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A Phenomenological Model of Volumetric and Free Volume Hole Properties in Supercooled Liquids: The *ortho*-Terphenyl CaseJ. Bartoš^{†,*} and J. Krištiak[‡]*Polymer Institute of SAS, Dúbravská cesta 9, SK-842 36 Bratislava, Slovak Republic, and Institute of Physics of SAS, Dúbravská cesta 9, SK 842 28 Bratislava**Received: October 27, 1999; In Final Form: February 18, 2000*

A phenomenological model linking the macroscopic volume from dilatometry with the microscopic free volume from positron annihilation lifetime spectroscopy is presented. The temperature dependences of both quantities enable to obtain the so-called initial temperature T_i at which dynamic free volume change sets in, the corresponding initial volume V_i , and subsequently, all free volume characteristics. Application of this model on the literature data of a typical low-molecular weight glass former, *o*-terphenyl, leads to the findings that (i) $T_i \cong T_K$ the Kauzmann temperature and (ii) a packing fraction of the extrapolated equilibrium liquid at T_i is close to the closest regular packing of hard spheres. The published viscosity–temperature data over 12 decades of magnitude are correlated with the free volume hole fraction f_h , as determined from the PALS results, via the WLF–Doolittle type equation. These findings indicate that the orthopositronium (*o*-Ps) is able to detect the part of the total free volume distribution which is relevant for the viscosity over the measured temperature interval from T_g up to $\sim 1.5T_g$. In addition, the change of the free volume hole behavior above $T_r = 1.25T_g$, lying in the vicinity of the crossover temperature T_c from the idealized version of mode-coupling theory, is critically analyzed within a modified bubble concept (the equilibrium interaction of *o*-Ps with the soft matrix).

I. Introduction

The physical nature of the dynamics of supercooled liquids as well as of the liquid–glass transition is still a very actual challenge of the condensed matter physics.^{1a–f} A wide spectrum of disordered materials ranging from inorganic (including metals) compounds to organic, both low- and high-molecular weight ones, exhibits this phenomenon. Despite their huge chemical diversity, thermodynamic and dynamic phenomenologies of the supercooled liquids have remarkably universal features: (i) thermodynamic properties such as volume and enthalpy give a bend at the conventionally defined glass transition temperature T_g , and (ii) transport (mobility) properties M , such as viscosity ($M = \eta$), relaxation time ($M = \tau$), and diffusion coefficient ($M = 1/D$) exhibit the deviations from the “ideal” Arrhenius and Debye laws for temperature or time dependences, respectively.

A number of models and theories have been formulated to explain these findings which are based on a variety concepts such as free volume,^{1c} excess entropy,^{1a} or purely dynamic change due to mode coupling.^{1d} To follow our approach, we review briefly the relevant phenomenology and some of the related treatments, especially those based on the free volume idea.

Volumetric and Free Volume Hole Properties. Dilatometry belongs to the classical methods to investigate a variety aspects

of the liquid–glass transition.² The most important phenomenon of any amorphous phase is characterized by an abrupt change in the slope on the V – T diagram, i.e., by a jump change in the macroscopic volume expansivity $\beta_V = \Delta V/\Delta T$ or in the macroscopic volume expansion coefficient $\alpha_V = (1/V_g)(\Delta V/\Delta T)$, see Figure 1.

On the other hand, positron annihilation lifetime spectroscopy (PALS) becomes a very powerful tool for extensive study of the free volume microstructure in disordered materials during the past decade.^{3,4} The orthopositronium (*o*-Ps) is a very sensitive microscopic probe to detect the defective regions such as holes, vacancies, cavities.⁵

A semiempirical quantum-mechanical model has been formulated which relates the orthopositronium lifetime τ_3 to the effective free volume hole radius R_h as follows:

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

where $R_0 = R_h + \Delta R$, $\Delta R = 1.66 \text{ \AA}$, is a fitting parameter from the observed *o*-Ps lifetimes for several groups of materials with the known hole radii such as zeolites and molecular crystals.

