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Universal scaling between structural relaxation and caged dynamics in glass-forming systems: Free volume and time scales

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ABSTRACT

It is shown that the Debye–Waller factor (DW), a measure of the cage dynamics, is contributed by free-volume in o-terphenyl (OTP) and glycerol. An elementary ansatz provides an alternative way to get the reduced DW from Positron Annihilation Lifetime Spectroscopy (PALS). The ansatz supports the scaling of the slow relaxation with the fast caged dynamics over about ten decades in relaxation times in OTP and glycerol. Both PALS and neutron scattering experiments show that, in order to evidence the scaling, the observation times must be shorter than the time scales of the relaxation processes.

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1. Introduction

Understanding the extraordinary viscous slow-down that accompanies glass formation is a major scientific challenge [1–3]. On approaching the glass transition (GT), trapping effects are more and more prominent. The average escape time from the cage of the first neighbors, i.e. the structural relaxation time τ_α , increases from a few picoseconds up to thousands of seconds. The rattling motion inside the cage occurs on picosecond time scales with amplitude $\langle u^2 \rangle^{1/2}$, the so called Debye–Waller factor (DW). At first sight, due to the extreme time-scale separation between the rattling motion ($\sim 10^{-12}$ s) and the relaxation ($\tau_\alpha \sim 10^2$ s at GT), one expects the complete independence of the two motions. Nonetheless, several authors investigated their correlations, emphasizing in particular the link with the bulk elastic properties (for a review see ref. [4]). From this respect, the universal scaling between the structural relaxation time, or the shear viscosity, and the DW factor was reported for several numerical models, including linear polymers, mixtures, prototypical glassformers like SiO₂ and o-terphenyl (OTP), and icosahedral glassformer [5,6]. The resulting master curve fits with the existing experimental data from supercooled liquids, polymers and metallic glasses over about eighteen decades of relaxation times and a very wide range of fragilities.

The closeness of the DW with free-volume concepts was noted in experiments [7–10], theories [11,12] and simulations [5,6,13]. The role of the free-volume in elastically-driven relaxation was recognized by Mooney and Bueche in fifties and later by Dyre and coworkers [4] who stated that the rearrangement only takes place when there is a local, temporary density decrease. Differently, Harrowell and coworkers concluded that relaxation in a supercooled liquid originates

from localized soft modes and that the spatial distribution of the free volume does not show any significant correlation with the spatial distribution of DW [14]. Ashton and Garrahan pointed out that free volume may be at the heart of both relaxation and soft modes with no causal link between them even in the presence of strong correlations [15].

The present paper aims at providing new elements to clarify the role of the free-volume. It follows several analyses of both the experimental [16,17] and the simulation [18–21] data on that topic by one of the authors and coworkers. To this aim, we consider results from the Positron Annihilation Lifetime Spectroscopy (PALS) [8,22]. PALS is a structural technique to parametrize the free volume. In fact, the orthopositronium bound state of a positron has a strong tendency to localize in holes of low electron density and decays with lifetime τ_3 being related to the average cavity size.

The paper first summarizes the results about the scaling between the structural relaxation and DW. Then, a simple ansatz to get information on DW from PALS is discussed. Finally, the conclusions are presented.

2. Scaling between structural relaxation and DW

Fig. 1 shows the scaling between the structural relaxation time τ_α and the viscosity η with respect to the reduced DW, $\langle u^2 \rangle / \langle u_g^2 \rangle$, with $\langle u_g^2 \rangle = \langle u^2 \rangle (T_g)$. The experimental data include supercooled liquids, polymers, metallic glasses over about eighteen decades of relaxation times and a very wide range of fragilities. The plot now includes the ionic liquid CKN as well. The master curve of Fig. 1 (black line) is expressed analytically by:

$$\log X = \alpha + \tilde{\beta} \frac{\langle u_g^2 \rangle}{\langle u^2 \rangle} + \tilde{\gamma} \left(\frac{\langle u_g^2 \rangle}{\langle u^2 \rangle} \right)^2 \quad (1)$$

