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Abstract.   A phenomenological model linking the macroscopic volumetric behaviour found from dilatometry to the microscopic free-volume hole properties found from positron annihilation lifetime spectroscopy is applied to a set of dynamic properties of a fragile low-molecular-weight glass former: ortho-terphenyl. A number of correlations between the free-volume hole fractions derived from this model and the various dynamic properties such as viscosity, self-rotational diffusion, and tracer translational diffusion can be established over the temperature range from the glass–liquid transition temperature T_g up to $\sim 1.2 T_g$ via a Williams–Landel–Ferry (WLF)– Doolittle-type equation.

1. Introduction

The structure of condensed matter and the dynamics of its constituents as well as the understanding of their mutual relationships determine our level of knowledge of a variety of physical and physico-chemical properties.

As regards the first aspect, the classical diffraction methods provide the inter- and intra-particle distances, at best. On the other hand, it is intuitively accepted that any motion of constituents requires some free space. For these reasons, the free-volume concept is widely used in interpretations of a variety of physical phenomena such as viscoelasticity and diffusion [1–3]. Recently, thanks to the development of positron annihilation lifetime spectroscopy (PALS), it became possible to measure this free volume directly via the annihilation characteristics of ortho-positronium (o-Ps), i.e., the o-Ps lifetime τ_3 and the o-Ps relative intensity I_3 [4]. Continued progress in PALS allows even better quantitative characterization of the free-volume hole microstructure in disordered systems. At present, the general direction in the methodological effort has been shifted from the free-volume hole size determination, where a semiempirical quantum-mechanical model [4–6] is widely used, to various attempts at free-volume hole fraction quantification [7–10].

As regards the second aspect of the mutual relationships between the structure and the dynamics, a huge amount of dynamical data obtained using various microscopic and macro-scopic techniques have been accumulated [11]. For these reasons, the problem actually now

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consists in a search for potential links between the two data sets via some physically acceptable model, using the determination of the free-volume hole fractions from the PALS data directly.

The aim of this paper is to demonstrate such a bridge between the free-volume microstructure and the various dynamic processes such as the viscosity, self-reorientational diffusion, and tracer translational diffusion for a prototypical fragile low-molecular-weight glass former: ortho-terphenyl (OTP).

2. Methods of PALS data analysis

2.1. The semiempirical quantum-mechanical model for the mean free-volume hole size

The first aspect of the free-volume microstructure, i.e., the mean free-volume hole size, has been evaluated by using the well known Tao–Eldrup–Jean model [4–6]. As a result, the o-Ps lifetime τ_3 is related to the spherical hole size R_h as follows:

$$\tau_3 = (1/2)[1 - R_h/R_0 + \{1/(2\pi)\} \sin(2\pi R_h/R_0)]^{-1} \tag{1}$$

where $R_h = R_0 - \Delta R$; here, ΔR is the thickness of the surface electron layer around the free-volume hole, for which the value 1.656 Å is derived from fitting the observed o-Ps lifetimes in molecular solids with known hole sizes such as those for molecular crystals and zeolites [4].

2.2. The phenomenological model of volumetric and free-volume hole behaviour and the free-volume hole fraction determination

The second aspect of the free-volume characterization, i.e. the free-volume hole fraction, has been determined by using our recently proposed phenomenological model [8, 10]. To briefly recapitulate, the starting expression is a linear dependence of the macroscopic volume V on temperature T for a liquid state above the glass transition temperature T_g:

$$V(T) = V_i + \beta_l(T - T_i) \tag{2}$$

where β_l is the liquid-state expansivity, and V_i and T_i are the so-called initial volume and initial temperature, respectively, at which the free volume (manifested as the excess volume $V_f(T) = V(T) - V_i$) begins to appear. These free parameters of our model can be determined from PALS data, and, consequently, their physical meanings have to be established. Continuing with the usual definitions for the free-volume fraction $f(T) = V_f(T)/V(T)$ and for its thermal expansion coefficient $\alpha_f = [1/f(T_g)][\Delta f(T)/\Delta T]$, one can arrive at a quadratic equation in T_i:

