On the origin of the non-exponential behaviour of the α-relaxation in glass-forming polymers:

incoherent neutron scattering and dielectric relaxation results

On the origin of the non-exponential behaviour of the α-relaxation in glass-forming polymers: incoherent neutron scattering and dielectric relaxation results

J Colmenero†§, A Arbe†, A Alegría†, M Monkenbusch‡ and D Richter‡

† Departamento de Física de Materiales, Universidad del País Vasco, Apartado 1072, 20080 San Sebastián, Spain
‡ Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany

Abstract. The question of whether the primary α-relaxation in glass-forming systems is homogeneous or heterogeneous in nature is investigated by incoherent neutron scattering techniques for glass-forming polymers. The results obtained for more than ten different polymers show that the incoherent intermediate-scattering function is well described by a Kohlrausch–Williams–Watts function with a constant shape parameter. Moreover, the momentum-transfer dependence of this function approximately follows the Gaussian approximation. These results do not agree with those expected from the heterogeneous picture usually invoked as the origin of the non-exponential behaviour of the α-process. It seems that the apparent stretching of the α-relaxation function in glass-forming polymers relates dominantly to sub-linear diffusion and is not a result of a superposition of single-exponential processes, at least in the mesoscopic timescale covered by neutron scattering techniques. Deviations from the Gaussian behaviour are evaluated for the different polymers investigated and interpreted in terms of distributions of stretched relaxation functions. The validity of the extension of these results to the low-temperature range close to the glass transition temperature, where neutron scattering measurements are not feasible, is discussed in the light of new dielectric results for this range.

1. Introduction

It is well established that the time correlation functions of supercooled glass-forming liquids exhibit non-exponential relaxation, even when the linear response approximation is fulfilled by the experimental conditions. For the main dynamical process, the so-called α-relaxation, the time dependence of the different correlation functions can be well approximated by the stretched exponential or Kohlrausch–Williams–Watts (KWW) function:

$$\phi(t) = \exp[-(t/\tau_w)^\beta] \tag{1}$$

where β is a phenomenological shape parameter measuring the deviation from a single-exponential decay ($\beta = 1$) and τ_w is the KWW relaxation time. The understanding of the microscopic mechanism giving raise to this peculiar behaviour is currently a topic of strong debate. Two limiting scenarios are invoked to explain the KWW functional form. Since a monotonic function can always be written as Laplace transform of a non-negative function,

§ Author to whom any correspondence should be addressed; telephone: +34 943 448205; fax: +34 943 212236; e-mail address: `wapcolej@sc.ehu.es`.

the KWW function can easily be interpreted as arising from the superposition of different simple exponential relaxations weighted by a broad distribution of relaxation times $g(\ln \tau)$:

$$\phi(t) = \exp[-(t/\tau_w)^\beta] = \int_{-\infty}^{+\infty} g(\ln \tau) \exp(-t/\tau) \, \mathrm{d}(\ln \tau). \qquad (2)$$

This picture is usually known as the 'heterogeneous' scenario. The distribution of relaxation times $g(\ln \tau)$ can be obtained from $\phi(t)$ by means of the inverse Laplace transformation methods [1] and for $\beta = 0.5$ it shows an exact analytical form. It is noteworthy that if this scenario is not correct, i.e., if the integral kernel, $\exp(-t/\tau)$, is conceptually inappropriate, $g(\ln \tau)$ becomes physically meaningless. The other extreme picture, the 'homogeneous' scenario, considers that all of the particles in the system relax identically but by an intrinsically non-exponential process.

