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## Some comments on heterogeneity at the glass transition

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**Abstract.** Different kinds of static and dynamic heterogeneity at the glass transition are discussed in relation to recent experiments. Heterogeneous lengths are distinguished from cooperative length scales—in particular, in geometrically confined systems—and these are compared with finite-size effects in computer simulations.

### 1. Introduction

Although heterogeneity at the glass transition has already been extensively reviewed in the recent literature [1–3] it may be useful to comment on some aspects that may help to clarify the meaning of ‘heterogeneity’ in different contexts. In particular, we discuss the various ways in which ‘dynamical heterogeneity’ arises in experiments and computer simulations, in contrast to static (long-lived) heterogeneities that have led to recent controversy, since it was concluded from neutron scattering that the stretching of the  $\alpha$ -relaxation function is *not* the result of heterogeneities in the material [4, 5].

### 2. Liquid mobility slowdown over four decades

In the time regime from about 1 ps to 10 ns, the ‘cage effect’ that is already present in the normal liquid is developing into a typical two-time behaviour, where the fast timescale relates to ‘in-cage’ motion whereas the slow timescale ( $\alpha$ -relaxation) relates to restructuring of the cages. Although this cage has a finite size that was determined in a recent computer simulation of a hard-sphere liquid [6], this size does not define a heterogeneity in the liquid, since *each* single molecule is the centre of its own cage, which defines a homogeneous scenario that can be quantified by particular higher-order correlation functions [6]. There is also the well known ‘back-flow’ effect responsible for the algebraic long-time tail of correlation functions in normal liquids [7]. As the liquid slows down, this may develop into the ‘stringlike cooperative motion’ seen in recent computer simulations of Lennard-Jones mixtures [8] where these regions of enhanced mobility are clearly exhibited. It is possible that the onset of ‘hopping’ processes dominating at lower temperatures is also contributing to this ‘dynamical heterogeneity’. A very interesting finding is that the size of the domains in which stringlike enhanced mobility is identified increases on lowering the temperature, and diverges if extrapolated to the ‘critical’ temperature,  $T_c$ , of the ‘idealized’ mode-coupling theory (MCT) of the glass transition [9].

It is important to note that the ‘dynamical heterogeneity’ observed in the ergodic regime at  $T > T_c$  may be qualitatively different from any heterogeneity in the nonergodic regime,  $T < T_c$ , where the  $\alpha$ -relaxation time increases by many decades on approaching the

calorimetric glass transition temperature  $T_g$ . In particular, the ‘ $\beta$ -relaxation’ attributed to the sub-diffusive time regime ( $\langle r(t)^2 \rangle \propto t^x$ ;  $x < 1$ ) of ‘in-cage’ motion within a homogeneous scenario at  $T > T_c$  should be clearly distinguished from the ‘ $\beta$ -relaxation’ of Johari and Goldstein as identified by dielectric and NMR relaxation at  $T \sim T_g$  [3]. This  $\beta$ -relaxation is clearly heterogeneous [10] and the lifetime of these heterogeneities given by the  $\alpha$ -relaxation time is ‘long lived’ in comparison with the microsecond timescale of the Johari–Goldstein  $\beta$ -relaxation process.

### 3. Higher-order correlation functions

The nonexponentiality of dielectric and other relaxation functions has been discussed in relation with heterogeneity for many decades. However, there was always the problem that the decomposition of a nonexponential decay function into a superposition of exponentials which defines a ‘distribution of relaxation times’ might just be a mathematical expansion with no justification in physics if relaxation is intrinsically nonexponential and each molecule is undergoing the same kind of complex motion in a ‘homogeneous’ scenario. This problem was resolved by a ‘reduced 4D-NMR’ experiment which made it possible to investigate fourth-order time correlation functions that probe a sub-ensemble ‘selected’ within a time interval  $t_2 - t_1$  after a waiting time  $t_w = t_3 - t_2$  in a second time interval  $t_4 - t_3$  [11]. This experiment clearly showed that the system studied was heterogeneous over a time of order  $t_w$ . Later on, it turned out that for all polymers and glass-forming liquids investigated, within a time domain of about 1 to 100 ms,  $t_w$  was of the order of the  $\alpha$ -relaxation time  $\tau_\alpha$  and that the systems can be considered as homogeneous for averages over much longer timescales [12, 13, 3]. This seemingly *universal* behaviour was confirmed by other experiments (see the references in [3]) except for a ‘deep-bleach’ experiment which was able to identify a small fraction of ‘slow’ fluorescent tracer molecules that remained slow for a time  $\tau_{\text{struct}} \sim 500\tau_\alpha$  at the glass transition temperature  $T_g$  of orthoterphenyl [14]. Although current experiments [15] show that  $\tau_{\text{struct}} \sim \tau_\alpha$  at the higher temperatures at which most of the other experiments were performed, the finding of the ‘deep-bleach’ experiment at  $T_g$  remains a challenge for the future.

