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Temperature dependence of three-point correlation functions of viscous liquids: the case of glycerol

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Abstract

What causes the dramatic slowing down of flow and relaxation that leads to glass formation in liquids as temperature decreases is hardly understood so far and is the subject of intensive research work. It is tempting to ascribe the strong temperature dependence of the dynamics, irrespective of molecular details, to a collective or cooperative behavior characterized by a length scale that grows as one approaches the glass transition. To access this length experimentally, we use the recently introduced three-point dynamic susceptibility, from which the number of molecules dynamically correlated during the structural relaxation, N_{corr} , can be extracted. The three-point functions are related to the sensitivity of the averaged two-time dynamics to external control parameters, such as temperature and density. We studied N_{corr} values in an important temperature range for a large number of liquids, and found that it systematically grows when approaching the glass transition. Here we specially emphasize the case of glycerol for which we combined dielectric and neutron spin echo spectroscopy to cover more than 16 decades in relaxation time.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

An important number of atomic, molecular and polymeric liquids can form a glass by decreasing their temperature fast enough to avoid crystallization. Associated to the glass formation, one can measure a dramatic increase of the viscosity, or of the structural relaxation time, of the system when the system is cooled. From one system to another, the relaxation time shows quantitatively different temperature dependencies. This can be quantified via the ‘fragility’, which is a measure of departure from an Arrhenius temperature dependence of the relaxation time as the temperature decreases [1], see figure 1. This departure may be described by an Arrhenius equation $\tau_{\alpha} = \tau_0 \exp(E_a(T)/RT)$ with a temperature-dependent effective activation energy

$E_a(T)$. An Arrhenius behavior of relaxation time corresponds to a temperature independent E_a and characterizes the strong systems, whereas a large departure from Arrhenius behavior, or so-called superArrhenian behavior, corresponds to a highly temperature-dependent $E_a(T)$ and characterizes the fragile ones. The origin of the superArrhenian behavior is often explained in theories by introducing a supramolecular length scale that increases when temperature decreases. Since the picture of Cooperatively Rearranging Regions proposed by Adam and Gibbs in 1965 [2], most theories of the glass transition [3–5] rely on this idea. The existence of such a length is still discussed and the subject of many experimental investigations.

The dramatic increase of the relaxation time at the glass transition is not the only interesting feature of the glass

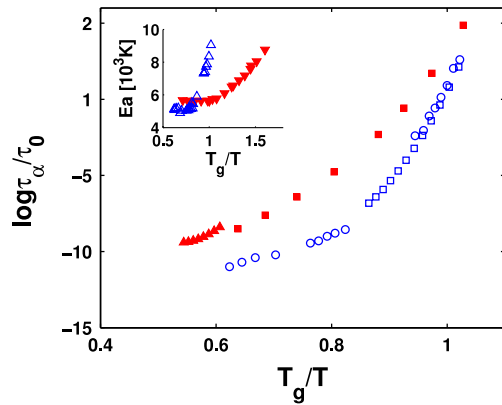


Figure 1. Classical Angell plot showing the logarithm of the average relaxation time τ_α/τ_0 where $\tau_0 = 1$ s versus T_g/T . Open symbols for m-toluidine (rounds for dynamic light scattering data and squares for dielectric spectroscopy data) and full symbols (squares for dielectric spectroscopy data and triangles for neutron spin echo data) for glycerol. The inset shows the apparent activation energy of both liquids as a function of T_g/T .

transition, there are other peculiarities such as the temporal behavior of the relaxation functions. The intermediate scattering function as measured by neutron scattering techniques (spin echo or time-of-flight measurements for example) gives us access experimentally to a relaxation function which has a non-Debye shape, and can be described by a stretched exponential, $\Phi(t) = A \exp(-(\frac{t}{\tau})^\beta)$. This non-exponential shape of the relaxation function at a given temperature is usually associated with a possible distribution of relaxation times in the system at this temperature.

Furthermore, the dynamics of many glass-formers was shown to be spatially heterogeneous close to the glass transition temperature T_g by different techniques such as 4D nuclear magnetic resonance, hole-burning techniques (see among others [6, 7] and [8]). These techniques have highlighted the coexistence of fast and slow regions in a glass-forming system at one temperature. This picture of having fast and slow coexisting regions is obviously time dependent, and as time passes a fast region may become a slow region and vice versa.