$$T_i^2 + bT_i + c = 0 \tag{3}$$

where the expressions for the coefficients containing only experimentally accessible quantities read as follows:

$$b = -[1 + \alpha_l(T + T_g)]/\alpha_l \tag{4}$$

$$c = [(1 + \alpha_l T)T_g]/\alpha_l + [(1 + \alpha_l T)T_g]/[\alpha_f(T - T_g)\alpha_l] - [(1 + \alpha_l T_g)T]/[\alpha_f(T - T_g)\alpha_l] \tag{5}$$

where α_l is the thermal expansion coefficient of the macroscopic volume obtained from dilatometry, and α_f is the free-volume-fraction expansion coefficient. In the context of the PALS method, the free-volume fraction $f(T)$ may be identified with the free-volume hole fraction $f_h(T)$ through the o-Ps annihilation data [4]:

$$f(T) \equiv f_h(T) = K_{V_h} V_h(T) I_3(T) \tag{6}$$

where K_{V_h} is the calibration coefficient, which can be determined from equations (3) and (2) using the EOS data, and $I_3(T)$ is the relative intensity of o-Ps, which is a measure of the number of free-volume hole sites [4]. $V_h(T)$ is the mean hole volume calculated simply as $V = (4\pi/3)R_h^3$ by using equation (1).

3. The volumetric, o-Ps, and dynamic data basis of our analysis

The $V-T$ liquid-state data for OTP from the dilatometric study made by Naoki and Koeda [12] were used in order to obtain the thermal expansion coefficient of the macroscopic volume of the liquid phase, α_l. The o-Ps lifetime τ_3 and the relative intensity I_3 for OTP were taken from the PALS investigation by Malhotra and Pethrick [13]. The results of the free-volume hole fraction determination by means of the above-mentioned model [8, 10] have been used to obtain a series of dynamic properties of OTP such as the viscosity η [14], self-rotational reorientation τ_{rot} [15], and tracer translational diffusion D_{tr} [15].

4. Results and discussion

Figure 1 shows the temperature dependence of the mean free-volume hole size V_h in OTP as evaluated from the o-Ps lifetime (τ_3) data [13] via equation (1). Comparison of these mean free-volume hole sizes with the van der Waals volume of the OTP molecule indicates a very effectively packed structure, and, consequently, that any dynamic process is probably highly cooperative. Two further features are evident: (i) the first abrupt break at around 240 K
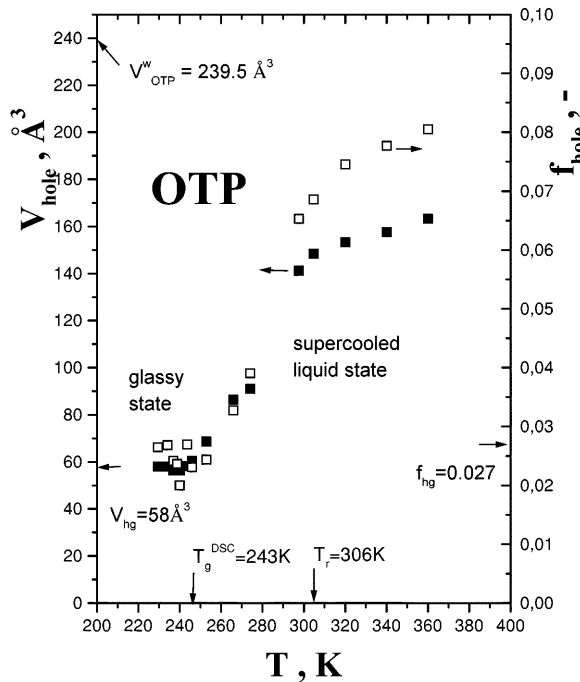

Figure 1. The temperature dependence of the mean free-volume hole size V_h in OTP derived from the PALS data and the quantum-mechanical model, and of the free-volume hole fractions f_h derived from the PALS data and the phenomenological model presented.