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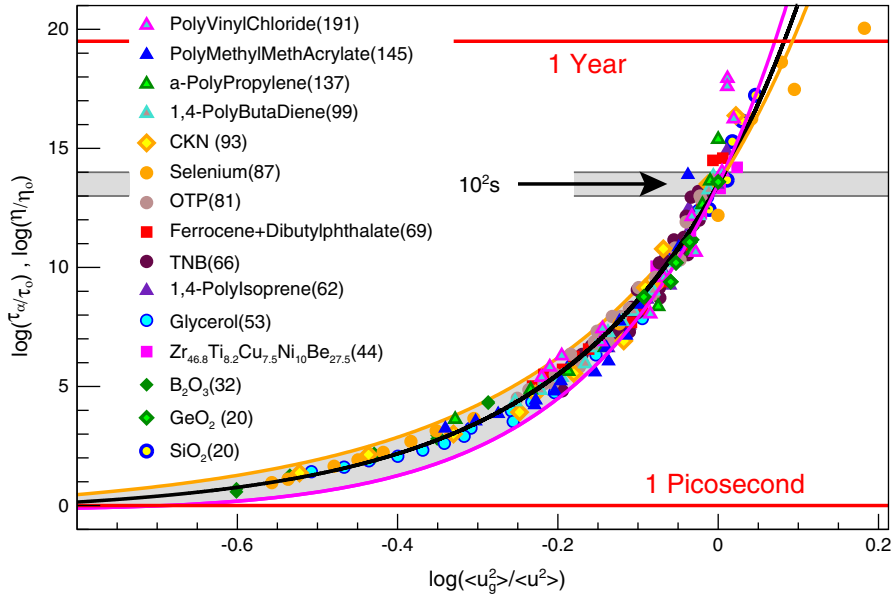


Fig. 1. Reduced relaxation time and viscosity vs reduced DW factor ($\langle u_g^2 \rangle = \langle u^2 \rangle(T_g)$). The numbers in parenthesis denote the fragility m . The black curve is Eq. (1). The colored curves bound the accuracy of Eq. (1) [5,6]. Refer to Table 1 for further details about the experiments.

with X equal to the reduced quantities τ_α/τ_0 or η/η_0 . The best-fit values ($\alpha = -0.424(1)$, $\tilde{\beta} = 1.62(6)$ and $\tilde{\gamma} = 12.3(1)$) were drawn by Molecular-Dynamics simulations (MD) on model polymeric systems [5] and mixtures, being confirmed by comparison with prototypical glassformers like SiO_2 and *o*-terphenyl, and icosahedral glassformer [6]. For the systems in Fig. 1, Table 1 lists the DW at the glass transition temperature, i.e. the temperature where $\tau_\alpha = 10^2$ s or $\eta = 10^2$ Pa s, and the conversion factors τ_0 and η_0 between the actual time and viscosity units and the corresponding MD units, respectively. Note

that the factors are the *only* adjustable parameters of the overall scaling procedure.

3. Free-volume and DW

The ratio between the volume that is accessible to the monomer center-of-mass and the monomer volume is $v_0^{(MD)} \sim \left(2\langle u_g^2 \rangle^{1/2}\right)^3$ in MD units [5,6]. From Table 1 one finds:

$$v_0^{(MD)} \sim 0.017 \quad (2)$$

Flory and coworkers proposed that the glass transition takes place under iso-free volume conditions with the universal value $v_0 \sim 0.025$ [53]. This suggests that DW and the free volume are related, as previously remarked [5–13]. To better elucidate the matter, we test the ansatz:

$$\langle u^2 \rangle = C\tau_3 \quad (3)$$

C is a constant and τ_3 is the PALS lifetime, which is related to the average size of the cavity where the annihilation takes place [8,22]. Eq. (3) yields the equality $\langle u_g^2 \rangle / \langle u^2 \rangle = \tau_{3g} / \tau_3$, with $\tau_{3g} = \tau_3(T_g)$, i.e. the reduced DW is equal to the reduced PALS lifetime τ_3 . In Fig. 2 the viscosity data of the well-known molecular liquids *o*-terphenyl (OTP) and glycerol were plotted by replacing the reduced DW with the reduced τ_3 and comparing the results to the master curve expressed by Eq. (1). Neither new adjustable parameter nor changes in τ_0 with respect to the ones in Fig. 1 (see Table 1) are involved, apart from the small adjustment of the vertical shift of the experimental data $\log \eta'_0 = \log \eta_0 - 1$. Fig. 2 shows that the reduced τ_3 and DW are quite close over about ten decades in relaxation times, thus reinforcing the conclusion that DW and free-volume are correlated. PALS data on OTP and glycerol from ref. [22] lead us to the same conclusion. Deviations are observed in Fig. 2 for glycerol when cage restructuring, and then the free-volume fluctuations, occur on time scales shorter than the PALS observation time, i.e. $\tau_\alpha \lesssim \tau_3 \sim 1$ ns (see also ref. [22]). In this regime the cage dynamics still takes place (it is detectable for $\tau_\alpha \gtrsim 1$ –10 ps) and DW is still well-defined [5,6] but the observation time τ_3 is too long and almost temperature-independent [8].

