

## Direct computation of the free volume fraction in amorphous polymers from positron lifetime measurements

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A model for computation of the free volume fraction from the temperature dependence of positron lifetime is presented. The model is based on the idea that the total free volume of the sample is expanding in the same rate as the volume of holes seen by positrons. Then, having the values of thermal expansion coefficients of bulk and free volume, it is possible to compute the temperature dependence of fraction of free volume  $f(T)$  and the thermal expansion coefficient of occupied volume  $\alpha_0$ . It is also possible to compute the Vogel temperature  $T_0$ , WLF coefficient  $c_{2g}$ , and the ratio  $c_{1g}/B$ , where  $c_{1g}$  is the WLF coefficient and  $B$  is the Doolittle constant. The paper also presents computed values of abovementioned parameters for six different polymers. In the case of poly(isobutylene) and cis-trans 1,4 poly(butadiene) the results are compared with that obtained from viscosity  $\eta(T)$  and temperature shift parameter  $a_T(T)$  measurements.

### I. INTRODUCTION

A free volume concept was developed to explain the non-Arrhenius dependence of the fluidity or viscosity of liquids on temperature<sup>1-3</sup> and also plays an important role in polymer physics. It successfully describes the mobility of polymer fluids, viscosity, etc. At the beginning the quantitative interpretation of the free and occupied volumes was not so obvious. Later Cohen and Turnbull<sup>4,5</sup> further developed this theory using the concept of cooperativity of motion. According to this theory the molecular transport occurs when a molecule moves into voids having a greater size than some critical volume. Voids are created by the redistribution of free volume arising from the cooperative motion of neighboring atoms.

Because of the success of the empirical free-volume relations in describing the behavior of glass-forming liquids, there have been many attempts to quantify the relevant free volume. Now it seems that the positron annihilation lifetime spectroscopy (PALS) is able to give us direct information about the free volume which is present in every polymer material.

PALS is based on the fact that the lifetime of positron and its bound form, positronium (Ps), is sensitive to the existence of structural inhomogeneities. In condensed media, in addition to  $e^+$  annihilation, a formation and annihilation of two forms of ( $e^+e^-$ ) bound system occurs in dependence on the mutual spin orientation of positron and electron. The singlet state of para-positronium ( $p$ -Ps) with antiparallel spin orientation has a lifetime  $\tau_{p-Ps} = 0.125$  ns in vacuo. Triplet state of ortho-positronium ( $o$ -Ps) lives in vacuo for  $\tau_{o-Ps} = 142$  ns. In liquid and solid substances  $\tau_{o-Ps}$  is shortened due to an interaction with electrons of surrounding medium to a few ns (pick-off annihilation). It is accepted fact that  $o$ -Ps is formed by  $e^+$  after very rapid thermalization and following capture in the regions with reduced electron density such as holes, vacancies, cavities.

The most important component is  $\tau_{o-Ps}$  which gives us information about the free volume holes in which annihilation

of positrons takes place. Using simple quantum mechanical model of particle in the spherical well<sup>6</sup> one can compute the radius of free volume hole  $R$  from  $o$ -Ps lifetime  $\tau_{o-Ps}$

$$\tau_{o-Ps} = \frac{1}{2} \left[ 1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + \Delta R}\right) \right]^{-1} \text{ [ns]}, \quad (1)$$

where  $\Delta R = 0.1656$  nm is empirically found constant. Next, we can compute the volume of the hole

$$V_d = \frac{4}{3} \pi R^3. \quad (2)$$

At present it is accepted that the relative intensity  $I_{o-Ps}$  corresponding to the  $o$ -Ps component  $\tau_{o-Ps}$  should reflect the number of free-volume holes in material. Using this assumption a semiempirical equation has been proposed to determine the fraction of free volume  $f$  in polymers<sup>7</sup>

$$f(T) = CV_d(T)I_{o-Ps}(T), \quad (3)$$

where  $C$  is a parameter which must be obtained by calibration. In our article we have used another approach for computation of the free volume fraction from lifetime data without any need of calibration constant.

### II. EXPERIMENTAL SECTION

#### A. Samples and treatment

We have measured following samples: cis 1,4 poly(butadiene) (cis 1,4 PBD), cis 1,4 poly(isoprene) (PIP), atactic poly(propylene) ( $a$ -PP), isotactic poly(propylene) ( $i$ -PP), poly(isobutylene) (PIB), cis-trans 1,4 poly(butadiene) (cis-trans 1,4 PBD). Their characteristics are summarized in Table I. The samples for PALS measurements were in a form of small discs with diameter of 10 mm and thickness of 5 mm.