In liquids close to their glass transition, the existence of spatially heterogeneous local dynamics (also called dynamical heterogeneities [9]) is now well established in experiments and simulations, see [6, 10, 11]. However, no consensus on their spatial definition exists. From 4D-NMR experiments length scales of 2–4 nm for *o*-terphenyl and polyvinylacetate, and of 1 nm for glycerol were determined [12]. Other experimental studies, based on the Adam–Gibbs theory have found that a rather low number of molecules (4 to 8) are involved in CRR [13].

Other length scales associated with supercooled liquid dynamics were found by numerical simulations at much shorter timescales (well above T_g). From molecular dynamics simulations on a binary Lennard-Jones mixture, Donati *et al* found noncompact regions, -strings-, whose size slightly increases upon cooling [14]. However, in both fragile (toluene)

and strong (SiO_2) liquids, these strings are observed [15, 16] and do not help in understanding the superArrhenian behavior.

More recently, several investigations focused on different length scales observable in liquid and glassy dynamics. Leonforte *et al* demonstrated the existence of elastic heterogeneities and showed that the classical elastic description breaks down under an intermediate length scale. By introducing new multipoint dynamical susceptibilities, Berthier *et al* provided a direct experimental evidence of a growing dynamic correlation length of few nanometers accompanying the glass formation [17]. All these definitions highlight some interesting questions about the coexistence of these different lengths, – their hierarchy or their coupling –, and the possible universal description of the viscous slowing down.

Following the temperature dependence of the static structure factor or the radial distribution function, while cooling to the glass transition temperature, no signature of any length scale of heterogeneities can be seen. These two-point correlation functions, such as the radial distribution function, do not seem to contain the relevant information to characterize these heterogeneities. One needs to use higher order correlation functions in order to be able to get any length scale growing when approaching the glass transition, as was proposed by Berthier *et al* in [17–19]. Four-point correlation functions have been measured for colloids by confocal microscopy images [20–22], for granular systems [23, 24] and for foams [25]. This four-point correlation function measures the spatial extent of the correlation between a fluctuation of energy at time 0 and at some point 0, and the change in the dynamics occurring at another point r between times 0 and t . It is directly related to the number of correlated molecules in the system. However for molecular or polymeric glass-formers, this four-point correlation function is not yet accessible nor a fortiori its temperature dependence. For this reason, one needs another way to extract this information. One possible approach proposed is the calculation of a three-point correlation function as presented here and in [17] and [26]. To answer the question of the temperature dependence of the length scale responsible for the glass formation, it is necessary to experimentally cover a wide range in relaxation time and temperature as we will show in this paper.

The paper is structured as follows. In the first part, we will describe the systems and the experimental techniques we used. In the second part, we will explain how to get a three-point correlation function for molecular liquids. In the third part, we will discuss more precisely our results, focusing on the particular case of glycerol.

2. Systems and experimental techniques

The fully deuterated d8-glycerol was bought from Cambridge Isotope Laboratories and used as purchased. The purity was 98% and the isotopic enrichment better than 99.5%. The sample was prepared in a glove box under inert gas. The high temperature data were measured by Neutron Spin Echo spectroscopy on SPAN (V5) at Hahn Meitner Institut, Berlin. We measured 5 K-temperature steps from 280 to 350 K. We worked mainly at a wavelength of 6.5 Å and for some

