

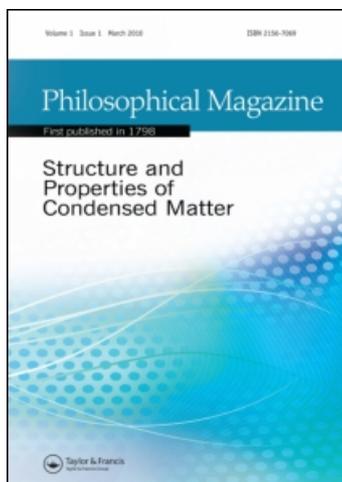
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Scaling between structural relaxation and caged dynamics in $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ and glycerol: free volume, time-scales and implications for pressure–energy correlations

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The scaling of slow structural relaxation with fast caged dynamics is seen in the molten salt $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ (CKN) over about 13 decades of the structural relaxation time. Glycerol scaling has been analysed in detail. In glycerol, the short-time mean-square displacement $\langle u^2 \rangle$, a measure of the caged dynamics, is contributed by the free volume. It is seen that, in order to see the scaling, the observation time of the fast dynamics must be shorter than the time-scales of the relaxation processes. Systems with both negligible (like CKN, glycerol and network glassformers) and high (like van der Waals liquids and polymers) pressure–energy correlations exhibit scaling between the slow relaxation and the fast caged dynamics. According to the available experiments, an isomorph-invariant expression of the master curve of the scaled data is indistinguishable from a simpler non-invariant expression. Instead, the latter agrees better with the simulations on a wide class of model polymers.

Keywords: glass transition; fast-dynamics; relaxation

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 neighbours, 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 $\langle u^2 \rangle^{1/2}$. This quantity is related to the Debye–Waller factor which, assuming harmonicity of thermal motion, takes the form $\exp(-q^2 \langle u^2 \rangle / 3)$ where q is the absolute value of the scattering vector. 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 complete independence of the two motions. Nonetheless, several authors have investigated their correlations, emphasising in particular the link with the bulk elastic properties (for a review see [4]). In this research field, universal scaling between the structural relaxation time, or the shear viscosity, and $\langle u^2 \rangle$ was reported for several numerical models, including linear

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polymers, mixtures, prototypical glassformers like SiO₂ and o-terphenyl (OTP), and icosahedral glassformers [5–7]. The resulting master curve fits with the available experimental data from supercooled liquids, polymers and metallic glasses over about 18 decades of relaxation times (or viscosity in non-polymeric systems) and a very wide range of fragilities.

The present paper shows that the scaling between the structural relaxation time and $\langle u^2 \rangle$ also holds for the molten salt Ca_{0.4}K_{0.6}(NO₃)_{1.4} (CKN) over about 13 decades of τ_α . Glycerol scaling was analysed in detail. The scaling of glycerol and, over a less wide range of relaxation times and viscosities, network glassformers like SiO₂, GeO₂ and B₂O₃, has also been reported [5–7]. Here, for the first time, the scaling of these systems and CKN will be discussed from the viewpoint of the pressure–energy correlations [8–10]. In addition, it is shown that the role of the free volume in glycerol is not negligible and that the scaling works only if the observation time of the fast dynamics is *shorter* than the time-scales of the relaxation processes [7].

The paper first summarises results about the scaling between the structural relaxation and $\langle u^2 \rangle$. Then, the results on glycerol and CKN are discussed in detail. Finally, the conclusions are presented.

2. Scaling between viscous flow, structural relaxation and $\langle u^2 \rangle$

Figure 1 shows the scaling between the structural relaxation time τ_α and the viscosity η with respect to the reduced mean-square displacement (MSD), $\langle u^2 \rangle / \langle u_g^2 \rangle$, with $\langle u_g^2 \rangle = \langle u^2(T_g) \rangle$. The experimental data include supercooled liquids, polymers, metallic glasses over about 18 decades of relaxation times and a very wide range

