Waals bonding liquid, a 5-polyphenyl ether (5PPE), which is a large molecule but with a similar behaviour and fragility as cumene^{34,44}. For 5PPE we present new MSD data and compare to earlier published shear mechanical data.

Cumene was from Sigma Aldrich, and 5PPE was from Santolubes. Both were used as acquired.

A. Mean-squared displacement

The MSD is measured by elastic incoherent neutron scattering. Elastic temperature scans at the backscattering instrument IN16B were performed for this study at the Institut Laue-Langevin (ILL).

Neutron backscattering can be used to study fast dynamics of atoms by measuring the incoherent intermediate scattering function, $I(Q, t)$. The incoherent intermediate scattering function is the space Fourier transform of the density self-correlation function, which gives the probability that an atom at some time, t , is at a new position at a new time, $t + t'$.

The elastic scans were performed with an energy resolution of $\Delta E \approx 0.75 \mu\text{eV}$, accessing a time scale of the dynamics of around 5 ns. The energy resolution of the instrument corresponds to studying the dynamics at a specific time, t . In elastic scans, $I(Q, t)$ is essentially time independent and only dependent on the scattering vector, Q and the temperature, T . We therefore introduce the incoherent intermediate scattering function notation $I(Q, T)$ used in incoherent elastic neutron scattering.

The MSD is obtained from the data using the Gaussian approximation⁴⁵

$$I(Q, T) = \exp\left(\frac{-Q^2 \langle u^2 \rangle(T)}{3}\right), \quad (7)$$

which is valid if the distributions of displacements is Gaussian, for example in the case for harmonic vibrations.

The MSD is calculated from the logarithm of the elastic intensity for each temperature as a function of Q^2 according to Eq. (7). The data for each temperature is normalized to the data at the lowest temperature, $T = 5$ K, thus removing any zero-point motion. The MSD of cumene as a function of temperature is shown in Fig. 1. Around the glass transition ($\tau_\alpha = 100$ s) for cumene³⁵ at $T_g = 127$ K there is a change in slope of the MSD as a function of temperature. We see a collapse of previous data measured on IN10 at ILL²⁹ with the new data with better statistics from IN16B.

B. Shear modulus

The shear modulus was measured as a function of frequency using a piezo-ceramic transducer⁴⁶ in the frequency interval $10^{-2} - 10^4$ Hz. The loss peak of the shear modulus for cumene is shown in Fig. 1 in the temperature interval 130 – 140 K probed in steps of 1 K. This temperature range corresponds to the shaded area in the MSD plot (Fig. 1). Note that within a temperature range of 10 K, the alpha relaxation time changes roughly five orders of magnitude.

The inverse of the frequency of the shear loss peak maximum, ν_{max} , gives a measure of the alpha relaxation time, $\tau_\alpha = 1/(2\pi\nu_{max})$. For studying the shoving model, we also need the elastic shear modulus (Eqs. (6) and (2)). To establish whether a plateau in the real part of the shear modulus is actually reached is not easy⁴⁷, especially for higher temperatures within the frequency range of this setup. However, if a liquid obeys TTS, the elastic shear modulus is proportional to the maximum loss³², $G_\infty(T) \propto G''_{max}(T)$, i.e., they have the same temperature dependence. Cumene obeys TTS with only a very small beta relaxation. Since the maximum of the loss peak is more readily accessible than the elastic (plateau) shear modulus, we will use the maximum of the loss in studying the elastic models throughout this paper.