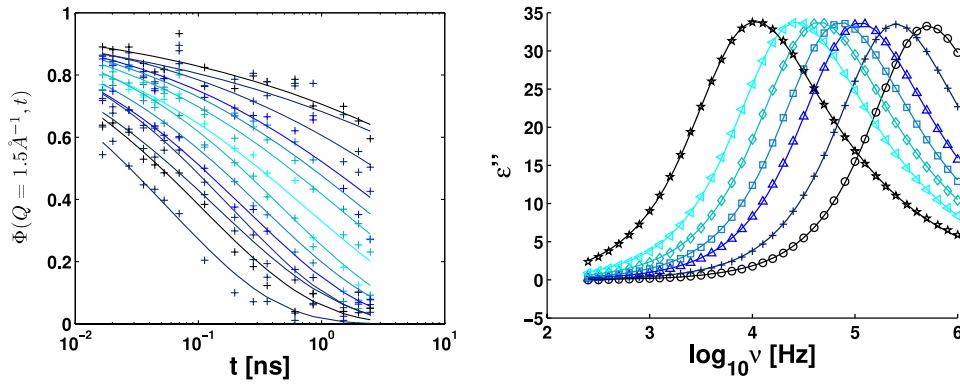


Figure 2. On the left, intermediate scattering function of glycerol obtained by neutron spin echo on SPAN, HMI at $\lambda = 6.5 \text{ \AA}$ at an average wavevector around 1.5 \AA^{-1} (symbols) and KWW fits of these data (full lines). The temperature range is from 280 to 350 K. On the right, semilog plot of the frequency-dependent dielectric loss of dibutylphthalate measured at different temperatures (205.6, 208.9, 210.8, 212.7, 214.6, 218.4, 222.2 K).

temperatures at 2.5 \AA in order to access shorter relaxation times. The average wavevector Q was 1.5 \AA^{-1} corresponding to the maximum of the structure factor of glycerol, measured by x-rays. The instrumental resolution was determined from the scattering of the sample at 10 K, which was purely elastic. The NSE data were divided by the resolution function to obtain the normalized intermediate dynamic structure factor $S(Q, t)/S(Q)$, see figure 2.

The dibutylphthalate (DBP) was acquired from Sigma-Aldrich (purity 99%). The dielectric spectra were measured using an HP 4284A LCR meter, which covers the frequency range from 100 Hz to 1 MHz, over a temperature range of 205–223 K, see figure 2.

The dielectric spectra were fitted by the normalized Havriliak Negami relaxation function generally used to describe the experimental frequency dependence of the dielectric spectra of glass-forming liquids [27]:

$$\epsilon_{HN,n}(\omega)^* = \frac{1}{[1 + (i\omega\tau_H)^\alpha]^\gamma} \quad (1)$$

with τ_H the characteristic relaxation time and α and γ parameters ranging from 0 to 1. In order to estimate the number of dynamically correlated molecules, the dielectric data measured in the frequency domain were converted to the time domain.

The time domain NSE data and the converted-to-time-domain dielectric data were fitted by a Kohlrausch–Williams–Watt (KWW) function $\Phi(t) = A \exp(-(\frac{t}{\tau})^\beta)$. The temperature dependence of the parameters of this function (A , τ and β) were fitted by polynomial functions, except for the temperature dependence of the average relaxation time τ fitted by a Vogel–Taumann–Fulcher form. This interpolation allowed us to have continuous results on the whole temperature range we measured, but we were careful not to extrapolate outside these measured ranges.

3. The three-point correlation function

3.1. Definition

Ideally to access the correlation length involved in glass transition or, more precisely, a number of correlated molecules we should measure a four-point correlation function over a large temperature range. As it is not yet easily directly accessible for molecular liquids and polymers we can use, thanks to fluctuation dissipation theorem, a trick proposed in [17, 18] and [19] via a three-point correlation function in the NPT ensemble. The relationship between the four-point correlation function χ_4^{NPT} and the three-point correlation function χ_T^{NPT} is given in equation (2).

$$\chi_4^{NPT} = \frac{k_B T^2}{C_p} (\chi_T^{NPT})^2 + \chi_4^{NPH}. \quad (2)$$

The four-point correlation function in the NPT ensemble is related to the three-point correlation function in the NPT ensemble via this equation, which also contains a third term: a four-point correlation function in the NPH ensemble, which can be neglected at least at lower temperatures as has been shown by numerical simulations [18]. The three-point correlation function can be obtained through the impact of a small perturbation of an external field, such as temperature or pressure, on a two-point correlation function. It may be calculated by the derivative of this two-point correlation function with respect to the external field. Several techniques which give access to two-point correlation functions are available to extract this three-point correlation function, such as dielectric spectroscopy, light scattering or neutron spin echo.