corresponding to the glass–liquid transition temperature $T_g = 243$ K; and (ii) the second one at around $T_r = 306$ K lying in the vicinity of the crossover temperature derived from various neutron and light scattering studies [16] as well as from other empirical findings [17]. A least-squares analysis gives the thermal expansion coefficient of the free-volume hole size above T_g up to around 300 K as $\alpha_{V_h} = 2.6 \times 10^{-2}$ K^{-1}. Comparison of this value with that for the thermal expansion coefficient of the macroscopic volume $\alpha_l = 7.3 \times 10^{-4}$ K^{-1} shows a difference of two orders of magnitude. On the other hand, the α_{V_h}-value is comparable with that for the thermal expansion of the mean square displacement $\langle u^2 \rangle$ of atomic scatterers from neutron scattering experiments [18], which is a geometric measure of the microscopic mobility: $\alpha_{\langle u \rangle}^2 = 2.1 \times 10^{-2}$ K^{-1}. The acceptable agreement seems to indicate a common origin of the two expansion phenomena.

Figure 1 also shows the temperature dependence of the free-volume hole fraction $f_h(T) \sim V_h(T) I_3(T)$ as calculated from the PALS data of reference [13] using equations (1) and (6). We can see the linearity of $f_h(T)$ between T_g and $\sim$300 K, which can be characterized by the thermal expansion coefficient of the free-volume hole fraction:

$$\alpha_{f_h} = [1/V_{h,g} I_{3,g}]\{[\Delta V_h(T) I_3(T)]/\Delta T\} = 2.8 \times 10^{-2} \text{ K}^{-1}.$$

Consequently, application of our phenomenological model (see equations (3)–(5)) provides the acceptably reasonable initial temperature $T_i = 209$ K.

This value is comparable with the Kauzmann temperatures $T_K = 206$ K and 204 K [19, 20] as well as with the onset temperature of the so-called fast motion in OTP derived from neutron scattering experiments, $T_f = 210 \pm 10$ K [18]. It is interesting to note that two different procedures based on quite different quantities lead to almost the same characteristic temperatures. The comparison between T_i and T_f, strictly speaking, indicates a relationship between the extrapolated equilibrium quantity and the glassy-state dynamic characteristic. Nevertheless, their accord might be considered an indication of the rest of the localized liquid-like dynamics, which persists only relatively slightly ($\sim$40 K) below T_g after cooling from the liquid state above T_g into the glassy one. In contrast, on going from the glassy state to the liquid phase, $T_i \simeq T_f$ coincidence can be considered as the first signature of the liquid-like dynamics in a transition zone of the glass–liquid transformation.

Knowing T_i, we can calculate the second free parameter of our model, V_i, using the liquid-state data, and, consequently, the packing coefficient $V_{\text{mol}}^w/V_i = 0.723$. This value is above that for the closest random packing 0.649, but close to that for the closest regular packing of hard spheres 0.7405 [21]. This fact, together with the above-mentioned $T_i \simeq T_K$ coincidence, may be considered as an argument in favour of the ideal-glass hypothesis; the ideal glass is a rather defective crystal state in accord with several model proposals [22, 23].

The free-volume fraction at T_g can be calculated to be 2.7% from the T_i-value (equations (3)–(5)) and the liquid-state data [12]. Consequently, the K_{V_h}-coefficient can be found to be 1.2×10^{-3} Å^{-3} from the mean o-Ps lifetime at T_g, τ_{3g}, and the corresponding free-volume hole size at T_g, $V_{h,g} = 58$ Å^3, and the relative o-Ps intensity at T_g, $I_{3g} = 0.40$ [13]. So figure 1 represents the absolute free-volume hole fraction f_h versus T as obtained from the PALS data directly via both the quantum-mechanical and phenomenological models—the latter with physically reasonable T_i- and V_i-values.