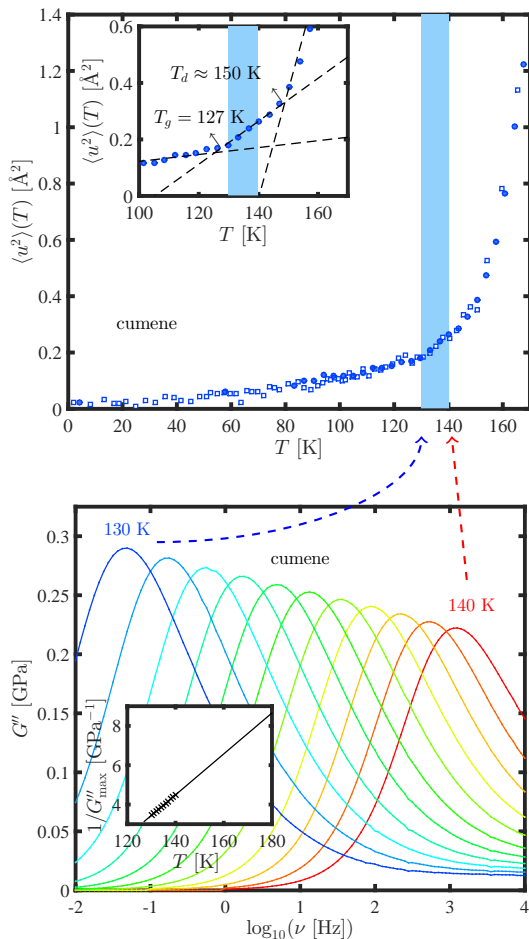


Figure 1. Top: The MSD of cumene as a function of temperature from IN16B (\bullet) and old data from IN10 (\square). The shaded area marks the temperature interval where the shear modulus was measured. Inset: The lines are guides to the eye to show the change in dynamics around T_g and $T_d \approx 150$ K. Bottom: Loss peak of the shear modulus of cumene measured in the temperature interval 130 – 140 K. The inset shows the extrapolation of the loss-peak moduli according to Eq. (8) into the higher-temperature liquid range that was used for neutron scattering.

The inset in Fig. 1 shows the extrapolation in temperature of the maximum shear loss for the entire liquid temperature range used in neutron scattering, i.e., up to 170 K. The relation from Barlow *et al.*^{48,49} is used to extrapolate to higher temperatures:

$$\frac{1}{G_\infty} = \frac{1}{G_0} + C(T - T_0), \quad (8)$$

where C is a constant. We will substitute G''_{max} for G_∞ . The extrapolation is used for testing Eq. (5) in the temperature range of the MSD in the liquid, i.e., above T_g .

IV. TESTING THE MODELS

A. The connection between G_∞ and MSD

To test Eq. (5), the MSD of cumene is plotted against the shear modulus scaled with temperature in Fig. 2. The black data points are in the interval where the shear data

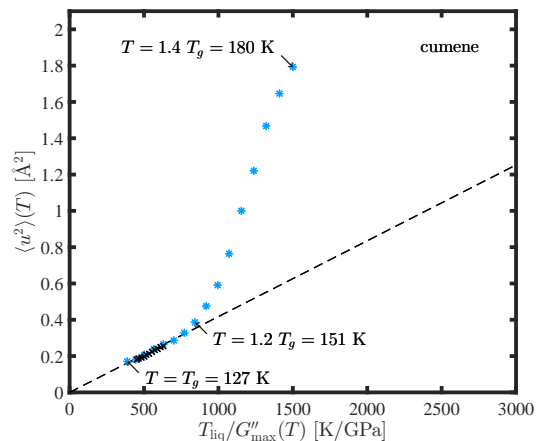


Figure 2. Testing Eq. (5) for cumene in the liquid. The black data points mark temperatures at which the shear modulus was measured. Equation (5) holds until the temperature $1.2 T_g$ where the alpha relaxation enters the neutron scattering window.

was actually measured, the rest is the extrapolation in temperature according to Eq. (8).

The straight line is a one parameter fit, in which only the slope of the line is fitted to the part of the data that clearly falls on a straight line. The line shows that the data follows the proportionality predicted by Eq. (5). This equation is valid under the assumption that the elastic constants measured in the kHz range agree with the elastic constants governing the MSD measured at roughly five orders of magnitude shorter times. The proportionality applies up until $1.2 T_g$. Our interpretation is that the alpha relaxation here enters the window of the neutron scattering instrument, causing a larger temperature dependence of the MSD than of the shear modulus, and that the MSD grows faster than predicted from the decrease of the shear modulus.