In the glass-liquid transition region, the free volume holes R_h (or V_h) behave in a similar way as the macroscopic volume exhibiting the rapid slope change at around T_g . An essential difference in the corresponding temperature expansion coefficients exists. While the macroscopic volume expansion coefficients α_V are of the order of magnitude of 10^{-4} K^{-1} for both

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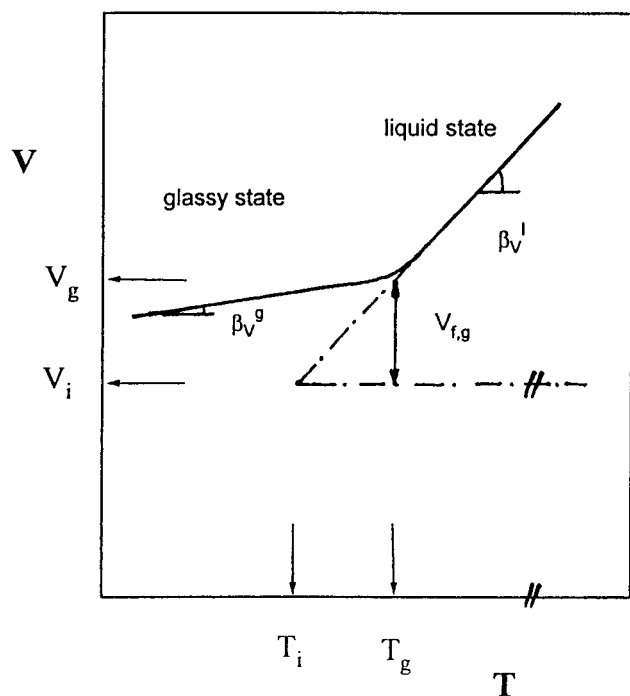


Figure 1. Schematic plot of the volumetric and free volume properties in the glass-liquid transition region of amorphous material.

glassy and viscous liquid state,² the free volume hole expansion coefficients $\alpha_{vh} = (1/V_{h,g})(\Delta V_h/\Delta T)$ are 1 or even 2 orders of magnitude higher below or above T_g , respectively.^{3,7-9} The second o-Ps annihilation quantity from PALS method, the relative o-Ps intensity I_3 , is believed to be related to the number of free volume holes and consequently, a semiempirical relationship between the free volume hole fraction $f_h(T)$ and both the annihilation characteristics has been presented:

$$f_h(T) = K_{vh} V_h(T) I_3(T) \quad (2)$$

^{10,11} where V_h is the mean free volume hole size obtained from eq 1 as $V_h = (4\pi/3)R_h^3$ and K_{vh} is a proportionality coefficient. This coefficient can be determined by various calibration procedures using other physical quantities such as the difference of the volume expansion coefficients below and above T_g ^{11,12} or by the present phenomenological approach.

Dynamic Properties. Phenomenologically, the dynamic behavior of supercooled liquids can be described in two different ways depending on the chosen independent variable. The first group of approaches is represented by various empirical formulas, such as the Vogel-Fulcher-Tammann-Hesse (VFTH) equation¹³ or, equivalently, by the Williams-Landel-Ferry (WLF) one,¹⁴ for both relatively low and high-temperature ranges with respect to T_g .¹⁵

$$\text{VFTH: } M(T) = A_T \exp[B_T/(T - T_0)] \quad (3)$$

or

$$\text{WLF: } a(T) = M(T)/M(T_g) = \exp[-C_{1g}(T - T_g)/(C_{2g} + T - T_g)] \quad (4)$$

The other description of the liquid mobilities is based on the free volume concept¹⁶ and is represented by the semiempirical Doolittle equation:¹⁷

$$M(T) = A_f \exp[B_f/f(T)] \quad (5)$$

where $f(T)$ is the free volume fraction defined as $f(T) = V_f(T)/V(T)$, V_f being appropriately defined free volume, and $V(T)$ is the macroscopic volume from dilatometric measurements. Formally, eqs 3 and 5 are equivalent, assuming:

$$f(T) = \beta_f^1(T - T_0) \quad (6)$$

where β_f^1 is the slope of f vs T dependence in the liquid state and T_0 is the Vogel temperature at which the corresponding mobility disappears due to $f \rightarrow 0$. In the above-mentioned eqs 3-5, all the quantities besides the liquid mobilities are parameters physical meaning of which needs to be established via various theoretical treatments or/and independent experiments.

One group of theoretical treatments¹⁶⁻²⁰ tries to connect the dynamics with thermodynamics based on the free volume¹⁶⁻¹⁹ or excess entropy²⁰ concept. The original free volume interpretation of the transport properties¹⁸ is based on a combination of the statistical-mechanical model of transport properties resulting into an exponential form for the mobility under assumption of linear temperature dependence of free volume. An extended version of the free volume model¹⁹ using percolation ideas leads to more complicated multiparameter form for $f(T)$ dependence.