3.2. Respective effects of temperature and density

By cooling a system one changes both its temperature and its density and this first equation relating χ_4^{NPT} and χ_T^{NPT} does not separate the two contributions. For a better understanding of the respective effect of density and temperature one can rewrite this equation with these two contributions [26]:

$$\chi_4^{NPT} = \frac{k_B T^2}{C_v} (\chi_T^{NVT})^2 + \rho^3 k_B T \kappa_T (\chi_\rho^{NPT})^2 + \chi_4^{NVE}. \quad (3)$$

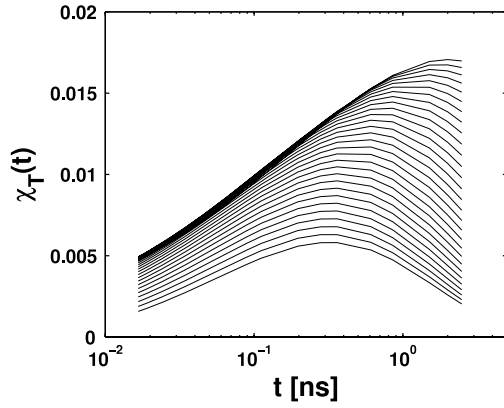


Figure 3. χ_T^{NPT} versus time at different temperatures for the NSE data of glycerol. These functions show a maximum around the average relaxation time τ_α at each temperature, which corresponds to the maximum number of correlated molecules $\chi_T^{NPT,*}$. On this plot for clarity reasons, we only presented the curves showing a maximum in the time range we measured.

The remaining term χ_4^{NVE} in equation (3) is then lower than χ_4^{NPH} in equation (2), as a part of the latter is included into the term representing the effect of temperature at constant density χ_ρ^{NPT} .

3.3. Experimental access to three-point correlation functions

To get a three-point correlation function from a two-point correlation function, one needs, for example, a set of dielectric spectra at different temperatures. The first step is to transform them in the time domain by Fourier transform as both equations (2) and (3) are written in time domain.

The time-dependent three-point correlation function is defined as the derivative of these time-dependent spectra with respect to temperature $\chi_T^{NPT}(t) = \frac{\partial \Phi(t)}{\partial T}$. The temperature derivative $\chi_T^{NPT}(t)$ of any experimental time-dependent relaxation function $\Phi(t)$ shows a maximum around the average relaxation time of the system, see figure 3. Its maximum $\chi_T^{NPT,*}$, at the structural relaxation time, enables us to get the maximal number of molecules dynamically correlated during the relaxation time as

$$N_{\text{corr},T} = \sqrt{\left(\frac{R}{C_P}\right) T \chi_T^{NPT,*}}. \quad (4)$$

We used this method to get the number of correlated molecules in glycerol over a wide temperature range from 190 to 350 K ($T_g = 190$ K at 100 s), covering almost 16 decades in relaxation time. For dibutylphthalate we focused on a more restricted temperature range, from 205 to 223 K ($T_g = 182$ K at 1 s). These two liquids are generally considered as intermediate for the former (with a fragility m_P around 50) and fragile for the latter (m_P around 80). The number of correlated molecules can be plotted versus the average relaxation time as in figure 4 or the temperature, as in figure 5 for glycerol. It increases as temperature decreases or relaxation time increases.

As a result, when this procedure is applied to different liquids one gets a general trend of the temperature and average

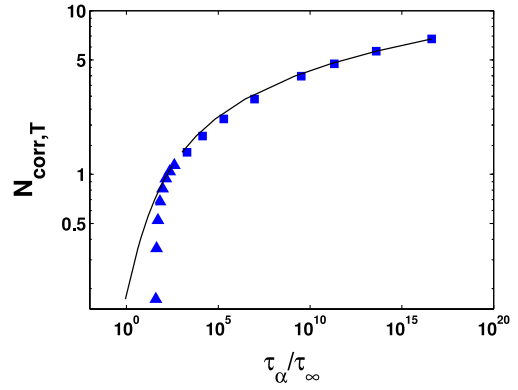


Figure 4. Number of dynamically correlated molecules $N_{\text{corr},T}$ for glycerol calculated from dielectric spectroscopy and neutron spin echo data versus $\log_{10}(\frac{\tau_\alpha}{\tau_\infty})$ with τ_∞ a microscopic relaxation time of the order of ps depending on the type of experiment.