The 'heterogeneous' picture was involved in some of the first theoretical approaches to the dynamics of supercooled liquids [2–4]. This scenario has also recently been invoked in connection with the question of the cooperative-rearrangement regions in glass-forming systems [5]. On the other hand, most of the experimental work accumulated over recent years was analysed in the framework of the mode-coupling theory [6] which does not address this question. Recent experimental results from different spectroscopic techniques (see, e.g., [7–10]) and computer simulations in Lennard-Jones systems [11, 12] have stimulated a new revival of the 'heterogeneous' picture which is usually related to some kind of spatial heterogeneity. It has been suggested [8] that the size of the spatial heterogeneities close to the glass transition temperature T_g should range in the nanometre scale (2–5 nm for low-molecular-weight glass-forming systems and up to about 10 nm for polymers). The above-mentioned results, in particular those related to the so-called rotation–translation paradox [13], seem also to suggest that the spatial heterogeneities mainly develop in the temperature range below about 1.2 T_g, while at higher temperatures the glass-forming matrix appears to be essentially homogeneous. For glass-forming polymers, on the other hand, it has also been suggested [14] that a heterogeneous structure should be present even at $T > 1.2T_g$.

The above-mentioned experimental results mainly correspond to spectroscopic techniques, which do not give direct information about the spatial scale of the molecular motions. The size of the spatial heterogeneities is estimated by indirect methods, such as from the sensitivity of the dynamics to the probe size or from the differences between translational and rotational diffusion coefficients (the rotation–translation paradox). Surprisingly, neutron scattering results, giving direct information about the spatial scales through the dependence on the momentum transfer (Q) of the dynamical magnitudes, still have not been exploited in order to address this question. In this work we show that incoherent neutron scattering results agree rather well with a 'homogeneous' scenario for the α-relaxation in glass-forming polymers, at least on the timescale covered by neutron scattering techniques.

Neutron scattering experiments measure the scattering function $S(Q, \omega)$, where Q and $\hbar\omega$ are the momentum and energy transfer respectively. $S(Q, \omega)$ is the Fourier transform of the intermediate-scattering function $S(Q, t)$ which in turn is the spatial Fourier transform of the pair and self-correlation functions of the moving nuclei. In some way $S(Q, t)$ can be considered as a spatially sensitive version of the correlation function $\phi(t)$. Both incoherent and coherent neutron scattering results, corresponding to different glass-forming systems, agree with an approximate KWW functional form for $S(Q, t)$ associated with the α-relaxation [15]. In the case of incoherent scattering, $S(Q, t)$ represents the self-part of the particle dynamics. At this point, it is worth emphasizing that when a spatially localized process is observed by means of quasielastic neutron scattering, the characteristic relaxation time does not depend on Q. However, the values found experimentally for the KWW relaxation time, τ_w, in the case

of the α-relaxation show a strong Q-dispersion, which indicates the diffusive nature of such a process.

In this paper, first of all, we examine the possibility of discriminating between homogeneous and spatially heterogeneous dynamics on the basis of the Q-dependence of τ_w. Second, we present a summary of incoherent neutron scattering results on glass-forming polymers accumulated over the last eight years. These results are finally discussed in the framework of the homogeneous-versus-heterogeneous-dynamics controversy.

2. Theoretical considerations

In the 'heterogeneous' scenario, and in parallel with the procedure followed for developing equation (2), we may consider a distribution of local diffusivities associated with the different regions of the sample. The resulting intermediate-scattering function can be expressed as

$$S(Q, t) = \exp[-(t/\tau_w)^\beta] = \int_{-\infty}^{+\infty} g(\ln D^{-1}) \exp(-Q^2 t/D^{-1}) \, \mathrm{d}(\ln D^{-1}) \tag{3}$$

where $\exp(-Q^2 D t)$ is the intermediate-scattering function corresponding to simple diffusion in the Gaussian approximation and D the corresponding diffusion coefficient. As in the case of equation (2), by properly choosing the distribution $g(\ln D^{-1})$ a KWW time dependence of the resulting $S(Q, t)$ can be easily reproduced. However, now the 'stretched variable' is $\chi = Q^2 t$, i.e., the 'conjugated' variable (showing the same dimension) of the distributed magnitude D^{-1}. As consequence, the resulting $S(Q, t)$ reads as

$$S(Q, t) = \exp[-(Q^2 t/D_w^{-1})^\beta] = \exp[-(Q^2 D_w t)^\beta] \tag{4}$$

which can also be written in the phenomenological KWW form of equation (1) with $\tau_w = Q^{-2} D_w^{-1}$. Therefore, in the 'heterogeneous' scenario the Q-dependence of the phenomenological KWW relaxation time turns out to be the same as the Q-dependence of each of the elementary diffusion times associated with each spatial region: $\tau = Q^{-2} D^{-1}$.