We see when the signal goes from being just elastic to also having an inelastic contribution by use of the fixed window scan (FWS) technique³⁹ available on IN16B at ILL. From this technique it is possible in, for example, a temperature scan to not only gain information about the change in elastic intensity, but also from the inelastic intensity by continuously changing the instrument settings. The change in elastic intensity (EFWS) and the inelastic intensity (IFWS) for three different settings, $\Delta E = 2, 5$ and $8 \mu\text{eV}$ are shown in Fig. 3 summed over Q and normalized to monitor.

The increase of the IFWS is a sign of the alpha relaxation entering the $2 \mu\text{eV}$ window, i.e. that it takes place at the nanosecond time scale. This happens at the temperature 150 K where the relation from Eq. (5) breaks down, causing a further increase in the elastic intensity (Fig. 2). This is also visible in the MSD (Fig. 1, inset of the top panel) where another change in slope in addition to the one at the glass transition can be seen at roughly 150 K. This change in slope signals the onset of the dynamics at the temperature T_d , which was also reported in Ref. 50.

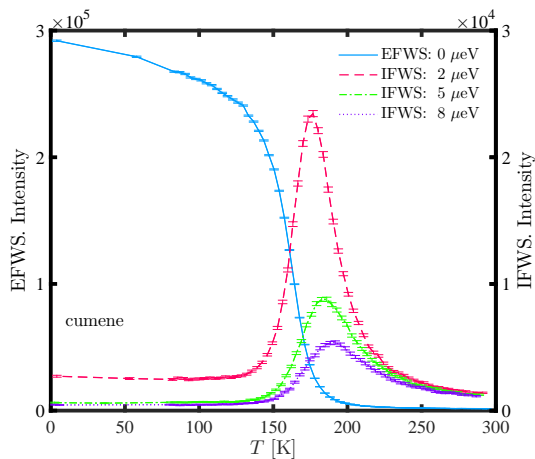


Figure 3. Fixed window scan on IN16B on cumene summed over Q . From the inelastic signal (IFWS: broken lines) we see the alpha relaxation entering the instrument window around 150 K causing a further increase in the elastic signal (EFWS: full line). Please note the different scales between the EFWs and IFWS.

B. Shoving model

Assuming that the characteristic volume V_c is constant in temperature, the shoving model predicts that the logarithm of the relaxation time is a linear function of $G_\infty(T)/T$. The prefactor, τ_0 , is given by a typical microscopic time scale. We set it to $\tau_0 = 10^{-14}$ s and define the glass transition temperature by $\tau_g = 100$ s. By doing this the linearity becomes³² (with all times in seconds)

$$\begin{aligned} \log_{10} \tau(T) &= (\log_{10} \tau_g - \log_{10} \tau_0) \frac{G_\infty(T)T_g}{G_\infty(T_g)T} + \log_{10} \tau_0 \\ &= 16 \frac{G_\infty(T)T_g}{G_\infty(T_g)T} - 14. \end{aligned} \quad (9)$$

This gives rise to a “shoving plot”; a way of testing the shoving model without free parameters by comparison of normalized data to the shoving model prediction.

A similar equation can be written up for the MSD version of the shoving model.

$$\log_{10} \tau(T) = 16 \frac{\langle u^2 \rangle_g}{\langle u^2 \rangle(T)} - 14. \quad (10)$$

Since the shoving model relates the relaxation time to the short-time liquid properties, the model is only tested in the temperature range of the shear measurements, i.e., from 130 – 140 K. In Fig. 4, the shoving plot with the black line as the prediction (Eq. (9)) is plotted along with the scaled shear modulus, the parameter $\frac{G_\infty(T)T_g}{G_\infty(T_g)T}$ from Eq. (9), and along with the MSD scaled to the MSD at the glass transition temperature (Eq. (10)). The MSD data points were interpolated to find the MSD at the temperatures where the shear modulus was measured. The prediction that the short-time dynamics scales linearly with the logarithm of the relaxation time all the way from the glass transition ($\tau = 100$ s) to microscopic time scales ($\tau_0 = 10^{-14}$ s) agrees with the data. Thus the figure shows that the shoving model works well for the MSD as well as the G_∞ .