Application of the Doolittle eq 5 becomes very useful in interpretation of the WLF eq 4, especially in polymer physics.^{1c,14} Under the assumption that

$$f(T) = f(T_g) + \beta_f^1(T - T_g) \quad (7)$$

one can arrive to the following free volume expressions for the C_{1g} and C_{2g} parameters:

$$C_{1g} = B_f/f_g \quad C_{2g} = f_g/\beta_f^1 \quad (8a,b)$$

And further, under the assumption that $B_f = 1$, one can estimate the free volume fraction at T_g , $f(T_g) \equiv f_g$, and the expansivity of the free volume fraction β_f^1 ; the former being about 2-3%, the latter $\beta_f^1 \cong \Delta\alpha_v = \alpha_v^l - \alpha_v^g \sim 10^{-4} \text{ K}^{-1}$, where α_v^l , α_v^g are the macroscopic volume expansion coefficients above and below T_g ¹⁴. Strictly speaking, the estimation of these free volume characteristics relies on both the mentioned assumptions and they are the results of the corresponding fits. Thus, their verification or determination of the f values by means of independent procedure is needed.

As for the Adam-Gibbs entropy model of dynamic behavior of supercooled liquids,^{20a} the excess configurational entropy of a liquid over that of the corresponding crystal from calorimetric studies is assumed to vanish at a temperature T_2 identified by Gibbs and DiMarzio as a second-order transition temperature.^{20b} So T_2 is closely related to the Kauzmann temperature T_K , at which an extrapolated liquid entropy reaches that of the crystal phase.²¹⁻²³ It is noteworthy that in many cases the Vogel divergence temperature T_0 lies in the vicinity of the Kauzmann temperature as reported by several authors.^{19b,22,23} The existence of the so-called ideal glass associated with an underlying phase transition below the measured glass transition temperature T_g is discussed topic until now.²⁴

From the above-mentioned review, direct verification of some basic assumptions of the free volume theory and of the related empirical equations is very actual. This paper presents a phenomenological model linking the macroscopic volumetric behavior of supercooled liquid to the microscopic free volume hole properties in order to quantify the free volume hole fraction, section II. This model is applied on a typical low-molecular

weight glass former of a van der Waals type: *o*-terphenyl (OTP), section III. OTP has been selected because it belongs to the widest studied and probably to the best understood fragile materials from the dynamic point of view. The wealth of the thermodynamic, o-Ps annihilation, and various dynamic data enables us not only to apply our approach but also to discuss its outputs from both microscopic, as well as macroscopic, dynamic viewpoints. Direct empirical relationship between the free volume hole data and typical transport quantity has been established. Finally, we discuss the model outputs from the points of view of the free volume and entropy models of dynamics in supercooled liquids, section IV.

II. Phenomenological Model

The macroscopic specific volume, $V(T)$, at a temperature T from the temperature range of the liquid state, $T > T_g$, can be represented in the simplest approximation in a linear form as follows:

$$V(T) = V_i[1 + \alpha_v^1(T - T_i)] \quad (9)$$

where α_v^1 is the macroscopic volume expansion coefficient and V_i and T_i are the free parameters of our model which have to be determined and their physical meanings established. Thus, the free volume $V_f(T)$ is the excess volume over some reference state V_i is given by

$$V_f(T) = V(T) - V_i = \alpha_v^1 V_i(T - T_i) \quad (10)$$

where T_i is the so-called initial temperature at which the free volume begins to appear, Figure 1. The free volume fraction $f(T)$ at the temperature T is defined as

$$f(T) = V_f(T)/V(T) \quad (11)$$

and after substitution of eq 10 we have

$$f(T) = \alpha_v^1(T - T_i)/[1 + \alpha_v^1(T - T_i)] \quad (12)$$

The expansion coefficient of the free volume fraction is defined as

$$\alpha_f = [1/f(T_1)]\{[f(T_2) - f(T_1)]/(T_2 - T_1)\} \quad (13)$$

After substitution of eq 12 and simple algebraic manipulations for $T_1 = T_g$ and $T_2 = T$, we obtain an expression,

$$\alpha_f^1 = [1/(T - T_g)]\{[(T - T_i)/(T_g - T_i)]\{[1 + \alpha_v^1(T_g - T_i)]/[1 + \alpha_v^1(T - T_i)] - 1\}\} \quad (14)$$