4.1. Correlations between the free-volume hole fractions and the various dynamic properties

Phenomenologically, the generalized mobility M, e.g., viscosity $M = \eta$, relaxation time $M = \tau$, and various diffusion coefficients $M = 1/D$, can be described at two heuristic levels: (1) in terms of the dependence on temperature, by the Vogel–Fulcher–Tammann–Hesse
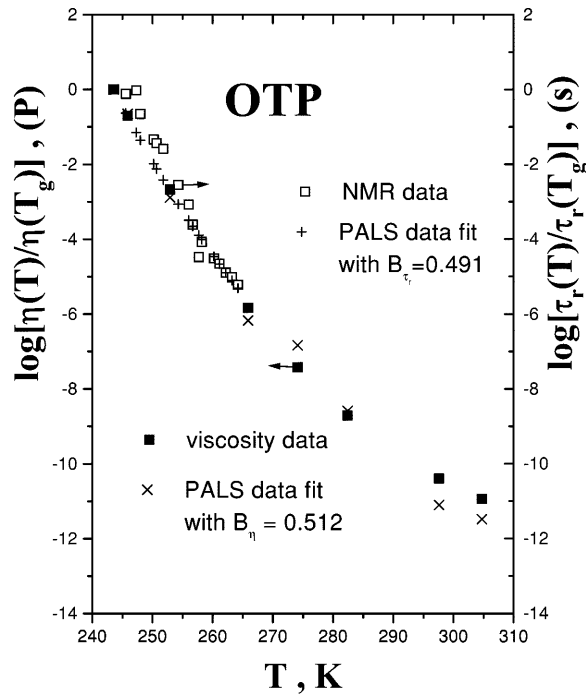
Figure 2. Correlations between the viscosity η and the reorientational correlation time τ_r of OTP and the free-volume hole fraction f_h obtained via the WLF–Doolittle expression.

(VFTH) equation or, equivalently, by the Williams–Landel–Ferry (WLF) equation for the shift factor $a(T)$ [24], or (2) in terms of the dependence on an operationally defined free-volume fraction $f(T)$, by means of the Doolittle equation [25]:

$$M(T) = A_{f,M} \exp[B_{f,M}/f(T)]. \tag{7}$$

By combining of the WLF equation with the Doolittle equation, we can arrive at the WLF–Doolittle form [2, 24]:

$$\log a(T) = \log[M(T)/M(T_g)] = B_{f,M}[1/f(T) - 1/f(T_g)]. \tag{8}$$

Originally, a free-volume interpretation of the WLF equation relied on two assumptions: (i) linearity of the free-volume fraction: $f(T) = f_g + \alpha_f(T - T_g)$; and (ii) $B_{f,M} = 1$ [24]. These allow one to estimate the free-volume fraction at T_g, $f_g \simeq 2.5\%$, and the expansion coefficient of the free volume $\alpha_f \simeq \alpha_l - \alpha_g \sim 10^{-4}\ \mathrm{K}^{-1}$. Our approach is quite different. We use the WLF–Doolittle equation functional form with the free-volume hole fractions $f_h(T)$ from figure 1 as the input quantities. In other words, we test the validity of the $B_{f,M} = $ constant condition in equation (8) on the basis of the mutual fitting of the PALS data and the dynamic quantity investigated. Figures 2 and 3 show the results of such fits of the published data for the viscosity of OTP [14], for the self-rotational diffusion of OTP as measured by means of ^{2}H NMR [15], as well as for the translational diffusion of the photochromic dyes TTI and ACR, which both have molecules of similar size to the TP molecule, from FRS measurements [15]. We can find satisfactory agreements over several decades of magnitude of the particular property change over the temperature range from T_g to $\sim 1.2T_g$ with the corresponding $B_{f,M}$-coefficients. Comparison of the $B_{f,M}$-coefficients provides information about the mutual relationships between the various dynamic phenomena considered. Thus, from $B_{f,\tau_{rot}} \simeq B_{f,\eta}$