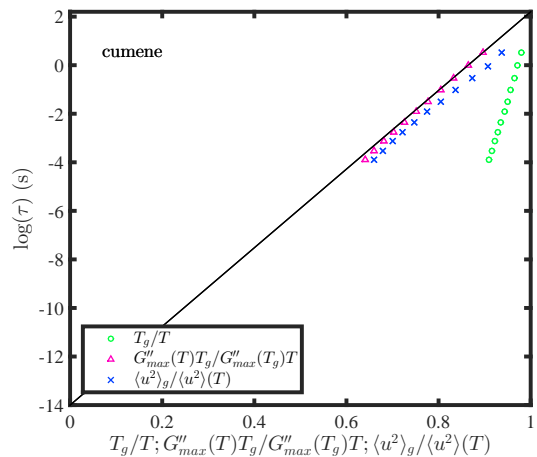


Figure 4. The shoving plot with the prediction (black line), relaxation time against $\frac{G_\infty(T)T_g}{G_\infty(T_g)T}$ (Δ), and $\langle u^2 \rangle_g / \langle u^2 \rangle(T)$ (\times). Relaxation time for cumene is plotted against temperature for the standard Angell plot (\circ).

C. Testing for another liquid

We also tested the elastic models for the glass-forming liquid 5PPE (5-polyphenyl ether). 5PPE has fragility of $m \approx 80$, similar to that of cumene, and it has a similar behaviour with only a tiny beta relaxation⁵¹. The glass transition temperature of 5PPE from shear modulus is 243 K. 5PPE has been shown to obey TTS⁵² and is found to have very simple behaviour in the sense defined by isomorph theory^{34,44}.

The MSD shown in Fig. 5 was measured at IN16 at ILL. The shear data is from Hecksher *et al.* (2013)⁵¹ and the shear loss peaks in the temperature interval $T = 245 - 265$ K are also shown in Fig. 5. The temperature range of the shear data is marked in the MSD plot as the shaded area. The inset shows the extrapolation into the higher temperature region according to Eq. (8).

The proportionality between MSD and $T/G_\infty(T)$, as well as the shoving plot, are shown in Fig. 6. The picture is the same as for cumene (Figs. 2 and 4): the elastic models work well. Regarding the proportionality between MSD and $T/G_\infty(T)$, we see the alpha relaxation entering the neutron scattering window at $1.15 T_g$, a slightly lower temperature than for cumene. This could be due to the higher fragility of 5PPE. The data follows the shoving prediction well. Clearly the scaled shear modulus and the MSD follow the general trend predicted by the shoving model, although not as nicely as for cumene.

V. DISCUSSION AND CONCLUSION

We have shown that the shoving model is confirmed in the case of the two liquids studied, and that there is good agreement between the two versions of the shoving model; one connecting the slow structural relaxation to the short-time elastic modulus and one connecting the slow structural relaxation to the short-time MSD. This correspondence holds even though the MSD and the shear modulus are measured at two very different time scales; the nanosecond and the millisecond, respectively.