The temperature range of measurement was from 15 up to 305 K, for some polymers up to 470 K. During the low temperature measurements (15–305 K) samples in holder

TABLE I. Main characteristics of measured polymers.  $\bar{M}_w$ , molecular weight;  $T_g$ , glass-transition temperature;  $\alpha_1(\alpha_2)$ , thermal expansion coefficients of total (bulk) volume  $V$  below (above)  $T_g$ , obtained from the given reference;  $\alpha_{v1}(\alpha_{v2})$ , thermal expansion coefficients of volume of holes  $V_d$  below (above)  $T_g$  obtained from our PALS measurements.

Polymer	$\bar{M}_w$ [ $0.10^5$ ]	$T_g^{\text{DSC}}$ [K]	$\alpha$		Ref.	$\alpha_v$		$T_g^{\text{PALS}}$ [K]
			$T < T_g$ [ $0.10^{-4} \text{ K}^{-1}$ ]	$T > T_g$ [ $0.10^{-4} \text{ K}^{-1}$ ]		$T < T_g$ [ $0.10^{-4} \text{ K}^{-1}$ ]	$T > T_g$ [ $0.10^{-4} \text{ K}^{-1}$ ]	
cis 1,4 PBD	8.1	168	1.93	7.52	21	$29.6 \pm 1.7$	$318.4 \pm 13.9$	$170 \pm 2$
cis 1,4 PIP	8	200	1.92	5.80	22	$19.9 \pm 0.5$	$155.4 \pm 3.9$	$196 \pm 1$
<i>a</i> -PP	1	258	1.94	7.14	23	$14.7 \pm 0.8$	$105.1 \pm 11.3$	$256 \pm 3$
<i>i</i> -PP	2.2	273	2.20	5.70	24	$31.2 \pm 3.7$	$132.6 \pm 18.5$	$271 \pm 7$
PIB	4.2	200	1.40	5.70	25	$8.1 \pm 1.7$	$180.1 \pm 7.4$	$199 \pm 2$
cis-trans 1,4 PBD	$2.1 \times 10^{-2}$	178	1.93	7.52	21	$36.9 \pm 1.2$	$201.3 \pm 7.2$	$176 \pm 1$

were fixed at the end of cold finger of a closed-cycle helium gas refrigerator with automatic temperature regulation. The source-sample assembly was kept in rotary pump vacuum. The high-temperature measurements (283–470 K) were performed with a home-made heater and the source-sample assembly was in air atmosphere.

Two different temperature measurement cycles were usually performed, heating and cooling. During the former one, samples were cooled down to 15 K in time about 2 h and then the temperature was being risen between measurements. During cooling cycle starting temperature was room temperature (305 K) and the temperature was being lowered between measurements.

We saw no difference in  $\tau_{o\text{-Ps}}(T)$  dependence between cooling and heating cycles in any sample. But we observed difference in  $I_{o\text{-Ps}}(T)$  dependence in some samples.

### B. Positron annihilation lifetime measurement

The positron annihilation lifetime spectra were obtained by the conventional fast-fast coincidence method using plastic scintillators coupled to Phillips XP2020 photomultipliers. The time resolution (FWHM) of prompt spectra was 320 ps. A model-independent instrumental resolution function was obtained from the decay curve of  $^{207}\text{Bi}$  isotope with a single lifetime of 186 ps. In the conventional three component analysis the Kirkegaard *et al.* PATFIT-88 software package<sup>8</sup> was used. The third component ( $\tau_3, I_3$ ) was attributed to the

pick-off annihilation of *o*-Ps. Results of PALS measurements have been partially published at several papers and conference contributions.<sup>9–12</sup>

The temperature dependence of volume of holes  $V_d(T)$  obtained from  $\tau_3(T)$  dependence is shown in Fig. 1 for PIB and cis-trans 1,4 PBD. We can see slow increase of  $V_d$  with temperature up to  $T_g$  and then rapid increase of  $V_d$  above  $T_g$ . This temperature marks the transition between thermal non-equilibrium (glassy) state and equilibrium (liquid) state in polymers.