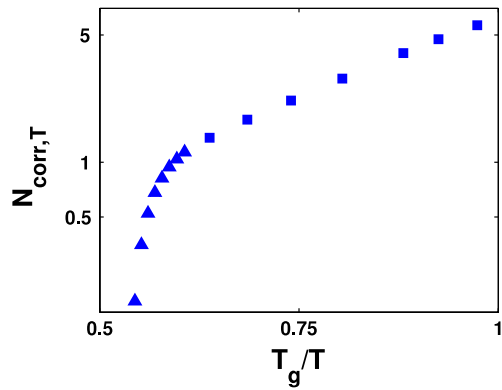


Figure 5. Number of dynamically correlated molecules $N_{\text{corr},T}$ for glycerol calculated from dielectric spectroscopy and neutron spin echo data versus T_g/T .

relaxation time evolution of $N_{\text{corr},T}$ as the glass transition is approached, see figure 4 in [26]. All the systems show a very similar behavior in the variation of this number of correlated molecules.

4. Discussion

The number of correlated molecules does not directly provide a typical length scale for the liquids. Indeed, the length scale can be expressed as a power law of the number of correlated molecules, but the value of the exponent is no simple question. One can even imagine a change of this exponent with temperature due to a change of the shape of the cooperatively rearranging regions as discussed in [28]. The number of correlated molecules is nonetheless compatible with the length scale of a few nanometers proposed in the literature for similar systems near the glass transition.

Both χ_4^{NPT} and χ_T^{NPT} can lead to a number of correlated molecules that we called respectively $N_{\text{corr},4}$ and $N_{\text{corr},T}$. However they do not correspond to the same value and do not even need to show the same temperature dependence. $N_{\text{corr},4}$ is the typical number of molecules whose dynamics

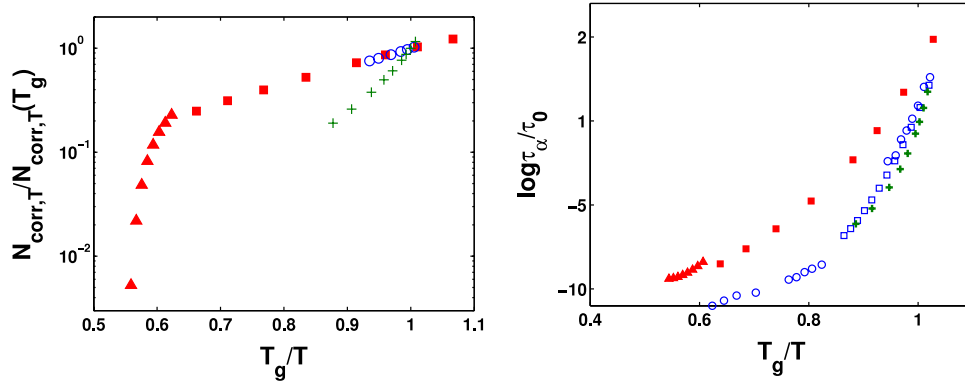


Figure 6. On the left, number of dynamically correlated molecules $N_{\text{corr},T}$ divided by the number of dynamically correlated molecules at the glass transition $N_{\text{corr},T}$ versus T_g/T for glycerol (full symbols), m-toluidine (empty symbols) and decalin (crosses). On the right, the same symbols for the same system, relaxation time (here again $\tau_0 = 1s$) versus T_g/T .

are correlated ‘among themselves’, $N_{\text{corr},T}$ the typical number of molecules whose dynamics are correlated ‘to a local fluctuation of enthalpy’. At low enough temperature, the term χ_4^{NPH} in equation (2) is negligible and then those two quantities are related by $N_{\text{corr},4} \approx N_{\text{corr},T}^2$. Both quantities are interesting [26], but as only $N_{\text{corr},T}$ is directly accessible from the experiments we mainly focus on this quantity.