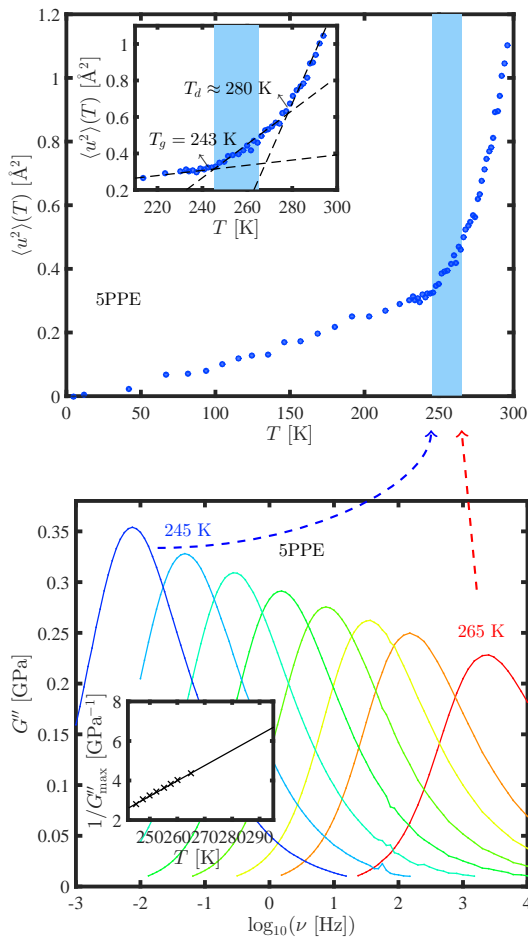


Figure 5. Top: The MSD of 5PPE as function of temperature. The shaded area illustrates the temperature interval of the measured shear modulus. Inset: Zoom, the lines are guides to the eye to show the change in dynamics around T_g and $T_d \approx 280$ K. The black lines are guides to the eye. Bottom: Loss peak of the shear modulus of 5PPE measured in the temperature interval 245 – 265 K. Inset shows the extrapolation of the loss peak moduli into the whole liquid temperature range that was used for neutron scattering.

For cumene, the relation between G_∞ and the MSD shows proportionality up to the temperature where the alpha relaxation as seen by IFWS enters the neutron scattering window, causing a stronger temperature dependence of the MSD than of the elastic modulus. In the case of 5PPE we do not have the IFWS data, but we see a similar development in the MSD. This supports the scenario proposed by Capaccioli *et al.*⁵⁰ referring to two transitions in the MSD of solvated proteins; the glass transition and the dynamic transition where the relaxation time and the resolution time of an instrument intersect.

In our view, the change in slope of the MSD at the glass transition temperature is not due to a change in the mechanism of the nanosecond dynamics. The dynamics is still vibrational. Rather, the modulus becomes much more temperature dependent because of going from the glassy to the liquid state. The temperature dependence just above T_g can be predicted by the change in the high-frequency modulus. The second change is in the liquid at T_d where the alpha relaxation enters the instrument window causing a further increase in the MSD.

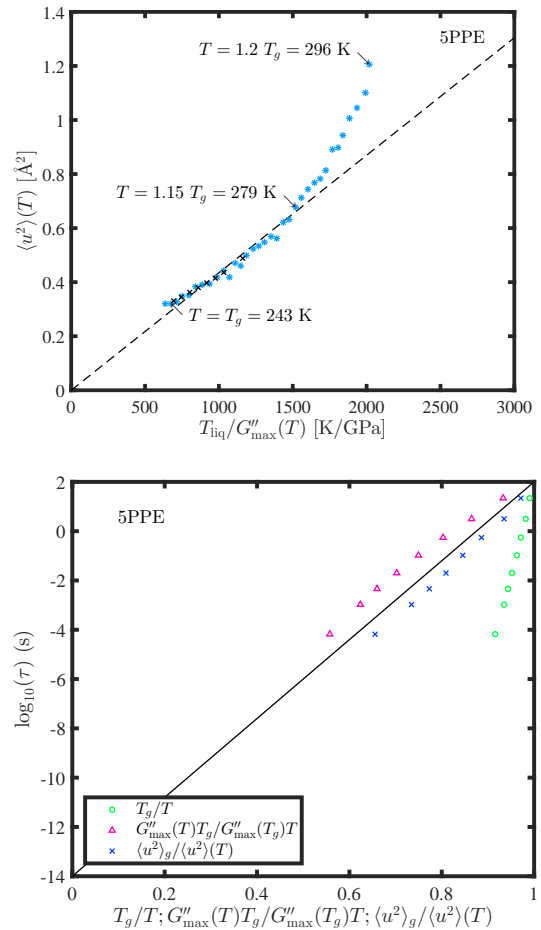


Figure 6. Top: Testing Eq. (5) for 5PPE in the liquid. The black data points marking temperatures at which the shear modulus was measured. Eq. (5) holds until $1.15 T_g$ where the alpha relaxation enters the neutron scattering window. Bottom: The shoving plot with the prediction (black line), relaxation time against $\frac{G''_{max}(T)T_g}{G''_{max}(T_g)T}$ (\triangle), and $\langle u^2 \rangle_g / \langle u^2 \rangle(T)$ (\times). Relaxation time for 5PPE is plotted against temperature for the standard Angell plot (\circ).