It is interesting to compare this dependence with the temperature dependence of total volume  $V(T)$ . Table I gives us information about the thermal expansion coefficients of  $V_d$  just below  $T_g$  ( $\alpha_{v1}$ ) and above  $T_g$  ( $\alpha_{v2}$ ) and the thermal expansion coefficients of total volume in glassy state  $\alpha_1$  and elastic state  $\alpha_2$ . We can see that there exists quite a big difference between these coefficients—one order below  $T_g$  and almost two orders above  $T_g$ . Now the question arises of which macroscopic quantity, if any, the expansion of free volume hole can reflect. In the next part we will present a model based on the assumption that the expansion of free volume holes seen by positrons reflects the expansion of total free volume of material.

### III. THEORETICAL SECTION

In the following part the model for direct computation of the fraction of free volume from positron annihilation data

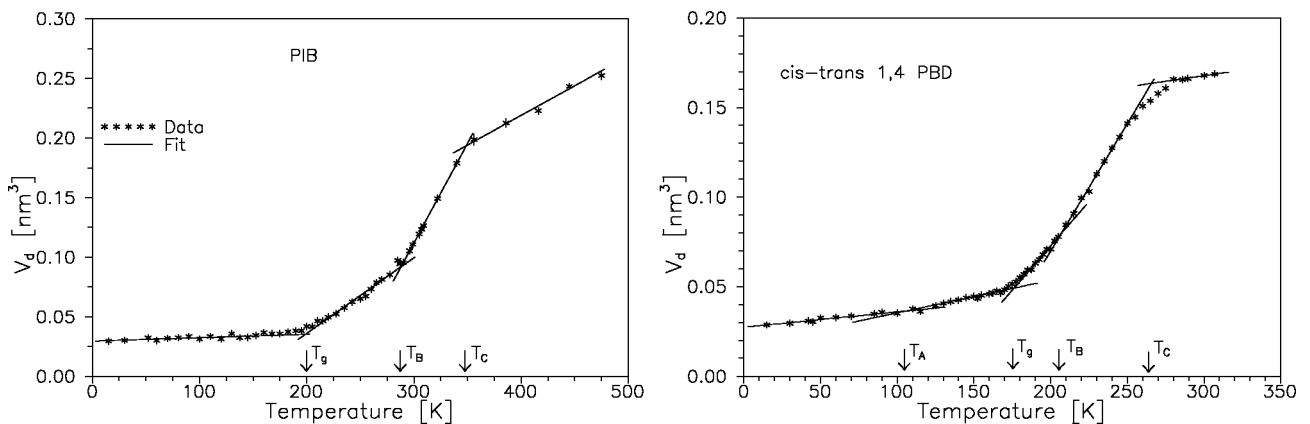


FIG. 1. Temperature dependence of  $V_d$  for PIB and cis-trans 1,4 PBD with linear fits.

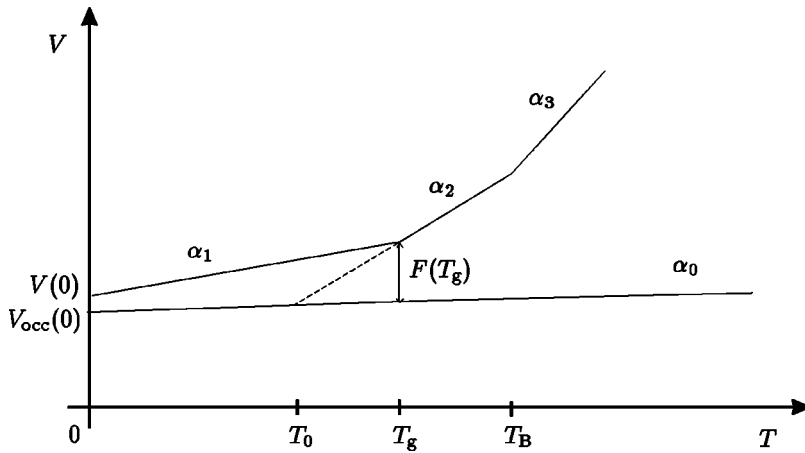


FIG. 2. Temperature dependence of volume.

will be presented. For a description of the temperature dependence of total and free volume we will use a well-known picture similar to that presented by Kovacs<sup>13</sup> (Fig. 2).