If we now invoke the 'homogeneous' scenario, a KWW intermediate-self-scattering function can be obtained by considering an anomalous diffusion process in which the mean squared displacement is sub-linear in time, i.e., $\langle r^2(t) \rangle \propto t^\beta$ with $\beta < 1$. The corresponding intermediate-scattering function in the Gaussian approximation can be written as

$$S(Q, t) = \exp(-Q^2 \langle r^2(t) \rangle / 6) = \exp[-Q^2 (\mathcal{D} t)^\beta] \tag{5}$$

where $\mathcal{D}$ is a factor giving the temperature dependence of $S(Q, t)$. Equation (5) is equivalent to equation (1) with a KWW relaxation time given by $\tau_w = Q^{-2/\beta} \mathcal{D}^{-1}$. For a typical value of $\beta = 0.5$ this expression gives a Q-dependence of $\tau_w \propto Q^{-4}$; it should be possible to discriminate between this and the Q^{-2}-law found in the 'heterogeneous' scenario.

It is noteworthy that an anomalous sub-linear time dependence of the mean squared displacement is obtained in the framework of many different theoretical approaches to transport in disordered systems in general (see, for example, reference [16] for a comprehensive review). Most of these approaches are based on random walks in fractal structures, which are considered as good models for the geometrical structure of most disordered materials. However, it is worth emphasizing that, independently of the geometrical structure considered, these approaches should be classified, according to our previous definition, as homogeneous, with the meaning that the sub-linear diffusion does not emerge as a consequence of a superposition of regular diffusion processes weighted by a distribution of local diffusivities.

3. Results and discussion

Over the last few years, the dynamics of the α-relaxation has been investigated by means of incoherent neutron scattering for several polymers with a Q-range usually between about 0.2 Å^{-1} and 2 Å^{-1} (see, e.g., [17–21]). The analysis of these results in terms of a KWW form for $S(Q, t)$ gives a Q-dependence of the characteristic time which, within the experimental uncertainties, can be well described by means of a power law in Q, $\tau_w \propto Q^{-n}$. In most of the cases, the values found for the exponent n are clearly higher than 2 and close to $2/\beta$, a value which indicates a Gaussian behaviour of $S(Q, t)$. It is worth emphasizing that this result, together with the KWW form of $S(Q, t)$, in fact implies a sub-linear time dependence of the mean squared displacement. Therefore, this dependence should be considered as an experimental result and not as an '*a priori*' assumption. Moreover, recent molecular dynamics (MD) simulations for different glass-forming polymer systems on the timescale covered by neutron scattering [22–24] also show a sub-linear time dependence of the mean squared displacement. It is noteworthy that, in this case, the atomic mean squared displacement is directly obtained from the atomic trajectories and not through $S(Q, t)$. On the other hand, the Q-dependence found for τ_w by incoherent neutron scattering is that expected in the framework of the above-described homogeneous scenario. As an example, figure 1 shows the Q-dependence of τ_w as observed by backscattering techniques applied to PVME (glass transition temperature: $T_g = 250$ K) [17]. This dependence is certainly much stronger than that predicted by the heterogeneous picture ($\tau_w \propto Q^{-2}$), and in the low-Q range can be well described by a power law $\tau_w \propto Q^{-2/\beta}$. Some deviations from this dependence can be observed at Q-values above 2 Å^{-1}. However, these deviations may occur due to an intrinsic jump-length distribution for the diffusive jumps. Finite jump lengths tend to cause a bending of the dispersion for the diffusive relaxation time away from the power law. For example, in the case of a sub-linear diffusion resulting from jumps with lengths ℓ distributed according to a function $f_0(\ell) = \ell \ell_0^{-2} \exp(-\ell/\ell_0)$, the resulting characteristic time is given by $\tau_w \propto [1 + (Q\ell_0)^{-2}]^{1/\beta}$, whose asymptotic low-$Q$ limit is $\tau_w \propto Q^{-2/\beta}$. As can be seen in figure 1, this kind of description holds perfectly for PVME. Therefore, the experimental results on this polymer
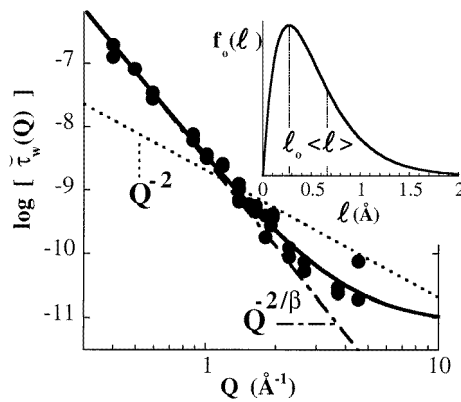