We find that $N_{\text{corr},T}$ increases as temperature decreases for all systems. The extent of spatial correlation in the dynamics therefore grows as one approaches the glass transition. Figure 6 shows the number of dynamically correlated molecules for three systems, divided by its value at the glass transition temperature. It can be compared to the Angell plot that illustrates the relative fragility of glass-formers for the same systems. A closer inspection, however, reveals no systematic correlation between the two plots, i.e., between the rapidity of the increase of $N_{\text{corr},T}(T)$ and the fragility.

In order to test the robustness of the analysis, we will now focus on a particular system: glycerol. We will discuss for this system different points such as the importance of the thermodynamical prefactor and the respective effect of density and temperature.

As we are interested in the temperature dependence of the number of correlated molecules, we should in principle use the temperature-dependent heat capacity in the calculation of the number of correlated molecules, via equation (4). We have shown in figure 2 in [26] that the use of a temperature-dependent heat capacity, or a constant heat capacity, evaluated at the glass transition temperature has almost no change on the temperature dependence of the number of correlated molecules. We also showed that the shape of the curve is the same with C_p or ΔC_p , even if the absolute value is obviously affected. The heat capacity takes into account all the modes of the system, whereas the heat capacity jump is limited to the modes frozen up at T_g . It is probably more sensible theoretically to use the heat capacity jump. For simplicity, we then used a constant heat capacity estimated at the glass transition temperature when comparing many different systems. One should keep in mind that it may affect the absolute value of the number of correlated molecules by a factor as large as two and be system dependent.

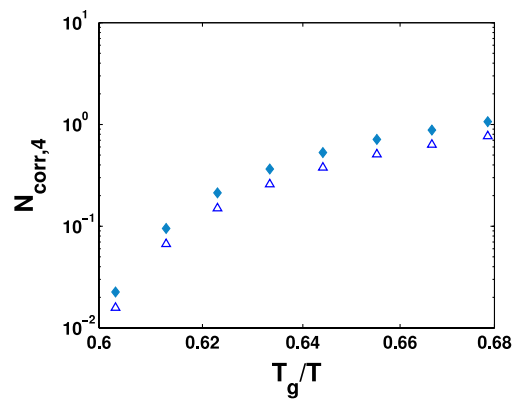


Figure 7. Comparison of the calculation of the number of correlated molecules obtained via equation (2) in open triangles and via equation (3) in full diamonds.

To be able to disentangle the density and the temperature contributions at atmospheric pressure, one can use the second expression for χ_4^{NPT} . By using this expression compared to the first one, one neglects a smaller term and for this reason obtain a number of correlated molecules $N_{\text{corr},4}$ including more physical processes than the one used before. These two ways of calculating the number of correlated molecules give a similar result, see figure 7. This calculation yields more additional information: the relative importance of density and temperature for this system. The factor R , defined in [26], being the ratio of the density fluctuation over the energy fluctuation, is low and almost constant with temperature for glycerol, as this system is dominated by thermal effects [29].

To complete the analysis of the number of correlated molecules at shorter average relaxation time, we used the intermediate scattering function obtained by neutron spin echo data. We found coherent results compared to the one obtained from the dielectric spectroscopy at lower temperature in [26], as can be seen in figure 5 when plotted versus T/T_g . One should keep in mind that the response functions measured by the two experimental methods are not exactly the same: this implies a rescaling of the data by a microscopic relaxation time τ_0 when plotting them versus relaxation time as shown

in figure 4. We now cover almost 16 decades for glycerol by combining these two sets of data.

The curve obtained shows two main regions. At low relaxation time, there is an important increase of the number of correlated molecules on a relatively narrow average relaxation time range, in this region the mode coupling theory formalism can be applied. At higher relaxation time the increase of the number of correlated molecules is much slower, we are in the regime of thermally activated dynamics [30].

These two regimes can be described by a unique equation combining the two types of variation:

$$\tau_\alpha \simeq A \left(\frac{N_{\text{corr},T}}{N_0} \right)^\gamma \exp \left[\left(\frac{N_{\text{corr},T}}{N_0} \right)^\psi \right]. \quad (5)$$

The first term describes an MCT like behavior and the second a thermally activated behavior. There might be two reasons for the small deviation of the fit from the data in figure 4 at really short timescale: it may be due to the effect of the H-bonds network in glycerol, which is not taken into account at all by the MCT formalism, or to the fact that the term we neglected in our calculation χ_4^{NPH} is no longer negligible in the relaxation time range we are looking at.