As it is clear from Fig. 2 we will use the concept of non-constant free volume below  $T_g$  and constantly expanding occupied volume  $V_{occ}$ , for which we can write

$$V_{occ}(T) = V_{occ}(T_g)[1 + \alpha_0(T - T_g)]. \quad (4)$$

Analogically for expansion of total volume we write

$$V(T) = V(T_g)[1 + \alpha_1(T - T_g)] \quad \text{for } T < T_g, \quad (5)$$

$$V(T) = V(T_g)[1 + \alpha_2(T - T_g)] \quad \text{for } T > T_g. \quad (6)$$

Free volume  $F$  is defined as a difference between total and occupied volume

$$F(T) = V(T) - V_{occ}(T) \quad (7)$$

and the fraction of free volume  $f$  as a ratio between free and occupied volume (Doolittle's fraction)

$$f(T) = \frac{F(T)}{V_{occ}(T)}. \quad (8)$$

From the definition of free volume  $F$  it implies that this quantity is also a linear function of temperature, e.g.,

$$F(T) = F(T_g)[1 + \alpha_{F1}(T - T_g)] \quad \text{for } T < T_g, \quad (9)$$

$$F(T) = F(T_g)[1 + \alpha_{F2}(T - T_g)] \quad \text{for } T > T_g. \quad (10)$$

After simple algebraic manipulations, using above mentioned equations, we obtain following expressions for  $\alpha_{F1}, \alpha_{F2}$ :

$$\alpha_{F1} = \frac{\alpha_1[f(T_g) + 1] - \alpha_0}{f(T_g)}, \quad (11)$$

$$\alpha_{F2} = \frac{\alpha_2[f(T_g) + 1] - \alpha_0}{f(T_g)}. \quad (12)$$

Up to this point we have only made an algebraic manipulation with definition relations implied from Fig. 2.

Now let us look closer on Eqs. (11), (12). Supposing that we know thermal expansion coefficients of total volume

$\alpha_1, \alpha_2$  from literature, we have two equations with four unknowns. To solve these equation we will make the supposition

$$\alpha_{F1} \equiv \alpha_{v1}, \quad \alpha_{F2} \equiv \alpha_{v2}, \quad (13)$$

which means that the holes of free volume seen by positrons  $V_d$  are expanding in the same rate as the total free volume  $F$ .

So, having the values of  $\alpha_{F1}, \alpha_{F2}$  from positron lifetime measurements, we can solve Eqs. (11), (12) for two unknowns  $\alpha_0, f(T_g)$

$$\alpha_0 = \frac{\alpha_1 \alpha_{F2} - \alpha_2 \alpha_{F1}}{(\alpha_{F2} - \alpha_{F1}) - (\alpha_2 - \alpha_1)}, \quad (14)$$

$$f(T_g) = \frac{\alpha_2 - \alpha_1}{(\alpha_{F2} - \alpha_{F1}) - (\alpha_2 - \alpha_1)}. \quad (15)$$

Now we also know the temperature dependence of fraction of free volume  $f(T)$

$$f(T) = f(T_g) \frac{1 + \alpha_{F1}(T - T_g)}{1 + \alpha_0(T - T_g)} \quad \text{for } T < T_g, \quad (16)$$

$$f(T) = f(T_g) \frac{1 + \alpha_{F2}(T - T_g)}{1 + \alpha_0(T - T_g)} \quad \text{for } T > T_g. \quad (17)$$

Using an extrapolation below  $T_g$  from above  $T_g$  we can further find temperature  $T_0$  at which the free volume would be zero

$$F(T_0) = 0 = F(T_g)[1 + \alpha_{F2}(T_0 - T_g)] \Rightarrow T_0 = T_g - \frac{1}{\alpha_{F2}}. \quad (18)$$

Temperature  $T_0$  is equivalent to the Vogel temperature which is defined as a temperature at which the viscosity would be infinity from the extrapolation from region above  $T_g$ . From the point of view of free volume theory this is equivalent to the statement that the free volume would be zero at this temperature. We must stress here that the real free volume is not equal to zero at this temperature because of inherent structural free space between molecules and finite dimension of  $o$ -Ps.

At this point we would like to stress that the value of  $\alpha_0$ , the thermal expansion of occupied volume, was never subjected to experimental investigation due to its experimental unaccessibility.