After several simple algebraic operations, we arrive to the final quadratic equation with respect to T_i :

$$T_i^2 + bT_i + c = 0 \quad (15)$$

where the coefficients read as

$$b = -[1 + \alpha_v^1(T_g + T)]/\alpha_v \quad (16a)$$

$$c = [(1 + \alpha_v^1 T_g)/\alpha_v^1 + [(1 + \alpha_v^1 T_g)T_g]/[\alpha_f^1(T - T_g)\alpha_v^1] - [(1 + \alpha_v^1 T_g)T]/[\alpha_f^1(T - T_g)\alpha_v^1] \quad (16b)$$

In the context of the PALS measurements, the free volume fraction $f(T)$ may be identified with the free volume hole fraction $f_h(T)$, given by eq 2 in section I. Then, the expansion coefficient

of the free volume hole fraction α_{fh}^1 can easily be obtained from the measured τ_3 and I_3 data using eqs 1 and 2:

$$\alpha_{fh}^1 = [1/(V_h I_3)] [\Delta(V_h I_3)/\Delta T] \quad (17)$$

Consequently, the quadratic eq 15 can be solved with respect to T_i .

III. Application on OTP

Dilatometric investigations on OTP were performed by several research groups.^{25–27}

The most extended and detailed data are given by Naoki and Koeda.²⁷ Their p – V – T results on OTP covering very wide temperature range from 220 up to 415 K, including both glassy and liquid phases, as well as the crystalline, are expressed in a polynomial form in T and p :

$$V(T, p) = \sum_{i=0} \sum_{j=0} c(i, j) T^i p^j \quad (18)$$

where $c(i, j)$ are the empirical parameters depending on the phase state considered.²⁷

The linearity of V on T required by eq 9 is satisfactorily fulfilled in a temperature region of our interest from 250 up to 290 K. Thus, one can obtain the mean expansion coefficient $\alpha_v^1 = 7.31 \times 10^{-4} \text{ K}^{-1}$.

The detailed PALS study on OTP in both glassy and liquid states from 220 up to 365 K was performed by Malhotra and Pethrick.^{28,29} The temperature dependences of both the relevant o-Ps annihilation quantities τ_3 and I_3 are presented in Figure 1 of ref 28. τ_3 – T plot for amorphous OTP exhibits three regions of different behavior:

(i) glassy region from 220 K up to about 240 K in accord with the glass transition temperature $T_g = 243 \text{ K}$,²⁵ (ii) low-temperature liquid region from 245 up to around $T_r \approx 304 \text{ K}$, and finally (iii) high-temperature liquid region above T_r continuing beyond the melting temperature of the crystalline form of OTP, $T_m = 331 \text{ K}$.²⁵ Therefore, we shall analyze these qualitatively different regions of liquid state separately.

Low-Temperature Viscous Liquid Region. In the context of our model just formulated in section II, we analyze the low-temperature region of viscous liquid (ii). The following higher temperature region of fluid liquid state iii will be discussed afterward.

The mean o-Ps lifetime τ_3 , the mean free volume hole radius R_h , calculated using eq 1 (Figure 2) and, consequently, the mean hole volumes $V_h = (4\pi/3)R_h^3$ can be represented by the following empirical equations:

$$\tau_3[\text{ns}] = 1.59 \times 10^{-2} T - 2.34 \quad r = 0.994 \quad (19a)$$

$$R_h[\text{\AA}] = 1.48 \times 10^{-2} T - 1.21 \quad r = 0.996 \quad (19b)$$

$$V_h[\text{\AA}^3] = 1.48 T - 307.38 \quad r = 0.989 \quad (19c)$$

where r is the regression coefficient. The corresponding free volume hole expansion coefficient α_{vh}^1 can be obtained from the slope of eq 19c and the value of free volume hole size at T_g , $V_{hg} = V_h(T_g) = 56 \text{ \AA}^3$, i.e., $2.56 \times 10^{-2} \text{ K}^{-1}$. This value is almost 2 orders of magnitude larger than that of the macroscopic volume $\alpha_v^1 = 7.31 \times 10^{-4} \text{ K}^{-1}$ in accord with the previous experiences.^{3,7–9} The second annihilation characteristic, the o-Ps relative intensity I_3 , is a measure of o-Ps formation probability and, thus, of the number of free volume holes detectable by this microscopic probe.^{3–7,10–12} Figure 1 of ref 28 shows that

the change of I_3 with the temperature is rather weak over a wide temperature range from below T_g through the viscous liquid