When going to higher temperature another interesting question is from which point in temperature it makes sense to calculate the number of correlated molecules in the liquid. At high temperature we expect the number of correlated molecules to be one, but as we do not perfectly control all the prefactors in the calculation, it seems difficult to numerically determine this point. Using the heat capacity C_p or heat capacity jump ΔC_p would, for example, change this point as it affects the absolute value of the number of correlated molecules obtained. One could propose starting the analysis at the point when the system becomes superArrhenian (see figure 1), or to use other criteria. One should look at this closer in the future but one needs more good quality high temperature data which are not available yet.

5. Conclusion

Thanks to the evaluation of a three-point correlation function as proposed in [17], we provided evidence of a growing correlation length over a wide range of relaxation time (16 decades), as glass transition is approached by cooling, by combining two sets of data. We tested its sensitivity to various thermodynamic factors, such as heat capacity, density and temperature. This study has been extended by others over a large number of systems (even polymers [31]).

It would be interesting now to study in more detail the crossover regime between the two regions, low and high average relaxation time, covered respectively by neutron spin echo and dielectric spectroscopy, as for the moment only very few experimental data are available in the short relaxation time limit.

Another interesting question, continuing the idea of comparing the pressure and temperature effect on a system, would be to study it under pressure, taking data covering the whole pressure temperature phase diagram. The pressure is

moreover another control parameter which enables us to tune the fragility without modifying the chemical interactions. It would allow us to extract new information, because it leads to a continuous change in the glass transition temperature, density and fragility.

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References

- [1] Angell C A 1991 Relaxation in liquids, polymers and plastic crystals strong/fragile patterns and problems *J. Non-Cryst. Solids* **131–133** 13–31
- [2] Adam G and Gibbs J H 1965 On the temperature dependence of cooperative relaxation properties in glass-forming liquids *J. Chem. Phys.* **43** 139–46
- [3] Debenedetti P G and Stillinger F H 2001 Supercooled liquids and the glass transition *Nature* **410** 259–67
- [4] Binder K and Kob W 2005 *Glassy Materials and Disordered Solids* (Singapore: World Scientific)
- [5] Kivelson D, Kivelson S A, Zhao X L, Nussinov Z and Tarjus G 1995 A thermodynamic theory of supercooled liquids *Physica A* **219** 27–38
- [6] Ediger M D 2000 Spatially heterogeneous dynamics in supercooled liquids *Annu. Rev. Phys. Chem.* **51** 99–128
- [7] Sillescu H 1999 Heterogeneity at the glass transition: a review *J. Non-Cryst. Solids* **243** 81–108
- [8] Richert R 2002 Heterogeneous dynamics in liquids: fluctuations in space and time *J. Phys.: Condens. Matter* **14** R703–38
- [9] Bohmer R, Chamberlin R V, Diezemann G, Geil B, Heuer A, Hinze G, Kuelbler S C, Richert R, Schiener B, Sillescu H, Spiess H W, Tracht U and Wilhem M 1998 Nature of the non-exponential primary relaxation in structural glass-formers probed by dynamically selective experiments *J. Non-Cryst. Solids* **235–237** 1–9
- [10] Tracht U, Wilhem M, Heuer A, Feng H, Schmidt-Rohr K and Spiess H W 1998 Length scale of dynamic heterogeneities at the glass transition determined by multidimensional nuclear magnetic resonance *Phys. Rev. Lett.* **81** 2727
- [11] Vollmayr-Lee K, Kob W, Binder K and Zippelius A 2002 Dynamical heterogeneities below the glass transition *J. Chem. Phys.* **116** 5158–66
- [12] Reinsberg S A, Heuer A, Doliwa B, Zimmermann H and Spiess H W 2002 Comparative study of the NMR length scale of dynamic heterogeneities of three different glass formers *J. Non-Cryst. Solids* **307–310** 208–14
- [13] Yamamuro O, Tsukuchi I, Lindqvist A, Takahara S, Ishikawa M and Matsuo T 1998 Calorimetric study of glassy and liquid toluene and ethylbenzene: thermodynamic approach to spatial heterogeneity in glass-forming molecular liquids *J. Phys. Chem. B* **102** 1605–9
- [14] Donati C, Douglas J F, Kob W, Plimpton S J, Poole P H and Glotzer S C 1998 Stringlike cooperative motion in a supercooled liquid *Phys. Rev. Lett.* **80** 2338
- [15] Glotzer S C 2000 Spatially heterogeneous dynamics in liquids: insights from simulation *J. Non-Cryst. Solids* **274** 342–55