Now, having all these values at the region of  $T_g$  we can move our attention to the next temperature point  $T_x$  which marks the change in the temperature dependence of  $V_d$ , respectively,  $V$ . If we know  $\alpha_{F3}$  ( $\equiv \alpha_{v3}$ ) from the PALS measurement,  $f(T_x)$  and  $\alpha_0$  calculated from Eqs. (17) and (14) then we are able to calculate macroscopic bulk  $\alpha_3$  from equation similar to that of Eq. (12):

$$\alpha_3(T_x) = \frac{\alpha_{F3}(T_x)f(T_x) + \alpha_0(T_x)}{f(T_x) + 1}. \quad (19)$$

All former mentioned expansion coefficients were connected with  $T_g$  [e.g.,  $\alpha \equiv \alpha(T_g)$ ]. We must remind here that thermal expansion coefficients must be recalculated for given temperature [in Eq. (19)  $\alpha_0$  from  $T_g$  to  $T_x$ , for example]. Following equation shows such recalculation in general:

$$\alpha_{(T_1)} = \frac{\alpha_{(T_2)}}{1 + \alpha_{(T_2)}(T_1 - T_2)}. \quad (20)$$

$\alpha_3$  is thermal expansion coefficient of total volume and its value calculated from Eq. (19) is correct under the assumption that expansion of  $V_d$  is the same as the expansion of free volume of the sample. Using this assumption and procedure described above we are able to calculate  $f(T)$  dependence and thermal expansion coefficients of total volume for the whole temperature interval of  $\tau_3$  measurement.

Now, having the temperature dependence of  $f(T)$  we can try to use this quantity for determination of the temperature dependence of viscosity, for example. Later we can compare these results with that obtained from experimental measurements of viscosity.

In the next part we will mention a couple of equations describing the temperature dependence of viscosity and we will express their coefficients through the above mentioned parameters. Vogel, Fulcher, Tamman, and Hess (VFTH) equation for viscosity<sup>14-16</sup> is using  $T_0$  parameter for its description:

$$\log \eta = A_{VFTH} + \frac{B_{VFTH}}{T - T_0} \quad A_{VFTH}, B_{VFTH} \text{ coefficients} \quad (21)$$

and another well-known description is the WLF equation<sup>17</sup>

$$\log \frac{\eta}{\eta_g} = -c_{1g} \frac{T - T_g}{c_{2g} + T - T_g}, \quad c_{1g}, c_{2g} \text{ coefficients.} \quad (22)$$

An alternative description of viscosity is based on the free volume concept. It is represented by the famous semiempirical Doolittle equation<sup>3</sup>

$$\eta(T) = A \exp B/f(T), \quad A, B \text{ coefficients.} \quad (23)$$

Combining both Eqs. (23), (22) and Eq. (17) we get following expressions for WLF coefficients:

$$c_{2g} = T_g - T_0 = \frac{1}{\alpha_{F2}}, \quad (24)$$

$$c_{1g} = \frac{B \left( 1 - \frac{\alpha_0}{\alpha_{F2}} \right) \log e}{f(T_g)} = \frac{B' \log e}{f(T_g)}, \quad (25)$$

where  $B' = B(1 - \alpha_0/\alpha_{F2})$ . From these last two equations we can also see that we are not able to compute coefficient  $c_{1g}$  from PALS data directly just the ratio  $c_{1g}/B$ , and that Vogel temperature can be expressed by the relation

$$T_0 = T_g - \frac{1}{\alpha_{F2}}. \quad (26)$$

We can see that usually used assumption  $B=1$  is not generally valid. From the above made analysis we can conclude that if we accept the approximation of equality of the thermal expansion coefficients of free volume and volume of holes seen by positrons [Eq. (13)], and having the values of thermal expansion coefficients of total volume below and above  $T_g$  ( $\alpha_1, \alpha_2$ ), we are able to compute the temperature dependence of free volume fraction  $f(T)$ , the expansion coefficient of occupied volume  $\alpha_0$ , Vogel temperature  $T_0$ , WLF coefficient  $c_{2g}$ , and the ratio  $c_{1g}/B$ . We are also able to compute the values of expansion coefficients of macroscopic volume for temperature regions different from that around  $T_g$ .

On the other hand if we have WLF coefficients  $c_{1g}, c_{2g}$  from viscosity measurement we can directly compute  $\alpha_{F2}$  and  $f(T_g)/B'$ . Other quantities [ $f(T_g), \alpha_0, \alpha_{F1}$ ] depend on the value of  $B$ . If we somehow choose the value of  $B$  we can obtain these quantities by solving Eqs. (11),(14),(15) and by using Eqs. (24),(25).