polybutadiene⁹ and the other limit is valid for asymmetric molecules. Since OTP molecules have a rather asymmetric shape we have applied the modified form of eq 21 with $\gamma(r)$ from eq 23 and $2\delta = R_{\text{cage}}(T)$. The last quantity was taken to be equal to the equivalent radius $R_{\text{eq}}^{\text{mol}}(T)$ calculated from the molar volume using $V-T$ data from ref 27. The results of calculations can be expressed by a linear equation, Comparison with eq 22

shows rather small change of the coefficients and suggests a relative insensitivity to the correction on the curvature of surface. We note that the proportion of the volume work, i.e., the second term in eq 21 is enhanced from 71.5% at 250 K up to 77.5% at 360 K. The calculated temperature dependence of the bubble radius from eq 24 is plotted in Figure 2.

IV. Discussion

Glass-Liquid Transition and Viscous Liquid Region. The T_i values obtained from eq 15 can be discussed as follows. Evidently, $T_{i,2} = 1693$ K has no physical meaning because it is far above the usual decomposition temperature of ordinary organic compounds. On the other hand, $T_{i,1} = 209$ K lies below T_g . To determine its physical nature, we compare this initial temperature of free volume change with several characteristic temperatures of OTP which are situated below the thermodynamic glass transition temperature T_g . These quantities have been determined by a large number of the authors using various thermodynamic and dynamic methods, and they are summarized in Table 1.

The $T_{i,1}$ value is comparable with the Kauzmann temperature $T_K = 200 \pm 10$ K^{22,37-39} at which the extrapolated liquid entropy reaches that of the corresponding crystalline form.²¹⁻²³ This fact suggests that infinitely slow cooling of the liquid could lead to some limiting state characterized by V_i . Knowing the macro-

TABLE 2: Volumetric, Empty, and Hole-Free Volume Characteristic of OTP at the Two Important Temperatures T_g and T_r

quantity/unit	$T_g = 243$ K	$T_r = 304$ K
V , cm ³ /g	0.8922	0.9320
$V_{f,e}$, cm ³ /g	0.2654	0.3052
f_e	0.298	0.328
τ_3 , ns	1.52	2.51
V_h , Å ³	56	149
V_h/V^w 100, % ^a	23.4	62.2
$V_{f,h}$, cm ³ /g	0.0236	0.0672
I_3	0.40	0.41
f_h	0.027	0.073
$c_h V$, holes/cm ³ ^b	4.82 10 ²⁰	4.90 10 ²⁰
l_h , Å ^c	12.8	12.7

^a Ratio of the mean hole volume V_h to the van der Waals volume V^w of OTP molecule; the latter being $V^w = 239.4$ Å³ using an additive group scheme from ref 41. ^b The mean volume concentration of free volume holes. ^c The mean distance between the mean free volume holes under assumption of their homogeneous distribution in the matrix.

the preference of $T_{i,1} \cong T_K$ identification over $T_{i,1} = T_0$ one. These findings may be considered as a support for the validity of one of the basic assumption of the original free volume model,^{14,16,18} i.e., a linearity between f and T , eqs 6 or 7, respectively, but with $T_i \cong T_K$ instead of T_0 . In other words, eq 10 implies that the free volume as measured by o-Ps probe and as treated by the present model seems to be simply an expansion volume of the supercooled liquid with respect to the initial volume V_i at T_i , where this excess dynamical free volume begins to appear due to some released degree of freedom, Figure 1.

Correlation between the Free Volume Hole Fraction and Viscosity. Calculating $V_g(T_g)$ from the $V-T$ data²⁷ and having both T_i and V_i from our model, we can calculate the free volume hole fraction $f_h(T)$ at the glass transition temperature T_g from eqs 10 and 11, then $f_h(T_g) = f_{h,g}$ is 2.7%. This value can be related to the so-called empty free volume $V_{f,e}$ at temperature T defined as⁴¹

$$V_{f,e}(T) = V(T) - V^w \quad (25)$$

which represents the maximal geometric free volume of the matrix. From Table 2 it follows that the dynamic free volume hole fraction at T_g represents about 9% of the total empty space. The knowledge of $f_{h,g}$ opens up the possibility to determine the calibration coefficient $K_{V,h}$ in eq 2; $K_{V,h} = 1.2 \times 10^{-3}$ Å⁻³ and, consequently, to calculate the free volume hole fractions $f_h(T)$ at any temperature T from the PALS data *directly*.