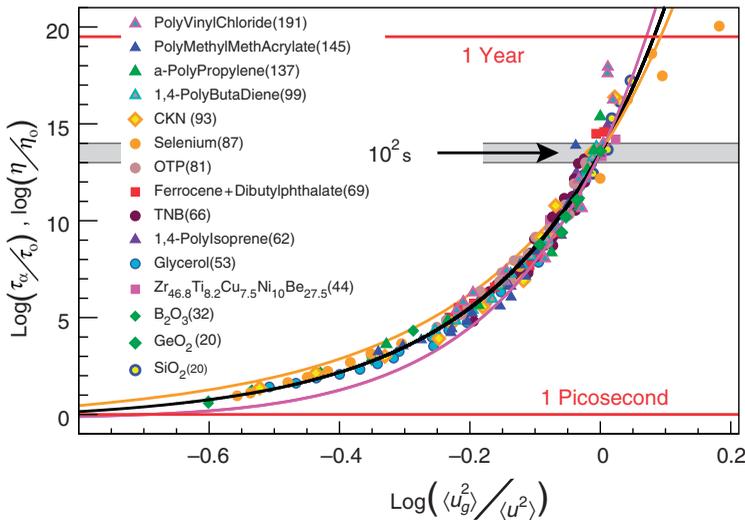


Figure 1. Reduced relaxation time and viscosity vs. reduced MSD factor ($\langle u_g^2 \rangle = \langle u^2(T_g) \rangle$). The numbers in parentheses denote the fragility m . The black curve is Equation (1). The coloured curves bound the accuracy of Equation (1) [5,6]. Refer to Table 1 for further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

of fragilities. The plot now includes the ionic liquid CKN as well. All the data in Figure 1 are at ambient pressure. The master curve of Figure 1 (black line) is expressed analytically by

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

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 (MD) simulations 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 Figure 1, Table 1 lists the MSD at the glass transition temperature, i.e. the temperature where $\tau_\alpha = 10^2$ s or $\eta = 10^{12}$ 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 conversion factors are the

Table 1. Details of the systems in Figure 1 (arranged in order of increasing fragility) and the MD simulations used to derive Equation (1). The experimental structural relaxation time τ_α is drawn by dielectric spectroscopy apart from B_2O_3 and CKN. 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 $-11 > \log \eta_0 > -12$. MSD is drawn by Incoherent Neutron Scattering (INS) or Mössbauer Spectroscopy (MS). The table lists the approximate observation time of the fast caged dynamics by experiment Δt , the MSD 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			MSD		
	Quantity	$\log \tau_0, \log \eta_0$	Ref.	Technique (Δt)	$\langle u_g^2 \rangle, -\ln f_g$	Ref.
MD	τ_α	0	[5,6]	MD	0.01667	[5,6]
SiO_2	η	-2	[11]	INS (40 ps)	0.081	[12]
GeO_2	η	-1	[13]	INS (0.4 ns)	0.191	[14]
B_2O_3	η	+2.2	[15]	INS (40 ps)	0.065	[16]
B_2O_3	τ_α^b	-8.4	[17]	INS (40 ps)	0.065	[16]
V4 ^a alloy	η	-1	[18]	MS (0.1 μs)	0.885	[19]
Glycerol	η	-1	[20]	INS (0.4 ns)	0.022	[21]
1,4 PI	τ_α	-12	[22]	INS (4 ns)	0.427	[23]
TNB	η	-2	[24]	INS (0.4 ns)	0.315	[25]
Fe + DBP	τ_α	-11	[26]	MS (0.1 μs)	3.15	[26]
Fe + DBP	η	-2	[27]	MS (0.1 μs)	3.05	[26]
OTP	τ_α	-11	[25]	INS (0.4 ns)	0.215	[28]
OTP	η	-1	[28]	INS (0.4 ns)	0.232	[28]
Selenium	η	-1.66	[29]	INS (20 ps)	0.155	[29]
CKN	τ_α^b	-13.5	[30]	INS (10 ps)	0.132	[31,32]
1,4 PBD	τ_α	-11	[33]	INS (4 ns)	0.102	[34,35]
a-PP	τ_α	-11.5	[36]	INS (0.2 ns)	0.13	[37]
PMMA	τ_α	-11.5	[38]	INS (5 ns)	1.1	[39]
PVC	τ_α	-11	[40]	INS (5 ns)	0.51	[39]

Notes: ^aZr_{46.8}Ti_{8.2}Cu_{7.5}Ni₁₀Be_{27.5}

^bData aggregated from different techniques.

only adjustable parameters of the overall scaling procedure. Table 1 also shows the (approximate) observation time of the fast dynamics by the experiments Δt . The structural relaxation times of the systems in Figure 1 are comparable with or longer than Δt . The Δt dependence of the scaling of glycerol is discussed in Section 5.