The analysis of third-order time correlation functions has provided a definition of heterogeneous and homogeneous contributions to the nonexponentiality of the corresponding second-order correlation functions [16]. This was applied to the dynamics of glass-forming polymer melts investigated by means of NMR experiments [17] and computer simulations [16]. The dynamical heterogeneities discovered in computer simulations (see section 2) have also been analysed in terms of higher-order correlation functions [6, 8]. In this respect it is noteworthy that the MCT analysis [9] carried out for the same time domain ( $\sim 1$  ps to 10 ns) yields primarily a density correlator which is a function of a single time interval and a single distance (or wave vector) and thus averages over the heterogeneity revealed by the computer experiments.

### 4. Heterogeneity versus cooperativity

Many theoretical concepts of complex molecular motion close to  $T_g$  focus on the concept of cooperativity with a cooperative length scale that may or may not diverge at the Kauzmann temperature  $T_K \leq T_g$ . Here, it is important to note that cooperativity or dynamical heterogeneity can occur within a spatially homogeneous system as exemplified by the ‘spin-facilitated kinetic Ising model’ [18, 19]. Therefore, one should distinguish regions of cooperative motion from domains defined by spatial heterogeneity. The question of whether

a correlation length  $\xi$  of cooperative motion can be identified via experiments in systems with geometrical confinements of size  $d \sim \xi$  has still not been answered unambiguously [20, 21]. Even a confinement which is neither wetting nor dewetting the confined liquid may not be appropriate for identifying the cooperative length  $\xi$ . A computer simulation of a model polymer melt (by Binder and co-workers [22–24]) showed a correlation length  $\xi$  if the system was confined by hard walls [24]. But finite-size effects of self-diffusion [22] could not be seen in the same (three-dimensional) model system as the lattice constant,  $d_1$ , of the periodic boundary condition was varied over a range from below to above  $\xi$  obtained from the confined system [23]. In this respect, systematic studies of finite-size effects may provide the ideal ‘confinement’ for probing the length scale,  $\xi$ , of the cooperative motion, since this length can be forced to diverge by reducing the spatial period,  $d_1$ , to the limit  $d_1 = \xi$  where the cooperativity starts to develop periodically through the infinite system.

It should be clear by now that more than one length scale can be found for a complex liquid. We refer the reader to recent reviews [1–3] for a more extensive discussion, and merely emphasize that all length scales determined near  $T_g$  in past experiments are based on theoretical concepts, where the existence of the respective length is assumed and the prescriptions for determining numbers (a few nm at  $T_g$ ) rely on further *ad hoc* assumptions. To my knowledge there is only one method by which a length scale of ‘slow’ domains can be measured directly, namely a 4D-NMR method determining this length via spin diffusion [25].

## 5. Energy landscapes

At temperatures below  $T_c \sim 1.2T_g$  one can associate different amorphous states with minima in a potential or free-energy landscape. The number of these minima grows exponentially with the size of the system and thus defines an extensive configurational entropy (complexity) [3, 26, 27]. From computer simulations of model systems, it is known that the minima define ‘inherent structures’ containing a relatively small number of molecules which can be looked upon as a special kind of heterogeneity, since ‘slow’ structures relate to deep wells and ‘fast’ structures to shallow wells [26]. If the transitions between these minima are associated with single-particle motion by assuming that each  $\varepsilon \rightarrow \varepsilon'$  transition between two minima is connected with a rotational jump by an angle  $\delta\phi$  and a translational jump by a distance  $\delta r$  of each molecule in the inherent structure, one can phenomenologically describe a number of puzzling experimental findings that are at variance with the assumption of long-lived domains [28, 29]. In particular, one can understand the apparent enhancement of translational over rotational diffusion in glass-forming systems without assuming the existence of local diffusion coefficients in the ‘slow’ and ‘fast’ domains [29] which was implied in the neutron scattering analysis mentioned above [4].

## 6. The experimentalist’s heterogeneity

During the last few years, a number of experimental methods have been developed whereby a dynamically distinguishable sub-ensemble can be selected in a supercooled liquid close to  $T_g$  and its return to the full equilibrium ensemble can be subsequently monitored [2, 3, 30]. These experiments provide a pragmatic way of quantifying heterogeneity via the selection procedure. For example, one can decompose a relaxation function,  $\Phi(t)$ , approximated by a stretched exponential into a superposition of *intrinsic* stretched exponentials:

$$\Phi(t) = \exp[-(t/\tau)^\beta] = \int w_{\text{in}}(\tau) \exp[-(t/\tau)^{\beta_{\text{in}}}] d\tau.$$

Here,  $w_{\text{in}}(\tau)$  is the weight of the intrinsic correlation function which is ‘filtered out’ in a selection experiment. The ‘degree of heterogeneity’

$$\eta = (\beta_{\text{in}} - \beta)/(1 - \beta)$$

with  $0 < \beta \leq 1$ ,  $\beta \leq \beta_{\text{in}} \leq 1$  and  $0 < \eta \leq 1$ , vanishes in the homogeneous limit and it is unity in the heterogeneous limit [30]. Of course,  $\eta$  may depend upon how sub-ensembles are filtered out in a particular selection experiment; however, it is of value for comparing different systems studied by the same experimental procedure. It should be noted that  $\eta$  has also been determined in studies of time-resolved solvation spectroscopy where no selection procedure is involved [30, 31].