Thus, we can test a possible relation between some representative dynamic quantity, e.g., viscosity and the measurable free volume hole fraction f_h from PALS method via the WLF–Doolittle-type equation by combining eqs 4 and 5. To make such a test we have to eliminate one of the three parameters by considering the ratio

$$\ln [\eta(T)/\eta(T_g)] = B_\eta [1/f_h(T) - 1/f_h(T_g)] \quad (26)$$

as usually made in the WLF approach.^{1c,14} If the viscosity η is governed by the free volume hole fraction from PALS, then the particular B_η coefficient is expected to be constant in the temperature range of the validity of eq 26. The result of such a test on the viscosity data of OTP from ref 46, which are considered to be the most precise ones, is shown in Figure 4. These data, as obtained by several authors over a wide T range, have been accounted for by two VFTH eqs; one for the low T region and the other for higher temperatures with intersection point at 283.3 K. We can found a quite satisfactory fit over

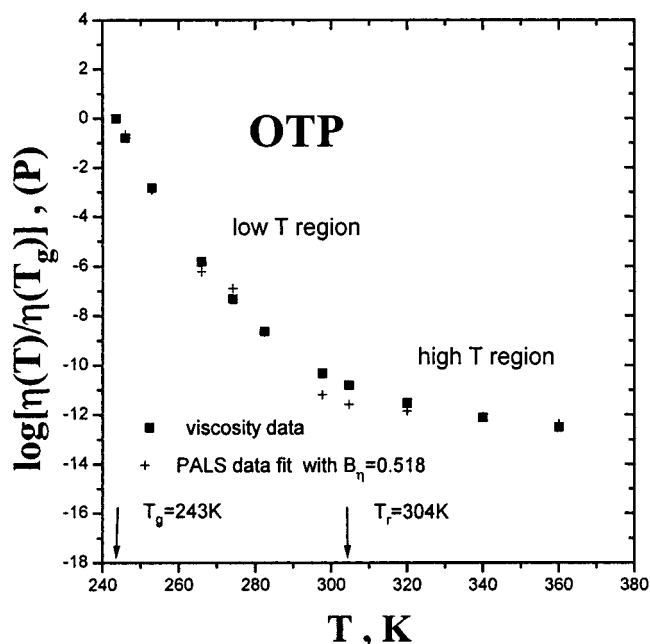


Figure 4. Correlation between the viscosity data of OTP from ref 46 and the free volume hole fraction f_h as determined from the PALS data (ref 28) by means of the presented model in terms of the WLF–Doolittle type equation.

12.5 decades of the change of viscosity between $T_g = 243$ and 360 K with $B_\eta = 0.518$. Note that although the T_i and V_i data and consequently, $K_{V,h}$ coefficient have been determined from the low T region PALS data only, the free volume hole fractions for the high T range have been calculated with the same coefficient. This correlation indicates that the free volume hole fraction $f_h(T)$ as measured by means of PALS method of the relevance to the viscosity over the whole temperature interval measured by both the methods so far.

Crossover Liquid–Liquid Transition and Fluid Liquid Region. The specific volume vs temperature plot for amorphous OTP in ref 27 shows the monotonic course from T_g up to T_m and beyond. On the other hand, the τ_3-T plot in ref 28 exhibits the relatively strong increase in the range between T_g and $T_r = 304$ K followed by relatively mild growth above T_r . This “decoupling” effect of the total volume and of the free volume holes above the characteristic temperature T_r seems to be indication of the change of o-Ps–matrix interaction mechanism as believed already in the original paper.²⁷ The results of our more realistic calculations using the modified bubble model in section IIIB plotted in Figure 2 can be discussed as follows.

In the low-temperature region from T_g up to T_r , the predicted bubble sizes exceed the mean free volume hole sizes from the PALS data as evaluated by eq 1. Simultaneously, the expansivity of bubble and that of free volume holes given by the corresponding slopes in eqs 24 and 19b differ essentially; the former being 1 order of magnitude lower than the latter. It indicates that at temperatures below T_r , the o-Ps probes indeed feel the original preexisting holes and that the matrix has relatively rigid character. As for the higher temperature region, the predicted bubble sizes exceed the mean free volume hole over 26%, although the corresponding expansivities are similar. Evidently, the first finding means that the modified bubble concept does not work for the fluid liquid state of OTP. Moreover, the above-mentioned correlation between the free volume hole fraction and viscosity (Sect.IVB) holds for both the low and high T regions. Thus, we conclude that the bubbles can be excluded in the high-temperature region of OTP.

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