Section 4. Glass transition: length scales

Comparative study of the NMR length scale of dynamic heterogeneities of three different glass formers

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Abstract

This article presents a comparison of the determination of the length scale of dynamic heterogeneities in different glass formers by means of a multidimensional 13C solid-state exchange NMR experiment. So far, results for poly(vinyl acetate) and glycerol have been reported. The existing data together with new results for o-terphenyl have been reanalysed in a slightly revised procedure. This revision is rationalised by computer experiments which are performed on hard-sphere systems in analogy to the NMR experiment. While we find domains in the region of 2–4 nm for PVAc and o-terphenyl, glycerol has a smaller domain of ≈1 nm.

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1. Introduction

The field of glass formation has experienced intense research in the past decades due to its practical implications as well as fundamental importance in many areas of science [1–3]. Our understanding of glassy phenomena has advanced considerably: it is now widely accepted that supercooled liquids near the glass transition temperature, Tg, exhibit spatial heterogeneity [4,5]. The life time of these transient heterogeneities is on the scale of the α-relaxation time [6,7] but there also exists experimental evidence for long-lived heterogeneities very close to Tg [8]. However, to gain information about the spatial extent of dynamic heterogeneities proved difficult and only recently experimental efforts yielded first results. These now allow a comparison of this length scale for different glass formers.

The length scale of the dynamic heterogeneity, ξhet, is now directly accessible by an advanced solid-state NMR experiment introduced by Tracht et al. [9]. It makes use of the fact that the NMR frequency monitors the orientation of the residue under investigation. In this way one may obtain information about reorientation times. Furthermore, the length scale of regions which differ in
their dynamic characteristics can be measured by spin diffusion [10]. In the reduced four-dimensional spin-diffusion experiment (4D3CP) of Tracht et al. these two aspects are combined.

After a short recapitulation of the essentials of the 4D3CP experiment, we sketch the data-analysis procedure for extracting the length scale. Following experimental procedures, we state our results for o-terphenyl. To better visualise the meaning of the length scale determined by means of NMR, we present computer experiments conducted in analogy to the NMR 4D3CP experiment for a simulated hard-sphere systems. Finally, we compare our results to studies earlier performed for a simulated hard-sphere systems. Finally, we compare our results to studies earlier performed on PVAc and glycerol.

The experiment by Tracht et al. utilises, as a core ingredient, dynamic filters [11] that allow the selection of slow subensembles. Initially, magnetisation diffusion within the entire sample occurs and is monitored selectively at locations of slow entities after various waiting times, t_{n2}. Hence, we can understand the qualitative behaviour displayed in Fig. 2 as follows: as magnetisation is only detected at \(^{13}\)C but reaches a state of homogeneous distribution over the entire sample by diffusion, only the portion that is proximate to \(^{13}\)C atoms will be detected after a long enough waiting time of \(\approx t_{m2} > r_{CC}^2/(6D)\), where \(r_{CC}\) is the distance of labelled carbons and \(D\) is the spin-diffusion coefficient. While this explains the decay of the curve with both dynamic filters switched off (upper curve), the experiment with dynamic selection (lower curve) experiences a further decay, after approximately \(t_{m2} > \zeta_{het}^2/(6D)\). After that time, magnetisation has left the slow domains and, due to the second filter, is suppressed for detection.

Tracht et al. (see Appendix of Ref. [12]) have published an analytical treatment that allows the detected magnetisation to be described by

\[
M_{\text{detect}}(t) = \frac{1}{N} \int \text{d}x \rho(x) \int \text{d}r \rho(x + r) M_{\text{point}}(r, t),
\]

where \(\rho(x) = \sum_i \delta(x - x_i)\) picks only magnetisation at selected particle locations \(x_i\), and \(M_{\text{point}}(r, t)\) is the magnetisation experienced at a point \(r\) from a point source. We note in passing, that two parameters (diffusion constant, \(D\), and the magnetisation spread after cross-polarisation, \(a\)) of \(M_{\text{point}}(r, t)\) can be determined from the diffusion curve without selection in a self-consistent fashion. From Eq. (1) we see that ultimately the pair-correlation function, \(p(r_{ij}) = \langle \rho(0) \rho(r_{ij}) \rangle / \langle \rho(0) \rangle\), governs the detected magnetisation. For the purpose of data analysis one can assume