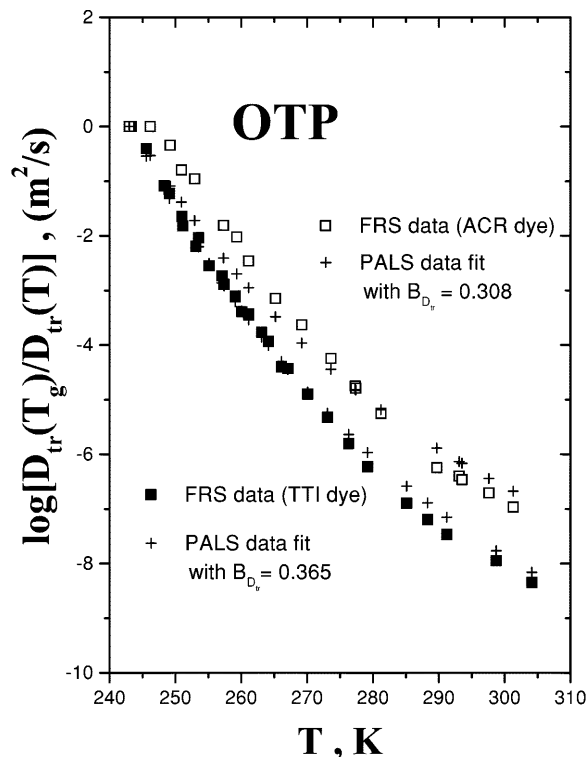**Figure 3.** Relationships between the translational diffusion coefficients D_{tr} of TTI and ACR dyes in OTP and the free-volume hole fraction f_h obtained using a WLF–Doolittle-type equation.

it follows that the two processes respond in a similar way to the free-volume hole fraction. Consequently, the viscosity process probably includes the reorientation of OTP molecules. This seems to be consistent with the effectively packed structure of the OTP matrix derived from figure 1. On the other hand, the finding that $B_{f,D_{tr}} < B_{f,\eta}$ indicates a different influence of the free-volume fraction on the tracer translation in comparison with the viscosity. This is consistent with the finding of the so-called decoupling effect of the translational diffusion and the viscosity or, equivalently, with the fractional Stokes–Einstein model, $D_{tr} \sim \eta^{-\xi}$, where $\xi < 1$ [15]. Since all three processes investigated can be represented by the Doolittle equation, as demonstrated in figures 2 and 3, it can easily be shown that $\xi_M = B_{f,M}/B_{f,\eta}$. For example, in the case of TTI dye in OTP, the $\xi_{D_{tr}}$-exponent can be calculated to be 0.71, in good agreement with that derived from the phenomenological scaling between D_{tr} and η, namely 0.75 ± 0.03 [15]. In the case of ACR dye, we obtain $\xi = 0.61$, but this value is loaded with possible non-equilibrium effects occurring during the measurement in the vicinity of T_g, as mentioned in the original paper [15], and by our normalization of the D_{tr}-value at T_g. In any case, our results suggest that translation and viscosity seem to be influenced differently by free-volume redistribution. Therefore, more insight into the microscopic basis of the difference between the $B_{f,D_{tr}}$- and $B_{f,\eta}$-coefficients requires the determination of the free-volume hole size distributions in the OTP matrix.

5. Conclusions

Application of the recently formulated phenomenological model linking the volumetric behaviour derived from dilatometry to the free-volume hole properties derived from the PALS method to the OTP data revealed its physically reasonable basis; it consisted in plausible identifications of the output quantities: the initial temperature T_i is comparable with the Kauzmann temperature T_K, and the initial volume V_i falls between the limits of the closest regular and the closest random packing arrangements. Consequently, the calibration of the o-Ps annihilation data can be carried out, allowing us to determine the free-volume hole fraction directly from them. A number of correlations between the free-volume hole fractions and the various mobilities in OTP have been established via a WLF–Doolittle-type expression. These correlations indicate that the quantified free volume detectable by the PALS method is of relevance for many motional processes in the supercooled liquids.

Acknowledgments

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