For other systems with more complex behaviour such as large beta relaxations, it is likely that the picture is more complicated. Here we would expect a discrepancy between the temperature dependence of the MSD at the nanosecond and the modulus measured in the kHz range. Based on the shoving model, one expects the properties at short time scales to be the best predictor of the temperature dependence of the alpha relaxation time. However, literature findings do not always support this prediction^{29,30}. Another possibility is that the MSD at the nanosecond time scale has a larger relaxational component in liquids with a more complex relaxation map. If this fast relaxation has a weak temperature dependence, it could lead to a relatively weaker temperature dependence of the MSD as compared to the activation energy and thus a deviation from Eq. (6). Finally it is also possible, as suggested by Buchenau³⁰, that the elastic models do not explain the full temperature dependence of the activation energy in the general case. In the future it is therefore important to test the different versions of the shoving model with liquids of different behaviour, including variations in fragility.

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- ¹ C. A. Angell, in *Relaxations in complex systems*, edited by K. Ngai and G. Wright (US Dpt of Commerce, 1985).
- ² J. C. Dyre, *Reviews of Modern Physics* **78**, 953 (2006).
- ³ M. Goldstein, *Journal of Chemical Physics* **51**, 3728 (1969).
- ⁴ F. H. Stillinger and P. G. Debenedetti, *Annual Review of Condensed Matter Physics* **4**, 263 (2013).
- ⁵ J. S. Langer, *Reports on Progress in Physics* **77**, 042501 (2014).
- ⁶ J. C. Dyre, N. B. Olsen, and T. Christensen, *Physical Review B* **53**, 2171 (1996).
- ⁷ J. C. Dyre and N. B. Olsen, *Physical Review E: Statistical, Nonlinear, and Soft Matter Physics* **69**, 042501 (2004).
- ⁸ U. Buchenau and R. Zorn, *Europhysics Letters* **18**, 523 (1992).
- ⁹ A. P. Sokolov, E. Rössler, A. Kisliuk, and D. Quitmann, *Physical Review Letters* **71**, 2062 (1993).
- ¹⁰ T. Scopigno, G. Ruocco, and F. Sette, *Science* **302**, 849 (2003).
- ¹¹ V. N. Novikov and A. P. Sokolov, *Nature* **431**, 961 (2004).
- ¹² L. Larini, A. Ottochian, C. de Michele, and D. Leporini, *Nature Physics* **4**, 42 (2008).
- ¹³ K. L. Ngai, *Philosophical Magazine* **84**, 1341 (2004).
- ¹⁴ S. Bernini, F. Puosi, and D. Leporini, *Journal of Chemical Physics* **142**, 124504 (2015).
- ¹⁵ L. Yan, G. Düring, and M. Wyart, *Proceedings of the National Academy of Sciences* **110**, 6307 (2013).
- ¹⁶ S. Mirigian and K. S. Schweizer, *Journal of Physical Chemistry Letters* **4**, 3648 (2013).
- ¹⁷ W. Schirmacher, G. Ruocco, and V. Mazzone, *Physical Review Letters* **115**, 015901 (2015).
- ¹⁸ P. A. Betancourt, P. Z. H. F. Starr, and J. F. Douglas, *Proceedings of the National Academy of Sciences* **112**, 2966 (2015).
- ¹⁹ T. Rouxel, *Journal of Chemical Physics* **135**, 184501 (2011).
- ²⁰ B. Xu and G. B. McKenna, *Journal of Chemical Physics* **134**, 124902 (2011).
- ²¹ M. Potuzak, X. Guo, M. M. Smedskjaer, and J. C. Mauro, *Journal of Chemical Physics* **138**, 12A501 (2013).
- ²² S. Mirigian and K. S. Schweizer, *Journal of Chemical Physics* **141**, 161103 (2014).