Table 1

Details about the systems in Fig. 1 (arranged in order of increasing fragility) and the MD simulations used to derive Eq. (1). The experimental structural relaxation time τ_α is drawn by dielectric spectroscopy apart from B_2O_3 . τ_0 and η_0 are the conversion factors between the actual time and viscosity units and the corresponding MD units, respectively. Note that, apart from B_2O_3 and CKN, $\log \tau_0$ and $\log \eta_0$ cover the narrow ranges $-1 > \log \tau_0 > -2$ and $-11 > \log \eta_0 > -12$. DW is drawn by Incoherent Neutron Scattering (INS) or Mössbauer Spectroscopy (MS). The table lists the DW at the glass transition $\langle u_g^2 \rangle$ (in \AA^2) or, equivalently, the Lamb-Mössbauer factor $-\ln f_g$.

System	τ_α, η			DW		
	Quantity	$\log \tau_0, \log \eta_0$	Ref.	Technique	$\langle u_g^2 \rangle, -\ln f_g$	Ref.
MD	τ_α	0	[5,6]	MD	0.01667	[5,6]
SiO_2	η	-2	[23]	INS	0.081	[24]
GeO_2	η	-1	[25]	INS	0.191	[26]
B_2O_3	η	+2.2	[27]	INS	0.065	[28]
B_2O_3	τ_α^a	-8.4	[29]	INS	0.065	[28]
V4 alloy ^b	η	-1	[30]	MS	0.885	[31]
Glycerol	η	-1	[32]	INS	0.022	[33]
PI	τ_α	-12	[34]	INS	0.427	[35]
TNB	τ_α	-2	[36]	INS	0.315	[37]
Fe+DBP	τ_α	-11	[38]	MS	3.15	[38]
Fe+DBP	η	-2	[39]	MS	3.05	[38]
OTP	τ_α	-11	[37]	INS	0.215	[40]
OTP	η	-1	[40]	INS	0.232	[40]
Selenium	η	-1.66	[41]	INS	0.155	[41]
CKN	τ_α^a	-13.5	[42]	INS	0.132	[43,44]
1,4 PBD	τ_α	-11	[45]	INS	0.102	[46,47]
a-PP	τ_α	-11.5	[48]	INS	0.13	[49]
PMMA	τ_α	-11.5	[50]	INS	1.1	[51]
PVC	τ_α	-11	[52]	INS	0.51	[51]

^a Data aggregated from different techniques.

^b $\text{Zr}_{46.8}\text{Ti}_{8.2}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$.

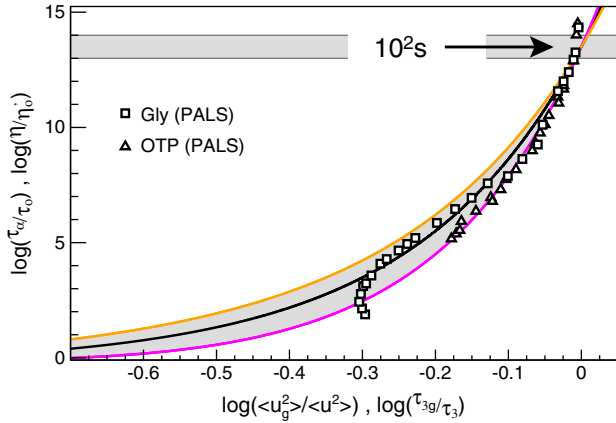


Fig. 2. Test of Eq. (3). The plots of the reduced glycerol (□) and OTP (Δ) viscosities vs. the reduced time τ_3 / τ_{3g} ($\tau_{3g} = \tau_3(T_g)$) are compared with the master curve Eq. (1) (black curve). The other curves have the same meaning of Fig. 1. $\log \eta_0 = \log \eta_0 - 1$. No new adjustable parameters with respect to Fig. 1 are involved. τ_0 and η_0 are given in Table 1. Deviations are observed for glycerol when the free-volume fluctuations become fast with respect to the PALS time-scale, i.e. $\tau_\alpha \leq \tau_3 - 1$ ns. PALS data from ref. [8].