3. Scaling and the pressure–energy correlations

Figure 2 shows that, when the CKN structural relaxation time and the glycerol shear viscosity are plotted vs. the reduced MSD, they collapse over about 13 decades in a single master curve well described by Equation (1) within the error bars.

There is competition between van der Waals and Coulombic terms in the interacting potential of CKN and glycerol. This feature deserves consideration from the viewpoint of the pressure–energy correlations [8–10]. Such correlations are expected to be weak for CKN and glycerol, thus leading to the absence of isomorphic states in these two systems.¹ Weak correlations are also expected for network glassformers like SiO_2 , GeO_2 and B_2O_3 which exhibit scaling (see Figure 1, not included in Figure 2 for clarity) [5–7].

Strongly correlating systems, e.g. van der Waals liquids, have isomorphic states. Rigorously, any general theory of the liquid state must end up in relations expressed only in terms of isomorph-invariants (constant quantities when evaluated over a set of isomorphic states) to deal with strongly correlating systems (a criterion also known as the ‘isomorph filter’ [10]). From this point of view, the master curve given

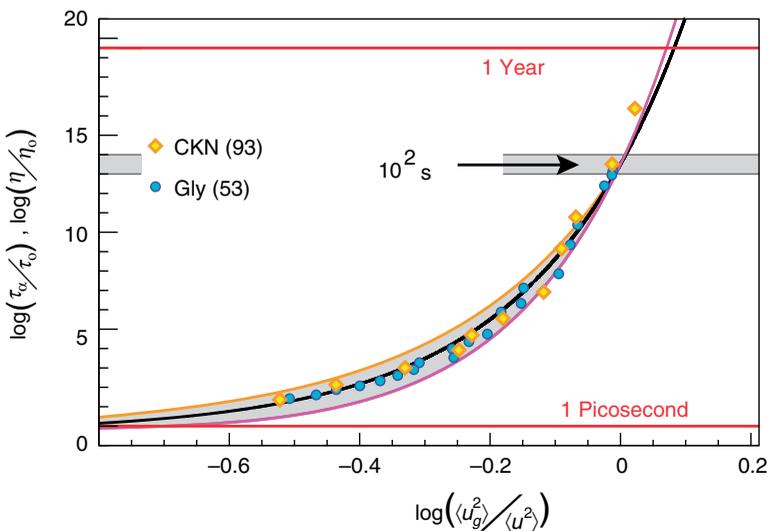


Figure 2. Reduced relaxation time (CKN) and viscosity (glycerol) vs. the reduced MSD. The other curves have the same meaning as in Figure 1. The numbers in parentheses denote the fragility m . Other parameters are listed in Table 1.

by Equation (1) with *constant* $\alpha, \tilde{\beta}, \tilde{\gamma}$ parameters does *not* pass the ‘isomorph filter’ and then should be unable to encompass strongly correlating systems since

$$\frac{\langle \tilde{u}_g^2 \rangle}{\langle \tilde{u}^2 \rangle} \neq \frac{\langle u_g^2 \rangle}{\langle u^2 \rangle}, \quad \log \tilde{X} \neq \log X, \quad (2)$$

where $\tilde{\zeta} \equiv \zeta/\zeta_0$ with ζ_0 equal to $\rho^{-1/3}$, $\rho^{-1/3}\sqrt{m/k_B T}$, $\rho^{2/3}\sqrt{mk_B T}$ for length, time and viscosity, respectively, and $\tilde{X} = \tilde{\tau}_\alpha/\tilde{\tau}_0$, $\tilde{\eta}/\tilde{\eta}_0$ (see previous footnote). A proper isomorph-invariant modification of Equation (1) is

$$\log \tilde{X} = C_1 + C_2 \frac{\langle \tilde{u}_g^2 \rangle}{\langle \tilde{u}^2 \rangle} + C_3 \left(\frac{\langle \tilde{u}_g^2 \rangle}{\langle \tilde{u}^2 \rangle} \right)^2, \quad (3)$$

where C_i , $i = 1, 2, 3$ are constants. The above equation is more complex in nature than Equation (1) since it needs the density as an additional input parameter.

