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Scaling between the rotational diffusion of tracers and the relaxation of polymers and glass formers

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Abstract. The rotational dynamics of subnanometric molecular tracers in glass formers with low molecular weight and polymers is discussed by presenting electron spin-resonance and time-resolved fluorescence studies. It is shown that the reorientation of the tracer is fully or partially coupled to the host relaxation processes. The degree of coupling is well described by the fractional scaling $\tau \propto \tau_i^{\xi_i}$ between the correlation time τ of the tracer and the host timescales τ_i . The crossovers between the different regimes are sharp. Remarkably, one crossover occurs systematically very close to the α - β splitting point of the dielectric relaxation or the critical temperature predicted by the mode-coupling theory of the glass transition.

1. Introduction

The rotational diffusion of molecular tracers in liquids approaching their glass transition is a topic of current interest. Studies have been carried out on both low-molecular-weight glass formers [1–6] and polymers [7–11]. It is usually found that *large* tracers, i.e. molecules of nanometre size at least, are well coupled to the viscosity or the α -relaxation even close to the glass temperature T_g [2, 7–9]. On the other hand, there is evidence collected by time-resolved fluorescence [3, 8] and electron spin-resonance (ESR) studies [4–6, 10, 11] that the reorientations of *small* tracers exhibit large decouplings.

The mechanism driving the decoupling is largely unknown although a role for the spatial and/or dynamical heterogeneities may be anticipated. The present paper discusses the correlation between the reorientation of *small* tracers and the relaxation properties of polymers and glass formers of low molecular weight.

These materials exhibit a variety of relaxations, either collective or local in nature. Flow and α -processes are of the former type whereas the so-called β -, γ - and δ -processes are of the latter type [12]. The timescale on which they occur will be denoted by τ_i with $i = \eta, \alpha, \beta, \gamma, \dots$. In particular, $\tau_\eta = \eta/G$ is a Maxwell relaxation time, where η and G are the shear viscosity and the elastic modulus, respectively.

It will be shown that the reorientation of the tracer is coupled to the host relaxation to different degrees. The degree of coupling is well described by a fractional scaling between the correlation time τ of the tracer and the host timescales τ_i :

$$\tau = C_i \tau_i^{\xi_i} \quad 0 < \xi_i \leq 1. \quad (1)$$

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$\xi_i = 1$ implies full coupling. Similar fractional relations involving translational diffusion [1, 13] and DC conductivity [14] have also been reported and have been known of for a long time [15, 16]. An obstruction model has been developed [17]. We believe that equation (1) may be validated as a general form of the coupling between a tagged particle and the host dynamics.

2. Experimental procedure

The low-molecular-weight glass former is o-terphenyl (OTP, Aldrich, $T_g = 243$ K). The tracer TEMPO (Aldrich), which is nearly spherical (semi-axis $r_{S\parallel} \approx 0.27$ nm, and $r_{S\perp} \approx 0.37$ nm), was dissolved to a concentration of 10^{-3} mol l⁻¹, corresponding to about 200 ppm.

The polymer under study is poly(vinyl acetate) (PVAc) which was obtained commercially and used as received. The weight-average molecular weight is $M_w = 197.6$ kg mol⁻¹ and the dispersity is 3.67. The calorimetric glass transition temperature is $T_g = 318$ K. The tracer dissolved in PVAc is the perdeuterated nitroxide 4-(hydroxyl)-2, 2, 6, 6-tetramethyl-piperidine, 1-¹⁵N-1 oxyl (¹⁵N-DTEMPOL, MSD Isotopes Incorporated) which is nearly spherical with a Van der Waals volume of about 180 Å³. The sample was prepared at the Max-Planck-Institut für Polymerforschung in Mainz. The tracer concentration was less than 0.5% by weight. Before the ESR measurements were performed, the sample was carefully dried at about 370 K in vacuum for 36 h and sealed in a standard ESR tube.

The ESR lineshape of the spin probes depends on their magnetic parameters and rotational diffusion constants. In short, owing to the anisotropy of the magnetic interactions, the reorientation of the spin probe results in random magnetic fields broadening the ESR transitions. Further details are given elsewhere [18].

The ESR measurements were carried out by using a Bruker spectrometer ER200D equipped with an X-band bridge ($\nu_0 = 10$ GHz), a NMR gaussmeter ER035M and a gas-flow variable-temperature unit with a temperature stability of about 0.1 K. All of the data were recorded on a computer and analysed off-line. The magnetic parameters of the tracer were carefully measured by fitting the powder ESR lineshape, i.e. the lineshape measured at very low temperature where the line broadening is not due to the reorientation of the tracer. The rotational diffusion constants were derived by numerical simulation of the ESR lineshape. Details of the algorithm are given elsewhere [19, 20].