It must be noted that PALS data are usually interpreted by a model assuming the spherical shape of the hole where the positron decays. The model relates τ_3 to the hole radius R [8]. We tested the relation $\langle u^2 \rangle \propto R^\delta$ and found good results with $\delta \sim 1$. However, being a model-dependent conclusion involving new adjustable parameters, we think that the analysis of the free-volume role in terms of Eq. (3) is more robust.

We now proceed and better clarify that the proper investigation of the cage dynamics is ensured if the observation time is shorter than the time scales of the relaxation processes. Fig. 3 shows the correlation between DW and the relaxation data of OTP and the viscosity data of glycerol. DW was taken as the mean square displacement within the time Δt , the latter depending on the energy resolution of the neutron scattering experiment. We first discuss glycerol. It is seen that the scaling between the long-time dynamics and $\langle u^2 \rangle_{\Delta t = 0.4 \text{ ns}}$ is rather good even for $\tau_\alpha / \Delta t \sim 1$, whereas using $\langle u^2 \rangle_{\Delta t = 5 \text{ ns}}$ leads to deviations from the universal master curve if $\tau_\alpha / \Delta t \leq 60$. This suggests that, if $\tau_\alpha \leq 300$ ns, $\langle u^2 \rangle_{\Delta t = 5 \text{ ns}}$ is contributed by components which are not related to the cage vibrational dynamics. One anticipates that these components have a relaxational character. For glycerol one observes that τ_3 from PALS tracks the universal master curve of the structural relaxation down to

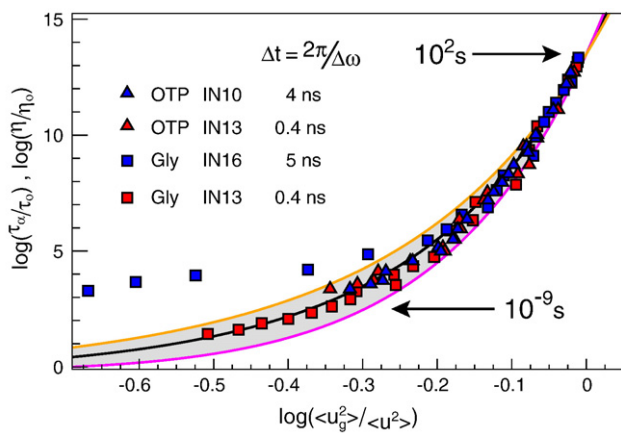


Fig. 3. Reduced glycerol (□) and OTP (Δ) viscosities vs. the reduced DW taken at two different timescales $\Delta t = h / \Delta E$ depending on the energy resolution of the neutron scattering experiment ΔE . All the curves have the same meaning of Fig. 1. τ_0 and η_0 are given in Table 1. Other details are in Table 2. The arrows point to states with the indicated τ_α values. Note that the scaling between the long-time dynamics and DW is apparent only if the latter is measured on Δt timescales shorter than τ_α .

Table 2

Details about the systems presented in Fig. 3. In addition to the fragility parameter m and T_g , information on their fast and slow DW, corresponding to different timescales $\Delta t = h / \Delta E$ due to the different energy resolutions of the neutron scattering experiments ΔE , is also given.

System	m	T_g	Fast DW			Slow DW		
			Set up	Δt (ns)	Ref.	Set up	Δt (ns)	Ref.
OTP	81	244	IN13	0.4	[40]	IN10	4	[54]
Gly	53	186	IN13	0.4	[33]	IN16	5	[55]

$\tau_\alpha \sim 3$ ns where $\tau_\alpha / \Delta t_{PALS} \sim \tau_\alpha / \tau_3 \sim 1$ (Fig. 2). The finding seems to indicate that in the range $3 \text{ ns} \lesssim \tau_\alpha \leq 300 \text{ ns}$ the free-volume of glycerol is less affected by the relaxation than MSD on the nanosecond time scale. The above discussion supports the conclusion that cage-rattling MSD must be measured on time scales Δt shorter than the time scales due to both the structural and the possible local relaxations. Shortening Δt results in a remarkable extension of the region where the scaling between the structural relaxation and the cage dynamics of glycerol is observed (Fig. 3). However, this effect is less apparent in OTP (Fig. 3).

4. Conclusions

It was shown that DW of glycerol and OTP is contributed by free-volume and that the elementary ansatz given by Eq. (3) provides an alternative way to get the reduced DW of that glass-forming liquids over about ten decades in relaxation times. Both PALS and neutron scattering experiments show that, in order to evidence the scaling of the slow relaxation with the fast caged dynamics, the observation times must be shorter than the time scales of the relaxation processes.

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