The fact that Equation (3) is constrained by the basic properties of strongly correlating systems, which are not accounted for by Equation (1), poses the question of the flexibility of these master curves to deal with systems with either strong (like OTP, TNB or polymers) or weak (like CKN, glycerol and the network glassformers SiO₂, GeO₂ and B₂O₃) pressure–energy correlations. Can Equations (1) and (3) be discriminated? To date, little help has been provided by experiments. The experimental data plotted in Figure 1 are taken at ambient pressure by sweeping the temperature in a limited range, thus resulting in small density changes. Owing to the much larger changes of the structural relaxation time, the viscosity and MSD, the equalities $\log \tilde{X} \simeq \log X$, $\langle \tilde{u}_g^2 \rangle / \langle \tilde{u}^2 \rangle \simeq \langle u_g^2 \rangle / \langle u^2 \rangle$ hold to a good approximation and Equations (1) and (3) are hardly distinguishable. To our knowledge, joint data concerning τ_α (or viscosity for non-polymeric systems) and MSD from high-pressure experiments spanning larger density changes are not yet available. If no clear-cut conclusion on the experimental side may yet be drawn, numerical studies offer more insight. In particular, Equations (1) and (3) were investigated in the temperature/density phase space of a class of model polymers with different chain lengths and generalised Lennard-Jones potentials having constant position and depth of their minima [6]. Note that pressure–energy correlations change with the potential and the physical state [41]. The different systems were compared with no MSD or τ_α rescaling and Equation (1) was used as the master curve by taking $\langle u_g^2 \rangle$ as a constant independent of the model polymer. These positions: (i) rely on the finding that the raw MD curves τ_α vs. $\langle u^2 \rangle$ for different systems superimpose very well, and (ii) fit in with the need to limit the number of adjustable parameters. To keep on an equal footing the comparison between the two master curves, an analogous position was adopted for Equation (3), i.e. $\langle \tilde{u}_g^2 \rangle$ was set to a constant independent of the model polymer (a step that still preserves the isomorph-invariance of Equation (3)). On this basis, Equation (1) was found to be more consistent with the numerical data (see Figure 11 of [6]). To summarise, if the experiments do not discriminate between the two versions of the master curve, the isomorph-invariant version (3), which is more complex in nature than Equation (1) as noted above, agrees less well with the simulations of a wide class of polymeric systems.

4. Free-volume effects in glycerol

The closeness of $\langle u^2 \rangle$ with free-volume concepts was noted in experiments [42,45–47], theories [4,48,49] and simulations [5,6,50], with some debate [51,52]. The basic question is about the existence of some critical displacement above which structural changes take place and it was stated that the rearrangement only takes place when there is a local, temporary density decrease [4]. We refer also to previous experimental [53,54], theoretical and simulation [55–58] work.

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

$$v_0^{(MD)} \sim 0.017. \quad (4)$$

Flory and coworkers proposed that the glass transition takes place under iso-free-volume conditions with the universal value $v_0 \sim 0.025$ [59]. This supports the conclusion that $\langle u^2 \rangle$ and the free volume are related, as noted above.