Figure 1. The momentum-transfer dependence of the characteristic time of the α-relaxation in PVME: the master curve obtained by shifting the timescale with the appropriate temperature shift factors (reference temperature: 350 K). Solid and dashed–dotted curves represent the fit to the Q-dependence expected in the homogeneous scenario when considering the distribution of jumping lengths shown in the inset and continuous diffusion respectively. The dotted line displays the behaviour expected in the heterogeneous case.

are compatible with a homogeneous scenario for the segmental relaxation with an underlying distribution of elemental jump lengths with a most probable value of $\ell_0 = 0.27$ Å.

As has already been mentioned, the power law $\tau_w \propto Q^{-2/\beta}$, i.e., the Gaussian approximation (equation (5)), holds approximately for glass-forming polymers. This general result implies that the observed stretching of the α-relaxation function is, at least in this case, mainly due to intrinsic anomalous diffusion (the homogeneous scenario). The experimentally determined values for the power-law exponent n of the characteristic time can be written as $n = 2x/\beta$, where we have introduced a new parameter, x, which measures the deviations from the pure Gaussian behaviour. If $x = 1$, the Gaussian approximation is perfectly fulfilled. In terms of this phenomenological parameter, $S(Q, t)$ can be expressed as

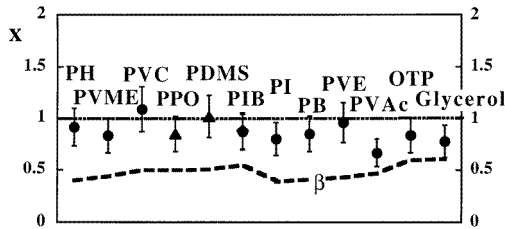$$S(Q, t) = \exp[-Q^{2x}(\mathcal{D}t)^\beta]. \tag{6}$$

Figure 2. Values of the x-parameter in comparison with the shape parameter β deduced from incoherent neutron scattering for the polymeric and low-molecular-weight glass-forming systems indicated.

Figure 2 shows a compilation of the values obtained for x for ten glass-forming polymers (for further details, see references [18, 20, 21, 25]). Among them, we would like to highlight PVE, PI, PIB and PB, whose Q-dependencies have been carefully investigated in a recent work [20], performing multiple-scattering corrections and avoiding possible contaminations from local processes [26]. It is clear from this figure that, with the possible exception of PVAc [25], all polymers exhibit x-values which are compatible with the Gaussian limit and therefore with the homogeneous picture. The values found in the literature for two low-molecular-weight glass formers, OTP [21] and glycerol [27], are also included. Their behaviour is similar to that observed for polymers, though the deviations from the Gaussian behaviour could be higher in these cases. These deviations, however, may also relate to a β-parameter which changes with Q.