Following equations give direct relations between two groups of values obtained from different experiments, namely,  $\alpha_{F1}, f(T_g), \alpha_0$  and  $c_{1g}, c_{2g}, B$ :

$$\alpha_{F1} = \frac{c_{1g}(\alpha_2 - \alpha_1)}{B c_{2g}(\alpha_2 - 1/c_{2g}) \log e} + \frac{1}{c_{2g}}, \quad (27)$$

$$f(T_g) = \frac{B c_{2g}(1/c_{2g} - \alpha_2) \log e}{c_{1g} + B c_{2g}(\alpha_2 - 1/c_{2g}) \log e}, \quad (28)$$

$$\alpha_0 = \frac{c_{1g} \alpha_2 + B(\alpha_2 - 1/c_{2g}) \log e}{c_{1g} + B c_{2g}(\alpha_2 - 1/c_{2g}) \log e}. \quad (29)$$

In the next section we will apply the presented model for six different polymers (Table I) and in the case of PIB and cis-trans 1,4 PBD we will compare our results from PALS measurements with that obtained from viscosity  $\eta(T)$  and temperature shift parameter  $a_T(T)$  measurements.

#### IV. RESULTS AND DISCUSSION

First let us look at the data obtained from our positron lifetime measurements. In Fig. 1 we can see a typical example of temperature dependence of volume of holes seen by positrons  $V_d(T)$  computed from  $o$ -Ps lifetime  $\tau_3(T)$  dependence using Eqs. (1) and (2). Table I gives us information about the thermal expansion coefficients just below ( $\alpha_{v1}$ )

TABLE II. Computed data from presented model using positron lifetime data ( $\alpha_v$ ) and thermal expansion coefficients from literature ( $\alpha$ ).  $\alpha_0$ , thermal expansion coefficient of occupied volume;  $f(T_g)$ , fraction of free volume at  $T_g$ ;  $T_0$ , Vogel temperature;  $c_{2g}, c_{1g}$ , WLF coefficients;  $B$ , Doolittle's coefficient.

Polymer	$\alpha_0$ [ $0.10^{-4} \text{ K}^{-1}$ ]	$f(T_g)$ [%]	$T_0$ [K]	$c_{2g}$ [K]	$c_{1g}/B$
cis 1,4 PBD	$1.38 \pm 0.05$	$2.0 \pm 0.1$	$138.6 \pm 2.4$	$31.4 \pm 1.4$	$21.9 \pm 1.1$
cis 1,4 PIP	$1.39 \pm 0.024$	$3.0 \pm 0.1$	$131.6 \pm 1.9$	$64.4 \pm 1.6$	$14.6 \pm 0.4$
a-PP	$1.14 \pm 0.09$	$4.4 \pm 0.2$	$189.1 \pm 2.6$	$69.9 \pm 2.4$	$9.8 \pm 0.4$
i-PP	$1.16 \pm 0.26$	$3.6 \pm 0.7$	$195.6 \pm 12.6$	$75.4 \pm 10.5$	$12.0 \pm 2.3$
PIB	$1.23 \pm 0.05$	$2.6 \pm 0.1$	$143.5 \pm 3.0$	$55.5 \pm 2.3$	$16.8 \pm 0.8$
cis-trans 1,4 PBD	$0.70 \pm 0.08$	$3.5 \pm 0.2$	$126.3 \pm 2.0$	$49.7 \pm 1.8$	$12.3 \pm 0.6$

and above ( $\alpha_{v2}$ ) $T_g$ , obtained from such dependences, together with the thermal expansion coefficients of total volume  $\alpha_1, \alpha_2$  obtained from literature.<sup>21–24</sup> Now, using the above mentioned model we are able to calculate the following values:  $\alpha_0, f(T_g), T_0, c_{2g}, c_{1g}/B$ . Results of these calculations are summarized in Table II for six different polymers.