Finally, we should be aware of the major difficulty of defining a ‘dynamical heterogeneity’ which decays on the same  $\alpha$ -relaxation timescale as molecular motion. If each molecule fluctuates between ‘slow’ and ‘fast’ states on the same timescale, why should this be called heterogeneous and not homogeneous? This conceptual ambiguity seems to be unavoidable. Nevertheless, the usage of the term ‘dynamical heterogeneity’ in relation to recent experiments is useful in order to describe what happens in structural glass formers close to the glass transition, and to distinguish that behaviour from homogeneous scenarios—e.g., the dynamics of self-similar (fractal) structures [3] or the above-mentioned ‘in-cage’ motion, which are also characterized by nonexponential second-order time correlation functions.

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### References

- [1] Ediger M C, Angell C A and Nagel S R 1996 *J. Phys. Chem.* **100** 13 200
- [2] Böhmer R 1998 *Curr. Opin. Solid State Mater. Sci.* **3** 378
- [3] Sillescu H 1999 *J. Non-Cryst. Solids* at press
- [4] Arbe A, Colmenero J, Monkenbusch M and Richter D 1998 *Phys. Rev. Lett.* **81** 590
- [5] Heuer A and Spiess H W 1998 *Phys. Rev. Lett.* at press
- [6] Doliwa B and Heuer A 1998 *Phys. Rev. Lett.* **80** 4915
- [7] Hansen J-P and McDonald I R 1986 *Theory of Simple Liquids* (London: Academic)
- [8] Donati C, Douglas J F, Kob W, Plimpton S J, Poole P H and Glotzer S C 1998 *Phys. Rev. Lett.* **80** 2338 and references therein
- [9] Götze W and Sjögren L 1992 *Rep. Prog. Phys.* **55** 241 and references therein
- [10] Schnauss W, Fujara F, Hartmann K and Sillescu H 1990 *Chem. Phys. Lett.* **166** 381
- [11] Schmidt-Rohr K and Spiess H W 1991 *Phys. Rev. Lett.* **66** 3020
- [12] Heuer A, Wilhelm M, Zimmermann H and Spiess H W 1995 *Phys. Rev. Lett.* **75** 2851
- [13] Böhmer R, Hinze G, Diezemann G, Geil B and Sillescu H 1996 *Europhys. Lett.* **36** 55
- [14] Cicerone M T and Ediger M D 1995 *J. Phys. Chem.* **103** 5684
- [15] Ediger M D 1998 Private communication
- [16] Heuer A and Okun K 1997 *J. Chem. Phys.* **106** 6176
- [17] Heuer A, Leisen J, Kuebler S C and Spiess H W 1996 *J. Chem. Phys.* **105** 7088
- [18] Fredrickson G H and Anderson H C 1984 *Phys. Rev. Lett.* **53** 1244  
Fredrickson G H and Anderson H C 1985 *J. Chem. Phys.* **83** 5822
- [19] Hurley M and Harrowell P 1997 *J. Chem. Phys.* **107** 8586 and references therein
- [20] Arndt M, Stannarius R, Groothues E, Hempel E and Kremer F 1997 *Phys. Rev. Lett.* **79** 2077
- [21] Streck C, Yan X and Richert R 1997 *Ber. Bunsenges. Phys. Chem.* **101** 1735
- [22] Ray P and Binder K 1994 *Europhys. Lett.* **27** 53
- [23] Binder K, Baschnagel J, Böhmer S and Paul W 1998 *Phil. Mag. B* **77** 591
- [24] Baschnagel J and Binder K 1996 *J. Physique I* **6** 1271
- [25] Tracht U, Wilhelm M, Heuer A, Feng H, Schmidt-Rohr K and Spiess H W 1998 *Phys. Rev. Lett.* **81** 2727

- [26] Stillinger F H 1995 *Science* **267** 1935 and references therein
- [27] Kirkpatrick T R, Thirumalai D and Wolynes P G 1989 *Phys. Rev. A* **40** 1045
- [28] Diezemann G 1997 *J. Chem. Phys.* **107** 10 112
- [29] Diezemann G, Sillescu H, Hinze G and Böhmer 1998 *Phys. Rev. E* **57** 4398  
Diezemann G, Sillescu H, Hinze G and Böhmer 1998 *J. Non-Cryst. Solids* **235–237** 121
- [30] Böhmer R, Chamberlin R V, Diezemann G, Geil B, Heuer A, Hinze G, Kuebler S C, Richert R, Schiener B,  
Sillescu H, Spiess H W, Tracht U and Wilhelm M 1998 *J. Non-Cryst. Solids* **235–237** 1
- [31] Richert R 1997 *J. Phys. Chem. B* **101** 6323  
Richert R 1998 *J. Non-Cryst. Solids* **235–237** 41