\[
p(r_{ij}) = \delta(r_{ij}) + \frac{1}{\xi_0^2} \left( p + (1 - p) \exp \left( -2 |r_{ij}| / \xi_{het} \right) \right),
\]

where \(p\) is the degree of selection. The choice of \(\xi_{het}^2/2\) as decay constant is motivated by \(\xi_{het}\) being a measure for the diameter of heterogeneous regions. This will be discussed in further detail below. Questions we would like to address with the simulation are: Is the exponential decay as given in Eq. (2) for clusters of low mobility justified? What is the meaning of the length scale \(\xi_{het}\)?

2. Experimental

OTP had to be labelled in a single position in order to avoid intra-molecular dipolar couplings. To reduce inter-molecular dipolar coupling, the sample was diluted with regular OTP. Fig. 1 sketches the nine steps of the complicated synthesis. \(\text{[}^{13}\text{]C}\)sodiumacetate (I) was prepared by carboxylation of the Grignard of \(^{13}\)C-methyl iodide (Isotec Inc.) in ether at \(-30^\circ\text{C}\), followed by neutralisation with NaOH. \(\text{[}^{13}\text{]C}\)acetophenone (II) was obtained by acylation of benzene with (I) and AlCl3 under reflux. After distillation, a chloromethylation followed with paraformaldehyde and conc. HCl at \(90^\circ\text{C}\) for \(6\) h resulting in \(\text{[}^{13}\text{]C}\)-3-chloropropiophenone (III) which was purified by column chromatography (silica, benzene). 2,3-diphenyl-1,3-butadiene (VI) was prepared in a conventional manner starting from diacetyl (IV) via 2,3-diphenyl-2,3-butandiol (V) followed by dehydration with KHSO4 at \(170^\circ\text{C}\). The diene was let to react with (III) and CH3COOK in boiling xylene.
(silica, CH₂Cl₂/n-hexane, 8:2), a colourless oil was obtained which crystallised on standing: 4[¹³C]-1, 2-diphenyl-4-benzoyl-cyclohexane (VII). Aromatisation of (VII) to 1[¹³C]-1-benzoyl-3,4-diphenyl-benzene (VIII) was accomplished by bromine in 80% yield in chloroform at ambient temperature (silica, CH₂Cl₂/n-hexane, 7:3). Reflux of (VIII) in isopropylbenzene with sodiumamide (180°C, 2 h) resulted in the desired 13C-o-terphenyl, 1,1₀₂₀₀-4[¹³C]terphenyl (IX). It was purified by chromatography (silica, CH₂Cl₂/n-hexane, 1:1) followed by distillation under reduced pressure. The problem of spontaneous crystallisation was overcome by thoroughly cleaning the sample. The substance was dissolved in acetone, filtered with a hydrophobic fluoropore membrane filter (PTFE, 0.2 μm pore size), and the solvent was then removed under vacuum prior to glass sealing the sample. To avoid extensively long T₁(¹H)-relaxation times the relaxation agent Cr(acac)₃ was added at a low concentration of 0.06%. As previously checked for glycerol [13] by means of a spatially selective 2D echo experiment, adding a relaxation agent at such a low concentration does not influence the dynamics.

NMR experiments were performed on a BRUKER DSX 500 spectrometer with a static, double-resonance HX probe. In order to immediately detect spontaneous crystallisation which sometimes occurred after some days of quenching the melted sample, correlation times were measured on an hourly basis (relaxation times of the crystalline sample diverge and the NMR signal is nearly completely lost because of a much prolonged T₁(¹H)-relaxation time). Constant monitoring by means of two-time correlation time experiments also allowed very sensitive detection of temperature drifts in the sample. The details of the static reduced 4D exchange experiment are described in [12].