3. Results and discussion

3.1. Low-molecular-weight glass formers

Figure 1 shows the temperature dependence of the rotational correlation time τ of TEMPO [4]. Three different regions are identified. In region I ($T > 298$ K) the data are well described by the Debye–Stokes–Einstein law (DSE):

$$\tau = \eta v / k_B T. \quad (2)$$

v is the effective volume of the tracer. k_B and T are the Boltzmann constant and the temperature, respectively. Equation (2) takes the form of equation (1) with $i = \eta$ and $\xi_\eta = 1$.

In region II (280 K $< T < 298$ K), which includes the MCT critical temperature $T_c = 290$ K, the reorientation of the tracer decouples from the viscosity. This region is magnified in the inset of figure 1. The decoupling is well described by equation (1) with $i = \eta$, $\xi_\eta = 0.28 \pm 0.04$. This special form of the scaling has been referred to as the *fractional DSE* (FDSE) form [4]. For region III ($T < 280$ K) previous studies obtained evidence that the spin probe rotates via activated jumps ($\Delta E = 18.7$ kJ mol⁻¹ for $T > T_g$) [20].

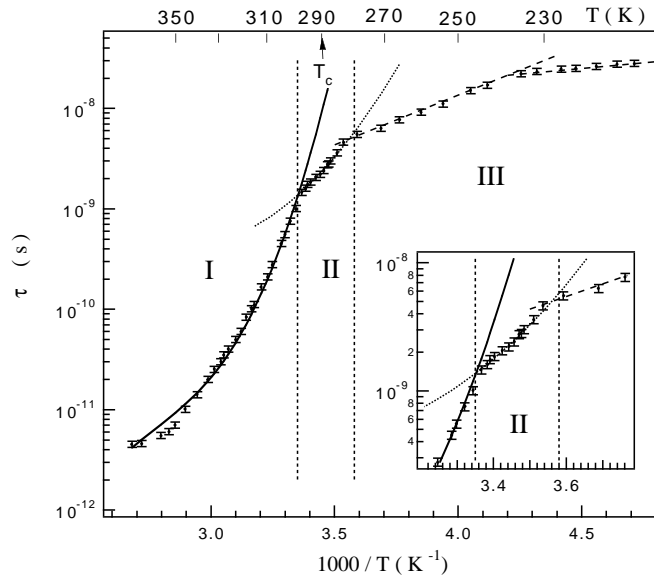


Figure 1. The rotational correlation time τ of TEMPO in OTP. Solid curves: the best fit with the DSE law, equation (2). Dot-dashed curve: the best fit with the FDSE law, equation (1) with $i = \eta$, $\xi_\eta = 0.28 \pm 0.04$. Dashed curves: Arrhenius laws. The MCT critical temperature is shown.

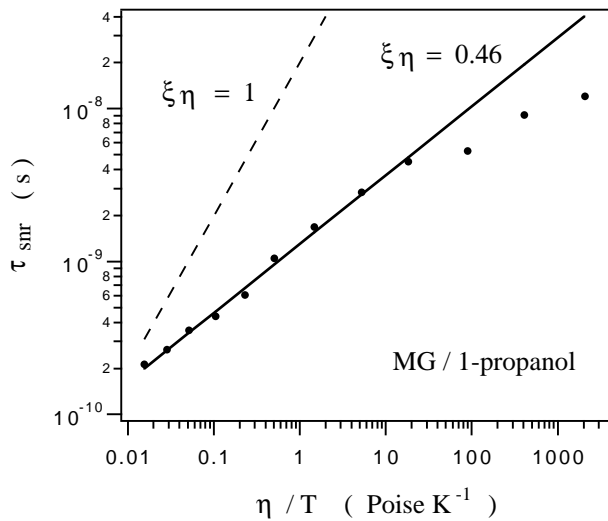


Figure 2. The non-radiative decay time of the slow component of malachite green in 1-propanol [3]. The slope predicted by the DSE law, equation (2), namely $\xi = 1$, is also shown.

Very recently, the decoupling of the reorientation of *small* tracers from the viscosity has been also observed by Ye *et al* via time-resolved fluorescence in different associated liquids [3]. Remarkably, the decoupling is well accounted for by the FDSE law (see figure 2). In particular, in agreement with the ESR studies (see figure 1), the existence of sharp crossovers (cusps) very close to the expected location of the MCT critical temperature T_c has been noted [3]. A recent numerical simulation by Nicodemi and Coniglio based on the frustrated percolation model

confirmed that the crossover from the usual liquid regime to the fractional Stokes–Einstein regime is signalled by cusps [21].