The discrimination between the homogeneous and heterogeneous scenarios can also be discussed in terms of the 'non-Gaussian' x-parameter defined above. By direct comparison of equations (4) and (6) it follows that in the heterogeneous case the value of x should be just the stretching parameter β. This heterogeneous-case limit is also depicted in figure 2. The experimental values of x determined for almost all glass-forming systems investigated clearly fall closer to the value 1 corresponding to the Gaussian case (and consequently to the homogeneous scenario) than to the value β which would be predicted for the heterogeneous picture. These values of x correspond to values of the well known non-Gaussian parameter α_2:

$$\alpha_2 = [(3\langle r^4(t)\rangle)/(5\langle r^2(t)\rangle^2)] - 1$$

of 0.1–0.2, which are in the range found by MD simulations of glass-forming polymers for a similar temperature range [22]. Similar values of α_2 have also been recently reported in the case of model glass-forming systems, as suspensions of hard spherical particles, and were considered as 'negligible deviations from Gaussian behaviour' [28]. Therefore, incoherent neutron scattering results indicate that the observed stretching of the α-relaxation function is mainly due to intrinsic anomalous diffusion and not to a superposition of single-exponential functions. Only the behaviour of PVAc and the low-molecular-weight systems would perhaps

be compatible with what we have defined here as the heterogeneous framework. In order to compare these results to those obtained by spectroscopic methods, it is worthy of remark that the timescale of the α-relaxation which is explored by incoherent neutron scattering is of the same order as that explored by, for example, dielectric spectroscopy. The values of τ_w measured by high-frequency dielectric spectroscopy usually correspond to those measured by incoherent neutron scattering over the same temperature range at Q-values of the order of $1\ \text{Å}^{-1}$ [29], i.e., more or less in the middle of the Q-range measured.

3.1. Interpretation of the deviations from Gaussian behaviour in terms of distributions of KWW-like processes

Now we will try to understand the observed deviations from the Gaussian behaviour in terms of the remaining heterogeneities in the system. First of all, let us consider a real and well known system where spatial heterogeneities are present in a controlled way: a miscible blend [30]. In such a system, concentration fluctuations with a characteristic time slower than that of the α-relaxation give rise to the existence of spatial regions with different concentrations, which on the timescale of the α-process are well defined. Due to the direct correlation between the blend concentration and the glass transition temperature, each of these regions shows a different T_g and, as a consequence, a different relaxation time for the α-process. Therefore, a distribution of relaxation times with an actual physical meaning is evident. The relaxation function of one of the components in the blend is given by the superposition of the relaxation functions of this component in the different regions of the blend. If the dynamics of this component in the pure homopolymer state is characterized by a stretching exponent β and behaves, as shown before, like a Gaussian system, i.e.,

$$S_{\text{pure}}(Q, t) = \exp[-(Q^{2/\beta} t / \mathcal{D}^{-1})^{\beta}] \tag{7}$$

in the blend we would observe

$$S_{\text{blend}}(Q, t) = \int_{-\infty}^{+\infty} g(\ln \mathcal{D}^{-1}) \exp[-(Q^{2/\beta} t / \mathcal{D}^{-1})^{\beta}] \, \mathrm{d}(\ln \mathcal{D}^{-1}) \tag{8}$$

and consequently the intermediate-scattering function for the blend will be more stretched than the one corresponding to the pure homopolymer. A description in terms of a KWW function reads

$$S_{\text{blend}}(Q, t) = \exp[-(Q^{2/\beta} t / \mathcal{D}_0^{-1})^{\beta_0}] = \exp[-Q^{2\beta_0/\beta} (\mathcal{D}_0 t)^{\beta_0}] \tag{9}$$

with $\beta_0 < \beta$. It can easily be deduced from a comparison between equations (7) and (9) that the effect of blending also induces the deviations from the Gaussian behaviour observed for the pure homopolymer. Expressed in terms of equation (6), the x-value exhibited by this polymer would be given by $x = \beta_0/\beta$.