To better elucidate the matter, we consider results from Positron Annihilation Lifetime Spectroscopy (PALS) [42,43,45]. PALS is a structural technique to parametrise the free volume. In fact, the orthopositronium bound state of a positron has a strong tendency to localise in holes of low electron density and decays with lifetime τ_3 , being related to the average cavity size. In particular, we test the ansatz

$$\langle u^2 \rangle = C \tau_3, \quad (5)$$

where C is a constant. This equation captures the essentials of the relation between τ_3 and $\langle u^2 \rangle$, both increasing with the free volume. Furthermore, it provides a simple procedure to compare PALS and $\langle u^2 \rangle$ data with no adjustable parameters. In fact, Equation (5) 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 MSD is equal to the reduced PALS lifetime τ_3 . In Figure 3, the viscosity data of glycerol are plotted by replacing the reduced MSD with the reduced τ_3 and comparing the results to the master curve expressed by Equation (1). The conversion factor between the actual and the MD viscosity units was adjusted to $\log \eta'_0 = \log \eta_0 - 1$. Other parameters are like in Table 1. Figure 3 shows that the scaling of the long-time dynamics by either the reduced τ_3 or the reduced MSD are quite close to each other over about 10 decades in relaxation times, thus leading to the conclusion that $\langle u^2 \rangle$ and the free volume are correlated. Deviations are observed for glycerol when cage restructuring, and then free-volume fluctuations, occur on time-scales shorter than the PALS observation time, i.e. $\tau_\alpha \lesssim \tau_3 \sim 2$ ns (see also [43]). In this regime, the cage dynamic still takes place (it is detectable for $\tau_\alpha \gtrsim 1 - 10$ ps) and $\langle u^2 \rangle$ is still well-defined [5,6] but the observation time τ_3 is too long and almost temperature-independent [42].

It should be noted that PALS data are usually interpreted by a model assuming a spherical shape of the hole where the positron decays. The model relates τ_3 to the hole radius R [42]. In addition to Equation (5), we also tested the relation $\langle u^2 \rangle \propto R^\delta$ (R drawn by the fit of τ_3 data) and found that the correlation plot between $\log \eta$ and R^δ agrees with the master curve expressed by Equation (1) with $\delta \sim 1$. However, being a model-dependent conclusion involving adjustable parameters, we

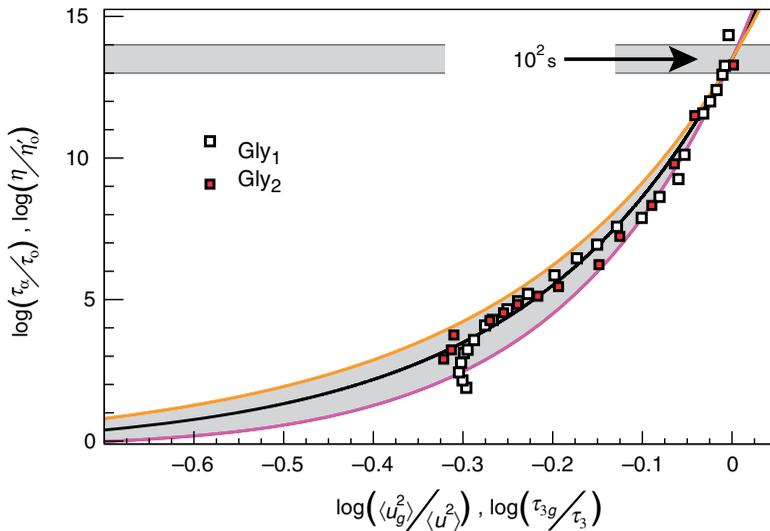


Figure 3. Test of Equation (5) for glycerol by using two different data sets for τ_3 , i.e. [42] (Gly1) and [43] (Gly2). The plots of the reduced glycerol viscosity vs. the reduced time τ_3/τ_{3g} ($\tau_{3g} = \tau_3(T_g)$) are compared with the master curve (1) (black curve). The other curves have the same meaning as in Figure 1. τ_0 and η_0 are given in Table 1. $\log \eta'_0 = \log \eta_0 - 1$. Deviations are observed when the free-volume fluctuations become fast with respect to the PALS time-scale, i.e. $\tau_\alpha \lesssim \tau_3 \sim 2$ ns.

think that the analysis of the free-volume role in terms of Equation (5) is more robust.