- [16] Kerrache A, Teboul V, Guichaoua D and Monteil A 2003 Aging effects in supercooled silica: a molecular dynamics investigation *J. Non-Cryst. Solids* **322** 41–5
- [17] Berthier L, Biroli G, Bouchaud J-P, Cipelletti L, El Masri D, L'Hôte D, Ladieu F and Pierno M 2005 Direct experimental evidence of a growing length scale accompanying the glass transition *Science* **310** 1797–800
- [18] Berthier L, Biroli G, Bouchaud J-P, Kob W, Miyazaki K and Reichman D R 2007 Spontaneous and induced dynamic fluctuations in glass formers. I. General results and dependence on ensemble and dynamics *J. Chem. Phys.* **126** 184503
- [19] Berthier L, Biroli G, Bouchaud J-P, Kob W, Miyazaki K and Reichman D R 2007 Spontaneous and induced dynamic fluctuations in glass formers. II. Model calculations and comparison to numerical simulations *J. Chem. Phys.* **126** 184504
- [20] Weeks E R, Crocker J C, Levitt A C, Schofield A and Weitz D A 2000 Three-dimensional direct imaging of structural relaxation near the colloidal glass transition *Science* **287** 627
- [21] Duri A and Cipelletti L 2006 Length scale dependence of dynamical heterogeneity in a colloidal fractal gel *Europhys. Lett.* **76** 972–8
- [22] Cipelletti L, Bissig H, Trappe V, Ballesta P and Mazoyer S 2003 Time-resolved correlation: a new tool for studying temporally heterogeneous dynamics *J. Phys.: Condens. Matter* **15** S257–62
- [23] Keys A S, Abate A R, Glotzer S C and Durian D J 2007 Measurement of growing dynamical length scales and prediction of the jamming transition in a granular material *Nat. Phys.* **3** 260–4
- [24] Dauchot O, Marty G and Biroli G 2005 Dynamical heterogeneity close to the jamming transition in a sheared granular material *Phys. Rev. Lett.* **95** 265701
- [25] Mayer P, Bissig H, Berthier L, Cipelletti L, Garrahan J P, Sollich P and Trappe V 2004 Heterogeneous dynamics of coarsening systems *Phys. Rev. Lett.* **93** 115701
- [26] Dalle-Ferrier C, Thibierge C, Alba-Simionesco C, Berthier L, Biroli G, Bouchaud J-P, Ladieu F, L'Hôte D and Tarjus G 2007 Spatial correlations in the dynamics of glassforming liquids: experimental determination of their temperature dependence *Phys. Rev. E* **76** 041510
- [27] Havriliak S and Negami S 1967 A complex plane representation of dielectric and mechanical relaxation processes in some polymers *Polymer* **8** 161–205
- [28] Stevenson J D, Schmalian J and Wolynes P G 2006 The shapes of cooperatively rearranging regions in glass-forming liquids *Nat. Phys.* **2** 268–74
- [29] Ferrer M L, Lawrence C, Demirjian B G, Kivelson D, Alba-Simionesco C and Tarjus G 1998 Supercooled liquids and the glass transition: temperature as the control variable *J. Chem. Phys.* **109** 8010
- [30] Biroli G and Bouchaud J-P 2004 Diverging length scale and upper critical dimension in mode-coupling theory of glass transition *Europhys. Lett.* **67** 21–7
- [31] Capaccioli S, Ruocco G and Zamponi F 2007 Dynamically correlated regions and configurational entropy in supercooled liquids arXiv:0710.1249v1