3.2. Polymers

In figure 3 the temperature dependence of the average rotational correlation time $\langle\tau\rangle$ of ^{15}N -DTEMPOL in PVAc is shown [11].

Three regions may be conveniently defined. For $T > 403$ K the temperature dependence of $\langle\tau\rangle$ is well fitted by the Vogel–Fulcher (VF) law:

$$\langle\tau\rangle = \tau_0 \exp\left(\frac{B}{T - T_\infty}\right) \quad (3)$$

with $\tau_0 = (7.8 \pm 0.8) \times 10^{-15}$ s, $B = 650 \pm 60$ K and $T_\infty = 265 \pm 18$ K. The parameters B and T_∞ compare nicely with the ones ($B = 660 \pm 50$ K, $T_\infty = 266 \pm 3.5$ K) derived from the dielectric α -relaxation [22]. The ratio $\langle\tau\rangle_\alpha/\langle\tau\rangle$ is about 300.

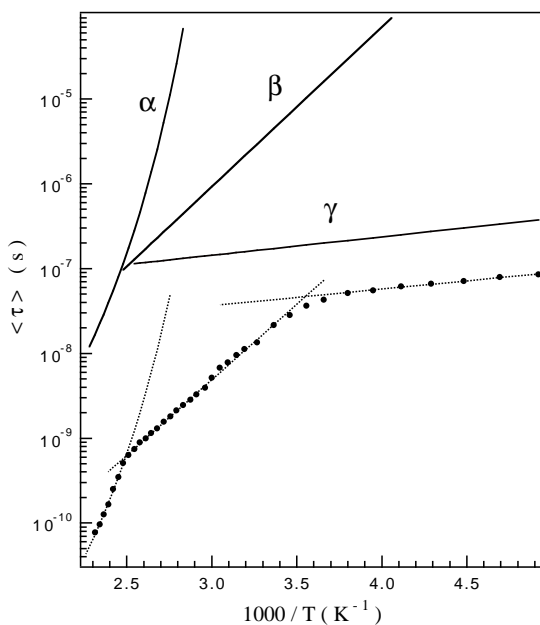


Figure 3. The average rotational correlation time $\langle\tau\rangle$ of ^{15}N -DTEMPOL in PVAc. For comparison the temperature dependence of the α -, β - and γ -relaxation times of PVAc are also shown as solid curves. The dashed curves are fits with equation (1) with $i = \alpha, \beta, \gamma$ and $\xi_\alpha = \xi_\beta = \xi_\gamma = 1$.

We interpret this as mainly due to there being different length scales involved. The length scale of the α -relaxation may be estimated by referring to recent NMR studies for PVAc on dynamic heterogeneities [23] and mechanical properties [24] which detect length scales of $\xi = 3 \pm 1$ nm. According to these studies, the α -relaxation involves regions with volumes of about 27 nm^3 , to be compared with the tracer volume of about 0.18 nm^3 . Interestingly, the volume ratio compares well with $\langle\tau\rangle_\alpha/\langle\tau\rangle$.

For $403 \text{ K} > T > 273 \text{ K}$, the reorientation of ^{15}N -DTEMPOL is activated, i.e. $\langle\tau\rangle = \tau_1 \exp(\Delta E/k_B T)$, with $\Delta E = 35 \pm 6 \text{ kJ mol}^{-1}$ and the apparent attempt time $\tau_1 = (2.21 \pm 0.7) \times 10^{-14}$ s. The value of ΔE compares quite well with the activation energy of the dielectric β -relaxation $\Delta E_\beta = 39 \pm 5 \text{ kJ mol}^{-1}$ [12,25]. It worth noting that the cusp separating

the regions where the tracer couples to the α - and β -processes is located at 403 K, i.e. very close to the temperature at which the α - and β -processes bifurcate, $T_{\alpha\beta} \simeq 395 \text{ K} = T_g + 77 \text{ K}$ (see figure 3) [12]. This is remarkable, since it is well known that dielectric relaxation does not readily investigate the α - β bifurcation region where the α - and β -peaks merge into a single broad structure. Finally, we note that the ratio $\langle\tau\rangle_\beta/\langle\tau\rangle \simeq 160$, to be compared to $\langle\tau\rangle_\alpha/\langle\tau\rangle \simeq 300$. This suggests that the β -relaxation has some non-local character. Ishida *et al* reached the conclusion that the β -relaxation arises from motions of the side groups which lead to, or are accompanied by, local distortions of the main chain [12, 25].