This real example suggests to us the possibility of interpreting the values of x for homopolymers as a measure of the distribution of KWW-like relaxations arising from the remaining heterogeneities in the sample. The observed deviations in the Q-dependence of $S(Q, t)$ from the Gaussian behaviour given by the x-value would reflect the difference between the experimentally observed stretching exponent β_0 and the actual β-value characteristic of the pure relaxation function. In this framework, we can calculate the distribution function $g(\ln \mathcal{D}^{-1})$ responsible for the additional observed stretching of the relaxation. This is shown in figure 3(a) for the case of PB, which could be considered as typical ($x \approx 0.8$). We would like to stress that this distribution corresponds to different diffusivities which relax intrinsically in a KWW-like form, not as single exponentials. The stretching exponent β characterizing the sub-linear behaviour of the elemental diffusive processes which are distributed, can be obtained from the
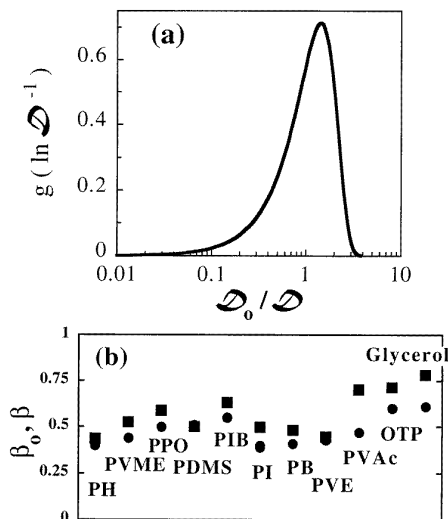
Figure 3. (a) The distribution of anomalous diffusion coefficients giving rise to the deviations from the homogeneous limit observed in PB. (b) Values of the observed (●) shape parameter (β_0) and the 'actual' ones (■) (β) deduced for the systems indicated (see the text).
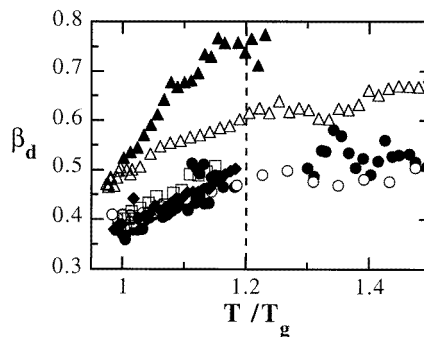
Figure 4. The temperature dependence of the shape parameter of the α-relaxation as determined from dielectric spectroscopy for several polymers: PVE (●), PVME (○), PB68 (◆), PH (□), PSF (▲) and PVAc (△).

observed stretching and the x-value: $\beta = \beta_0/x$. The resulting values for all of the polymers investigated are shown in figure 3(b); in general, they are quite close to the observed ones except for PVAc.

Last but not least, we would like to point out that the incoherent neutron scattering investigations of the α-relaxation are carried out at temperatures where the relaxation can be observed within the experimental window of the available spectrometers (typically, with average relaxation times of the order of a nanosecond). These temperatures usually correspond to the range close to or above $1.2\,T_g$. In this range, the value of the stretching parameter is approximately constant for most of the polymers and similar to that deduced by dielectric spectroscopy, β_d. Unfortunately, neutron measurements of the α-process usually cannot be extended to the range $T < 1.2T_g$. Therefore, we do not know anything about the evolution of the β-value determined by neutron scattering in this range. However, this temperature range can nicely be covered by broad-band dielectric spectroscopy. Recent careful measurements carried out on several polymers [31] indicate that the dielectric β-value, β_d, decreases as the temperature decreases towards T_g (see figure 4). This increase of the stretching below the temperature $\approx 1.2\,T_g$ could be interpreted in the framework proposed here as a progressive broadening of the distribution of stretched relaxation processes characteristic of the α-process. However, although this broadening could be related in some way to the development of solid-like spatial heterogeneities in this temperature range (e.g., in the landscape picture [32]), this does not imply that the origin of the α-stretching observed at $T > 1.2T_g$ is a distribution of simple exponential processes.

4. Conclusions

In summary, exploiting the space-time sensitivity of quasielastic neutron scattering, we have investigated the long-standing question of whether the primary relaxation in glass-forming

materials, here polymers, is heterogeneous or homogeneous in nature. From the Q-dependent KWW relaxation times τ_w it turns out that the apparent stretching of the α-relaxation function relates dominantly to sub-linear diffusion and is not a result of a superposition of single-exponential processes. Deviations from the homogeneous limit observed experimentally can be interpreted in terms of distributions of stretched elemental relaxation functions. Although, unfortunately, neutron scattering investigations of the α-process cannot be carried out in the range $T < 1.2T_g$, the decreasing of the β-value observed by dielectric spectroscopy for most of the polymers in this range suggests an increasing role of these distributions close to T_g.