3. Results

Experiments were performed at a constant temperature of T = Tₐ + 9 K. The selection level, p = Fₘ(∞), was set to 42%, 62%, and 82%. Fig. 2 shows the result of the 4D3CP experiment at a selection level of 62%. Displayed is the reference curve without dynamic selection (spheres) as well as the curve obtained with the two dynamic filters switched on (triangles). The two solid lines represent the simulation of the diffusion process using the best-fitting value for ζ_het. For the varied

![Fig. 1. Reaction scheme for ¹³C-labelled OTP.](image1.png)

![Fig. 2. Echo intensities for the 4D3CP NMR experiment on OTP at p = 62% as function of the second mixing time, t_m2. Displayed are the curves without (upper) and with (lower) dynamic selection. Also shown (——) are the simulations for the diffusion curves. The inset shows a histogram of obtained best fits for ζ_het, procedure detailed in the text.](image2.png)
levels of selection we obtain the following results for OTP: \( \xi_{\text{het}} = (2.2 \pm 1) \text{ nm for } p = 42\% \), \( \xi_{\text{het}} = (2.3 \pm 1) \text{ nm for } p = 62\% \), and \( \xi_{\text{het}} = (2.9 \pm 1) \text{ nm for } p = 82\% \). Quantitative analysis is based on the work of Tracht et al. [9] with a modification motivated by simulations and described below.

The inset shows a histogram of values for \( \xi_{\text{het}} \) as obtained from fitting a large set of 4D3CP curves derived from the one measured magnetisation decay. This set of decay curves was obtained from the original experimental curve by adding random noise that was distributed according to the statistical uncertainty of every data point as derived from the signal-to-noise ratio of the respective FID. This procedure directly shows how a statistical error of the intensity measured in the FID translates to a statistical error of the extracted fit parameter \( \xi_{\text{het}} \).

4. Discussion

Before we turn to the interpretation of the NMR result, it is instructive to explore the meaning of the extracted fit parameter, \( \xi_{\text{het}} \), by computer simulation, analysing ‘4D3CP experiments’ on highly controllable systems. For that we choose a hard-sphere system. At the same time, this exercise will validate the procedure of how the length scale is extracted from the NMR data if cross-checked against length scales extracted by other means from the same systems.

4.1. Simulation and theory

Magnetisation diffusion in a hard-sphere system provides an ideal model for aiding the analysis of the 4D3CP experiment. On the one hand, hard-sphere systems exhibit all the features of a glass former such as non-exponential relaxation, and most importantly dynamic heterogeneities. On the other hand, they promise to be tractable by a variety of tools that allow the extraction of experimental observables [14].

The diffusion experiment in a hard-sphere system consists – quite analogously to the 4D3CP experiment – of (i) a subensemble selection based on a criterion of free choice, (ii) a diffusion process, and (iii) a measurement of the magnetisation remaining at locations of the initially selected subensemble. As outlined in Section 1, once a selection criterion is translated into the corresponding pair-correlation function, the diffusion process is fully described. Initially, rather artificial selection criteria were attempted: Hard spheres inside of boxes, spheres, or lamellae of well-defined size (Fig. 3(a)) were labelled as ‘slow’. Fig. 3(b) shows length scales, \( \xi_{\text{het}} \), resulting from fits based on the pair-correlation function as given in Eq. (2). The value \( \xi_{\text{het}} \) shows a significant offset from the chosen geometric parameter, \( x \) (box side length, sphere diameter, or lamellae thickness).

This observation can be rationalised as follows: although the exponential form of the pair-correlation function in Eq. (2) is a reasonable assumption, it will certainly not be true for small \( |r| \). In other words, magnetisation cannot diffuse in the close proximity of \( r = 0 \). This region, that we term gap, corresponds to roughly twice the minimal particle radius. When the region of forbidden magnetisation is taken into account, the above described discrepancy can be rectified. Hence, the spatial extent of the regions of slower-than-average takes now the form

\[
p(r_{ij}) = \begin{cases} 
\delta(r_{ij}), & |r_{ij}| \leq g, \\
\xi_{\text{het}}^{-1}(p + (1 - p)e^{-2r_{ij}/\xi_{\text{het}}}), & |r_{ij}| > g,
\end{cases}
\]

where \( p \) represents the fraction of molecules designated as slow and \( g \) is the gap around a particle that cannot be entered by neighbours. The average \( ^{13}\text{C} \) density is reflected in the parameter \( \xi_{\text{het}}^{-1} \). Note that the limit of \( g \to 0 \) represents the pair-correlation function as given in Eq. (2).