- ²³ F. Klameth and M. Vogel, arXiv:1506.05568 (2015).
- ²⁴ J. Krausser, K. H. Samwer, and A. Zaccane, *Proceedings of the National Academy of Sciences* **112**, 13762 (2015).
- ²⁵ Y. P. Mitrofanov, D. P. Wang, A. S. Makarov, W. H. Wang, and V. A. Khonik, *Scientific Reports* **6**, 23026 (2016).
- ²⁶ M. Ikeda and M. Aniya, *Journal of Non-Crystalline Solids* **431**, 52 (2016).
- ²⁷ V. M. Syutkin, *Journal of Chemical Physics* **139**, 114506 (2013).
- ²⁸ B. Jakobsen, K. Niss, C. Maggi, N. B. Olsen, T. Christensen, and J. C. Dyre, *Journal of Non-Crystalline Solids* **357**, 267 (2011).
- ²⁹ K. Niss, C. Dalle-Ferrier, B. Frick, D. Russo, J. Dyre, and C. Alba-Simionesco, *Physical Review E: Statistical, Nonlinear, and Soft Matter Physics* **82**, 021508 (2010).
- ³⁰ U. Buchenau, R. Zorn, and M. A. Ramos, *Physical Review E* **90**, 042312 (2014).
- ³¹ C. Klieber, T. Hecksher, T. Pezeril, D. H. Torchinsky, J. Dyre, and K. A. Nelson, *Journal of Chemical Physics* **138**, 12A544 (2013).
- ³² T. Hecksher and J. C. Dyre, *Journal of Non-Crystalline Solids* **407**, 14 (2015).
- ³³ D. Gundermann, “Testing predictions of the isomorph theory by experiment,” (2013), PhD thesis, Roskilde University, DNRf centre “Glass & Time”.
- ³⁴ W. Xiao, J. Tofteskov, T. V. Christensen, J. C. Dyre, and K. Niss, *Journal of Non-Crystalline Solids* **407**, 190 (2015).
- ³⁵ H. W. Hansen, “(unpublished),”.
- ³⁶ B. Jakobsen, K. Niss, and N. B. Olsen, *The Journal of Chemical Physics* **123**, 234511 (2005).
- ³⁷ K. Niss, “Fast and slow dynamics of glass-forming liquids – What can we learn from high pressure experiment?” (2007), PhD thesis.
- ³⁸ J. C. Dyre, *Journal of Non-Crystalline Solids* **235-237**, 142 (1998).
- ³⁹ B. Frick, J. Combet, and L. van Eijck, *Nuclear Instruments and Methods in Physics Research A* **669**, 7 (2012).
- ⁴⁰ P. W. Bridgman, *Proceedings of the American Academy of Arts and Sciences* **77**, 129 (1949).
- ⁴¹ A. J. Barlow, J. Lamb, and A. J. Matheson, *Proceedings of the Royal Society of London. Series A, Mathematical, Physical and Engineering Sciences* **292**, 322 (1966).
- ⁴² G. Li, H. E. King, W. F. Oliver, C. A. Herbst, and H. Z. Cummins, *Physical Review Letters* **74**, 2280 (1995).
- ⁴³ M. Oguni, J. Sekine and H. Mine, *Journal of Non-Crystalline Solids* **352**, 4665 (2006).
- ⁴⁴ L. A. Roed, K. Niss, and B. Jakobsen, *The Journal of Chemical Physics* **143**, 221101 (2015).
- ⁴⁵ A. Rahman, K. Singwi, and A. Sjölander, *Physical Review* **126**, 986 (1962).
- ⁴⁶ T. Christensen and N. Olsen, *Review of Scientific Instruments* **66**, 5019 (1995).
- ⁴⁷ J. C. Dyre and W. H. Wang, *The Journal of Chemical Physics* **136**, 224108 (2012).
- ⁴⁸ A. J. Barlow, A. Erginsav, and J. Lamb, *Proceedings of the Royal Society A* **298**, 481 (1967).
- ⁴⁹ G. Harrison, *The Dynamic Properties of Supercooled Liquids* (Academic Press, New York, 1976).
- ⁵⁰ S. Capaccioli, K. L. Ngai, S. Ancherbak, and A. Paciaroni, *The Journal of Chemical Physics* **116**, 1745 (2012).
- ⁵¹ T. Hecksher, N. B. Olsen, K. A. Nelson, and J. C. Dyre, *Journal of Physical Chemistry* **138**, 12A543 (2013).
- ⁵² L. Roed, D. Gundermann, J. C. Dyre, and K. Niss, *Journal of Chemical Physics* **139**, 101101 (2013).