Acknowledgments

References

[1] See, e.g., Alvarez F, Alegría A and Colmenero J 1991 *Phys. Rev.* B **44** 7306 and references therein
[2] Adam G and Gibbs J H 1965 *J. Chem. Phys.* **43** 139
[3] Cohen M H and Grest G S 1981 *Phys. Rev.* B **24** 4091
[4] Alegría A, Barandiarán J M and Colmenero J 1984 *Phys. Status Solidi* b **125** 409
[5] Fischer E W, Donth E and Steffen W 1992 *Phys. Rev. Lett.* **68** 2344
[6] Götze W and Sjögren L 1992 *Rep. Prog. Phys.* **55** 241
[7] Schmidt-Rohr K and Spiess H W 1991 *Phys. Rev. Lett.* **66** 3020
[8] Cicerone M T, Blackburn F R and Ediger M D 1995 *J. Chem. Phys.* **102** 471
[9] Williams G and Fournier J 1996 *J. Chem. Phys.* **104** 5690
[10] Schiener B, Böhmer R, Loidl A and Chamberlin R V 1996 *Science* **274** 752
[11] Kob W, Donati C, Plimpton S J, Poole P H and Glotzer S C 1997 *Phys. Rev. Lett.* **79** 2827
[12] Doliwa B and Heuer A 1998 *Phys. Rev. Lett.* **80** 4915
[13] Hall D B, Dhinojwala A and Torkelson J M 1997 *Phys. Rev. Lett.* **79** 107
[14] Cicerone M T and Ediger M D 1996 *J. Chem. Phys.* **104** 7210
[15] See, e.g., *Science* 1995 **267** (Special Issue on glasses and glass-forming liquids)
[16] Havlin S and Ben-Avraham D 1987 *Adv. Phys.* **36** 695
[17] Colmenero J, Alegría A, Alberdi J M, Alvarez F and Frick B 1991 *Phys. Rev.* B **44** 7321
[18] Colmenero J, Alegría A, Arbe A and Frick B 1992 *Phys. Rev. Lett.* **69** 478
[19] Zorn R, Richter D, Frick B and Farago B 1993 *Physica* A **201** 52
[20] Arbe A, Colmenero J, Monkenbusch M and Richter D 1998 *Phys. Rev. Lett.* **81** 590
[21] Colmenero J, Arbe A, Alegría A and Ngai K L 1994 *J. Non-Cryst. Solids* **172–174** 229
[22] Roe R J 1994 *J. Chem. Phys.* **100** 1610
     Roe R J 1998 *J. Non-Cryst. Solids* **235–237** 308
[23] van Zon A and de Leeuw S W 1998 *Phys. Rev.* E **58** R4100
[24] Binder K, Baschnagel J, Bennemann C and Paul W 1999 *J. Phys.: Condens. Matter* **11** A47 and references therein
[25] Colmenero J, Alegría A, Alvarez F and Alberdi J M 1999 to be published
[26] Arbe A, Buchenau U, Willner L, Richter D, Farago B and Colmenero J 1996 *Phys. Rev. Lett.* **76** 1872
[27] Wuttke J, Chang I, Fujara F and Petry W 1997 *Physica* B **234–236** 431
[28] van Megen W, Mortensen T C, Williams S R and Müller J 1998 *Phys. Rev.* E **58** 6073
[29] Colmenero J, Arbe A and Alegría A 1994 *J. Non-Cryst. Solids* **172–174** 126
[30] Alegría A, Cendoya I, Colmenero J, Alberdi J M, Grimm H, Richter D and Frick B 1999 *Macromolecules* submitted
[31] Alegría A, Colmenero J, Mari P O and Campbell I A 1999 *Phys. Rev.* E submitted
[32] See, e.g., Angell C A 1997 *Complex Behaviour of Glassy Systems (Springer Lecture Notes in Physics, vol 402)* ed M Rubi and C Prez-Vicente (Springer: Heidelberg) p 1