Fig. 3(c) shows how the improved procedure yields values for \( \xi_{\text{het}} \) that match the geometric input parameters, \( x \). It is noteworthy that \( \xi_{\text{het}} \) has to be plotted against diameters (spheres) or side length (cubes) in order for \( \xi_{\text{het}} \) to directly represent the geometry parameter. This motivated the particular decay constant, \( \xi_{\text{het}}/2 \), in Eq. (2). One can also see that structures that are heterogeneous in all three dimensions (spheres, cubes) give the expected 1:1 relationship between \( \xi_{\text{het}} \) and \( d \) whereas
one-dimensional heterogeneities (lamellae) deviate from the expected curve \( \eta_{\text{het}} = d \).

To apply more realistic selection criteria to our hard-sphere system, all particles were selected that perform less than 10 nearest-neighbour (NN) changes during a given time, \( t_{\text{select}} \), on the order of an \( \alpha \)-relaxation time, \( \tau_\alpha \). This criterion mimics quite well the selection of slow particles. Fig. 4 shows clusters of low mobility based on this selection. For the hard-sphere system under study (15 422 particles at a density of \( \rho = 0.53 \), for further details see Ref. [14]), at \( t_{\text{select}} = \tau_\alpha \) we selected 76% of the ensemble which decreases down to 0.1% at a waiting time of \( t_{\text{select}} = 9 \tau_\alpha \). We performed a simulation of magnetisation starting to diffuse from (and detected at) a subensemble selected by the change of NN criterion over a varied time period, \( t_{\text{select}} = (1-9)\tau_\alpha \). The heterogeneity length scale was extracted using Eq. (3). Due to the drastic change of selection we can, thus, measure the heterogeneity length scale of subensembles representing different portions of the entire sample. As expected, Fig. 5 shows that the length scale, \( \xi_{\text{het}} \), increases when the selection level, \( p \), is increased. However, it quickly levels off at about 30%. The beauty of performing this experiment in a hard-sphere system is that one can check the result by other observables measuring the length.
scale. We followed a procedure previously applied by Donati et al. [15]: The ‘structure factor’, \( S_{\text{sub}}(g) \), is calculated from the normalised pair correlation function \( \Gamma(r) = g_a(r)/g(r) - 1 \). The Fourier transform \( S_{\text{sub}}(q) = \mathcal{F}(\Gamma(r)) \) can be fit with a Lorentzian function \( 1/(1 + (\xi_{\text{het}}/2)^2 q^2) \) which yields values (see Fig. 5, triangles) that closely follow the ones obtained by applying the analysis scheme for extraction length scales from magnetisation–decay curves.

4.2. The 4D3CP experiment

Before applying the modified data analysis as described in Section 4.1, one has to determine a reasonable parameter for the gap size, \( g \). By fitting reference diffusion curves it was found that the gap has to be smaller than the centre distance of two NNs, \( r_{\text{NN}} \). The exponential approximation (Eq. (3)) best accounts for deviation from the real pair-correlation function (see, e.g., Ref. [16]) if a gap of \( g = \frac{1}{2} r_{\text{NN}} \) is used. Fortunately, the parameter \( r_{\text{NN}} \) is directly accessible from MD simulation studies performed on the molecules that we study: Root and Stillinger [16] find a carbon–carbon distance \( r_{\text{NN}} \approx 3.5 \text{ Å} \) for glycerol and Mossa et al. [17] find a centre-of-ring distance \( r_{\text{NN}} \approx 5 \text{ Å} \) for OTP. Both figures are sufficiently good measures for the carbon–carbon distance of the molecules we study. This leads to \( g_{\text{glycerol}} := 0.2 \text{ nm} \) and \( g_{\text{OTP}} := 0.3 \text{ nm} \).