Let us have a look at these values and decide how “reasonable” they are, e.g., to legalize our assumption about the equality of expansion coefficients of holes seen by positrons and expansion coefficients of total free volume [Eq. (13)]. Table 11-II from Ref. 18 gives following ranges of values of  $c_{1g}, c_{2g}$  and  $f(T_g)/B$  coefficients obtained from  $a_T$  measurements for different polymers:  $c_{1g} = 6.1 - 32.2, c_{2g} = 17.6 - 129.4 \text{ K}, f(T_g)/B = 1.3 - 7.1 \%$ . From our PALS measurements and model calculations for our polymer samples we received following ranges of coefficients:  $c_{1g}/B = 9.8 - 21.9, c_{2g} = 31.4 - 74.5 \text{ K}, f(T_g) = 2.0 - 4.4 \%$ . Taking into account the fact that the value of  $B$  should be close to 1 (Ref. 18) we can conclude that our calculated values are “reasonable” enough, and that positrons “feel” free volume which also governs such macroscopic quantity as viscoelasticity.

Thermal expansion coefficients of occupied volume  $\alpha_0$  are smaller than that of total volume below  $T_g, \alpha_1$ , as one would expect, and the ratio  $\alpha_0/\alpha_1$  vary from 0.36 for cis-

trans 1,4 PBD up to 0.88 for PIB. This observation reflects the different speed of expansion (e.g., a different tightness) of free volume below  $T_g$  in different polymers.

Next we will focus our attention to two polymers, PIB and cis-trans 1,4 PBD and we will present calculated values of macroscopic expansion coefficients for regions different from that around  $T_g$  and the  $f(T)$  dependence for the whole measured interval of PALS. Table III gives us the values of thermal expansion coefficients of total ( $\alpha$ ) and free volume ( $\alpha_F \equiv \alpha_v$ ) together with the fraction of free volume at given temperature. Calculation procedure was as follows: first we performed calculations for temperature region around  $T_g$  using  $\alpha_1, \alpha_2$  values from literature and  $\alpha_{v1}, \alpha_{v2}$  from our PALS measurement. Applying Eqs. (13), (14), (15) we received  $\alpha_0(T_g)$  and  $f(T_g)$  values. Further we moved to the next temperature region using Eqs. (16), (17), (20) for calculation of  $f(T)$ , and Eq. (19), (20) for calculation of thermal expansion coefficient of total volume  $\alpha$ . In such a way we were able to cover the whole measured temperature interval and to obtain  $f(T)$  dependence. Value of fraction of free volume at 0 K is of course just extrapolation. Figure 3 shows the temperature dependence of  $f(T)$  for the whole temperature interval of PALS measurements.

We must remind here that assumption behind these calcu-

TABLE III. Thermal expansion coefficients ( $\alpha$ , macroscopic volume;  $\alpha_F$ , free volume) and the fractions of free volume  $f(T_x)$  for PIB and cis-trans 1,4 PBD.

	$T_x$ [K]	$\alpha_{(T_x)}(T < T_x)$ [ $0.10^{-4} \text{ K}^{-1}$ ]	$\alpha_{(T_x)}(T > T_x)$ [ $0.10^{-4} \text{ K}^{-1}$ ]	$\alpha_F(T_x)(T < T_x)$ [ $0.10^{-4} \text{ K}^{-1}$ ]	$\alpha_F(T_x)(T > T_x)$ [ $0.10^{-4} \text{ K}^{-1}$ ]	$f(T_x)$ [%]
PIB						
	0		$1.4 \pm 0.0$		$9.6 \pm 2.5^a$	$2.2 \pm 0.1$
$T_g =$	$199 \pm 2^a$	$1.4 \pm 0.0^b$	$5.7 \pm 0.0^b$	$8.1 \pm 1.7^a$	$180.1 \pm 7.4^a$	$2.6 \pm 0.1$
$T_B =$	$288 \pm 1^a$	$5.4 \pm 0.0$	$12.4 \pm 0.6$	$69.1 \pm 1.2^a$	$181.7 \pm 3.5^a$	$6.6 \pm 0.7$
$T_C =$	$349 \pm 4^a$	$11.5 \pm 0.5$	$4.2 \pm 0.5$	$86.2 \pm 3.0^a$	$25.7 \pm 3.6^a$	$13.8 \pm 1.9$
cis-trans 1,4 PBD						
	0		$1.3 \pm 0.1$		$31.3 \pm 2.0^a$	$2.0 \pm 0.1$
$T_A =$	$105 \pm 5^a$	$1.3 \pm 0.1$	$2.0 \pm 0.0$	$23.6 \pm 0.9^a$	$50.0 \pm 1.8^a$	$2.6 \pm 0.4$
$T_g =$	$176 \pm 1^a$	$1.9 \pm 0.0^b$	$7.5 \pm 0.0^b$	$36.9 \pm 1.2^a$	$201.3 \pm 7.2^a$	$3.5 \pm 0.2$
$T_B =$	$207 \pm 2^a$	$7.4 \pm 0.0$	$10.3 \pm 0.6$	$124.6 \pm 3.8^a$	$179.1 \pm 4.0^a$	$5.7 \pm 1.3$
$T_C =$	$266 \pm 1^a$	$9.7 \pm 0.5$	$1.4 \pm 0.1$	$87.1 \pm 1.6^a$	$7.8 \pm 0.8^a$	$11.6 \pm 0.9$