5. Time-scales of $\langle u^2 \rangle$ in glycerol

We now proceed and better clarify that the correct investigation of the cage rattling is ensured if the observation time of the fast dynamics is *shorter* than τ_α . Figure 4 shows the correlation between $\langle u^2 \rangle$ and the viscosity data of glycerol. $\langle u^2 \rangle$ was taken as the mean-square displacement within the time Δt , the latter depending on the energy resolution of the neutron scattering (NS) experiment. 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 $\tau_\alpha/\Delta t \lesssim 60$. This suggests that, if $\tau_\alpha \lesssim 300$ ns, $\langle u^2 \rangle_{\Delta t=5\text{ ns}}$ is influenced by components which are not related to the cage vibrational dynamics. One anticipates that these components have a relaxational character. Interestingly, τ_3 from PALS tracks the universal master curve of the structural relaxation down to $\tau_\alpha \sim 3$ ns where $\tau_\alpha/\Delta t_{\text{PALS}} \sim \tau_\alpha/\tau_3 \sim 1$ (Figure 3). This finding seems to indicate that, in the range $3\text{ ns} \lesssim \tau_\alpha \lesssim 300$ ns, the free volume 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

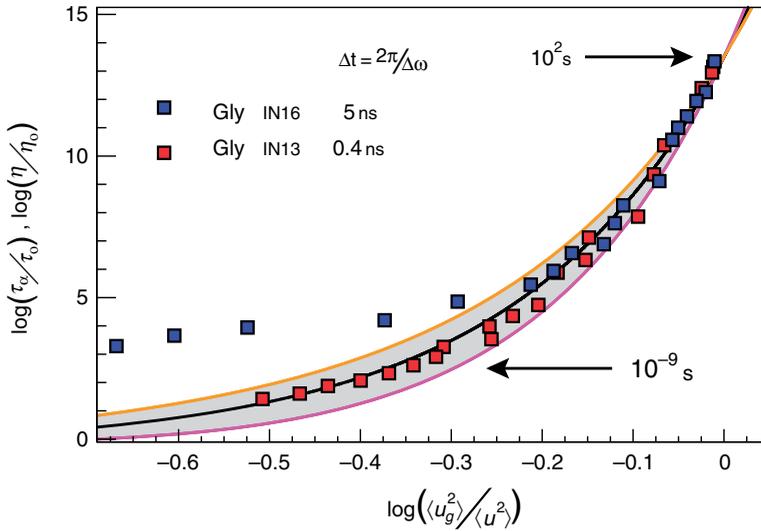


Figure 4. Reduced glycerol viscosity vs. the reduced MSD taken at two different time-scales $\Delta t = h/\Delta E$ depending on the energy resolution of the neutron scattering experiment ΔE (IN13 and IN16 data are from [21] and [44], respectively). All the curves have the same meaning as in Figure 1. τ_0 and η_0 are given in Table 1. The arrows point to states with the indicated τ_α values.

relaxation and the cage dynamics of glycerol is observed (Figure 4). However, this effect is less apparent in OTP [7].

6. Conclusions

It is shown that one molten salt (CKN) and one hydrogen-bonded liquid (glycerol) exhibit scaling between the mean-square displacement due to cage rattling, $\langle u^2 \rangle$, and the structural relaxation time or viscosity already observed in supercooled liquids, polymers and metallic glasses. Systems with both negligible (like CKN, glycerol, SiO_2 , GeO_2 and B_2O_3) and high pressure–energy correlations (like OTP, TNB or polymers) exhibit this scaling. According to the available experiments, an isomorph-invariant expression of the master curve of the scaled data is indistinguishable from a simpler non-invariant expression. Instead, the latter agrees better with the simulations of a wide class of model polymers. The cage rattling of glycerol is influenced by the free-volume over about 10 decades in relaxation times. Both PALS and neutron scattering experiments show that, in order to see scaling, the observation time of the fast dynamics must be shorter than the time-scales of the relaxation processes.

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Note

1. In a system with N particles and density ρ , two system states, say $(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ and $(r'_1, r'_2, \dots, r'_N)$, are isomorphic under the prescription that, if $\tilde{r}_i = \tilde{r}'_i$, $i = 1, \dots, N$ ($r_i \equiv \rho^{1/3} r_i$), then they have proportional configurational NVT Boltzmann factors [10].

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