For $T < 273 \text{ K}$ the temperature dependence is well described by the Arrhenius law with the activation energy $\Delta E = 3.7 \pm 0.6 \text{ kJ mol}^{-1}$ and the attempt time $\tau_1 = (9.5 \pm 1) \times 10^{-7} \text{ s}$. This value compares well with the activation energy of the γ -relaxation $\Delta E_\gamma = 4.1 \pm 0.7 \text{ kJ mol}^{-1}$ [12, 26]. The ratio $\langle\tau\rangle_\gamma/\langle\tau\rangle \simeq 2.7$. This suggests that the reorientation of the tracer relaxes due to the molecular units being of comparable size. The dielectric γ -relaxation has been occasionally ascribed to the methyl group located in the side chain of PVAc. Colmenero and co-workers found by means of inelastic neutron scattering that the activation energy of the methyl group rotation of PVAc is $3.74 \pm 0.27 \text{ kJ mol}^{-1}$, in nice agreement with our value, but the attempt time is in the picosecond region, i.e. six orders of magnitude faster than the γ -relaxation [27]. This leads to the conclusion that the question of the molecular interpretation of the γ -relaxation in PVAc remains open [12].

The above discussion points to the overall conclusion that the tracer is well coupled to the relaxation mechanisms driving the dielectric response of PVAc. As the latter is mainly due to the polar groups of the side chains, one concludes that the tracer is located preferentially close to the latter.

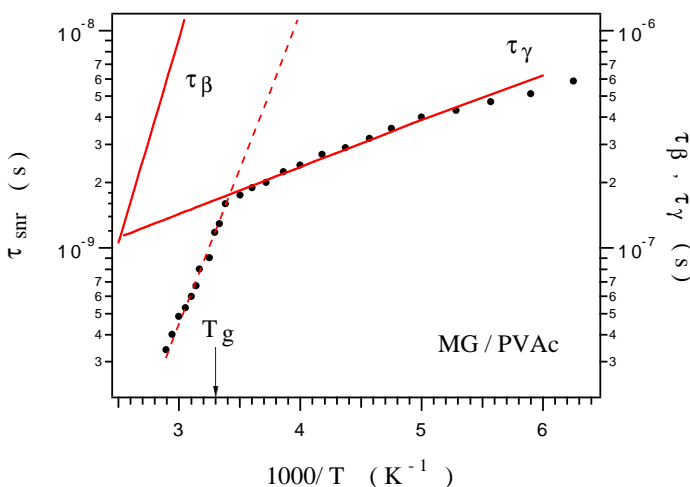


Figure 4. The non-radiative decay time of the slow component of malachite green in PVAc [3]. The temperature dependences of the β - and γ -relaxation times of PVAc are also shown as solid curves. A vertical shift of two decades makes τ_γ and τ_{snr} coincide. The superimposed dashed curve is the best fit with the Arrhenius law.

Very recently, the reorientation of the tracer malachite green in PVAc has also been studied by Ye *et al* via time-resolved fluorescence [3]. In figure 4 their data are compared to the secondary relaxations of PVAc. Below T_g the reorientation is activated with the activation energy $\Delta E = 4.6 \text{ kJ mol}^{-1}$ which is quite close to $\Delta E_\gamma = 4.1 \pm 0.7 \text{ kJ mol}^{-1}$ [12, 26]. The ratio τ_γ/τ_{snr} is about 10^2 . Above T_g a fit with the Arrhenius law yields the activation law

$\Delta E = 27 \text{ kJ mol}^{-1}$, which is lower than the activation energy of the dielectric β -relaxation $\Delta E_{\beta} = 39 \pm 5 \text{ kJ mol}^{-1}$. The discrepancy may follow from the large timescale separation: $\tau_{\beta}/\tau_{snr} \simeq 10^3$. It must be pointed out that the transient fluorescence of malachite green which was investigated by Ye *et al* is not due to the overall rotation of the tracer but only to a *part* of it. On the one hand this leads to a decrease of the 'effective' size of the tracer; on the other hand it must be appreciated that the interaction of that part with PVAc may be *screened* by the rest of the tracer. This argument may help to understand why the reorientation times of malachite green exhibit a large offset from the secondary relaxations of PVAc.

4. Conclusions

The rotational dynamics of subnanometric molecular tracers in glass formers and polymers has been discussed. The studies that we presented support the conclusion that the scaling can be described by equation (1). Different dynamical regimes are observed with sharp crossovers. Remarkably, some crossovers occur very close to the α - β splitting point of the dielectric relaxation or the critical temperature predicted by the mode-coupling theory of the glass transition.

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