With the additional parameter \( g \) being fixed, we now fit \( \xi_{\text{het}} = (2.2 \pm 1) \text{ nm} \), \( \xi_{\text{het}} = (2.3 \pm 1) \text{ nm} \), and \( \xi_{\text{het}} = (2.9 \pm 1) \text{ nm} \) for 42%, 62%, and 82% selection, respectively. Data previously presented for PVAc [9] and glycerol [13] has been re-analysed with the modified procedures. The results changed marginally: the length scale of heterogeneities in PVAc at \( T = T_g + 9 \text{ K} \) yields \( \xi_{\text{het}} = (3.7 \pm 1) \text{ nm} \). Values for glycerol (\( T_g = 189 \text{ K} \)) remain nearly unchanged at \( (1.3 \pm 0.5) \text{ nm} \) for \( T = T_g + 10 \text{ K} \), \( (1.1 \pm 0.5) \text{ nm} \) for \( T = T_g + 14 \text{ K} \), and \( (1.0 \pm 0.5) \text{ nm} \) for \( T = T_g + 18 \text{ K} \). Please note that one cannot straightforwardly predict for the general case in which direction \( \xi_{\text{het}} \) changes using the refined instead of the conventional analysis method. This is due to the fact that the diffusion constant, \( D \), as well as the magnetisation spread, \( a \), have to be fit using the new diffusion model. However, all three examples show that the change is within the estimated error bars and, thus, has no implications on the conclusions drawn from the results to date. Our value for the heterogeneity length scale is slightly smaller but within the error bars of the values obtained by Hempel et al. [18]. Our values are higher than results from broadband dielectric spectroscopy on a number of molecular glass-forming liquids by Kremer et al. [19].

Of course, it would be highly desirable to learn something about the shape of the domains under scrutiny. In principle, information about that could be gathered from selection level-dependent determination of \( \xi_{\text{het}} \). In fact, this seems feasible for the hard-sphere system. Fig. 5 tells us that, above 30% selection, slow domains do not simply increase by scaling their size. Instead they grow dendritic-like sprouts which leads to the characteristic length scale being \textit{constant} at \( \approx 3.5 \text{ Å} \). However, it is impossible to come up with a definite statement of that sort for the three glass formers OTP, glycerol, and PVAc merely based on the NMR results. Molecular systems near \( T_g \) could exhibit the same features of shape as hard-sphere systems. An indisputable analogy cannot be drawn because the dynamics of molecular glass formers differ from the fast dynamics of hard-sphere systems. We only
know that $\xi_{\text{het}}$ gives the shortest dimension of a likely fractal moiety of slow molecules. Under conditions of 70% selection this fractal object could well be one fully percolating cluster.

5. Conclusion

In summary, the simulations of spin diffusion in hard spheres strongly support the data-analysis method applied to extract a heterogeneity length scale from experimental NMR data. If one assumes artificial heterogeneous regions in the shape of, e.g., spheres, we find that the heterogeneous length scale exactly matches the geometric parameter, e.g., sphere diameter, in a 1:1 relationship. Of course, heterogeneous structures of such regular (spheric, cubic, lamellar) shape will not be found in a dynamically heterogeneous sample such as the subensemble in a hard-sphere system that shows fewer than average NN changes. Nevertheless, a length scale can be attributed to such likely fractal structures by means of the diffusion experiment as well as analysing the static ‘structure factor’. Again, both figures match. Additionally, from studies on lamellae we learn that $\xi_{\text{het}}$ represents something like the ‘smallest’ dimension of a heterogeneity. Furthermore, a modification of the analysis procedure including a gap, $g$, around the origin of magnetisation spread much better explains diffusion data on model systems. Due to the experimental scatter of the NMR data the modified analysis has only marginal impact on the extracted heterogeneity length scales, $\xi_{\text{het}}$.

From the 4D3CP NMR experiment on OTP one can conclude that heterogeneities are comparable to the one previously found in PVAc. However, the length scale as found for glycerol is notably smaller. This becomes especially apparent if one compares the numbers of molecules per slow domain: While we find 390 monomer units of PVAc or 76 molecules of OTP in one domain, there are only as little as 10 molecules in a slow domain of glycerol. Without offering an explanation we point out that glycerol is not as fragile a glass former as is PVAc or OTP. Furthermore, the distribution of relaxation rates is narrower for glycerol ($\beta = 0.55$) than it is for either PVAc ($\beta = 0.45$) or OTP ($\beta = 0.41$).

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References