<sup>a</sup>Values calculated from  $V_d(T)$  dependence (PALS data, see Eq. 13).

<sup>b</sup>Values obtained from literature, other values were calculated from the proposed model using both the above mentioned data sets.



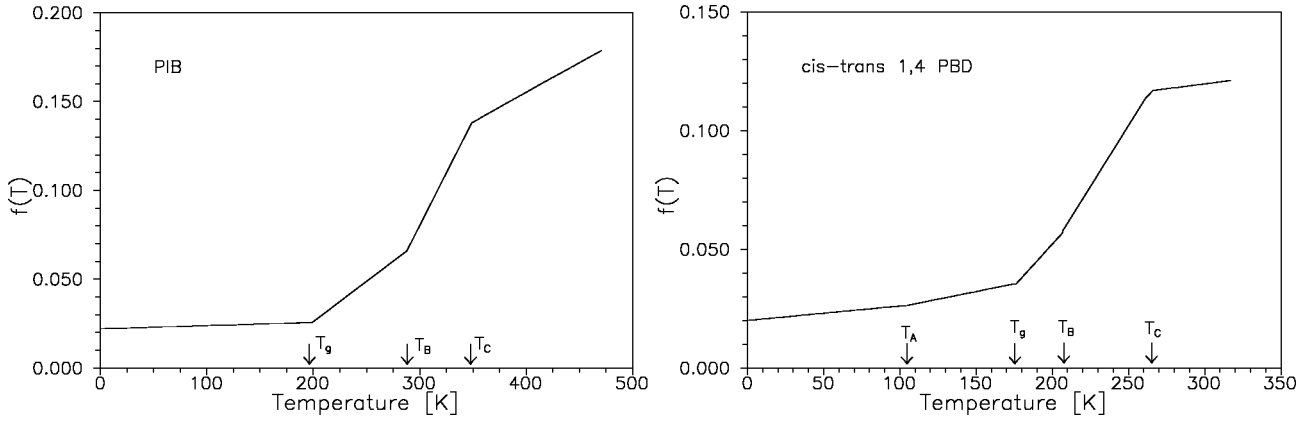


FIG. 3. Temperature dependence of fraction of free volume  $f(T)$  for PIB and cis-trans 1,4 PBD.

lations is that the expansion of holes of free volume seen by positrons ( $\alpha_v$ ) reflects the expansion of total free volume ( $\alpha_F$ ) [Eq. (13)]. This is obviously not the case for regions above  $T_C$  because there is no clear reason for  $f(T)$  and  $V$  to almost stop rising. This effect is maybe connected with the behavior of positron itself in soft medium, probably with the creation of holes of free volume by positronium atoms themselves. From Fig. 3 and Table III it is also clear that cis-trans 1,4 PBD is a much “softer” material than PIB and this fact leads to a much bigger increase of  $f(T)$  in a similar temperature region.

In the next step we will compare our abovementioned calculated parameters from PALS measurements with that obtained from  $\eta(T)$ , respectively,  $a_T(T)$  measurements for PIB and cis-trans 1,4 PBD. In the case of PIB we took data from Ref. 19 and made the fits of WLF equation in the temperature region  $\langle T_g; T_B \rangle$ . They used PIB with  $T_g = 200.4$  K,  $\bar{M}_w = 7.85 \times 10^4$ , and our sample had  $T_g = 200$  K,  $\bar{M}_w = 4.2 \cdot 10^5$ . So, one must keep in mind this difference in  $\bar{M}_w$  during comparison of  $c_{1g}, c_{2g}$  parameters. Table IV gives us results of WLF fit to  $a_T(T)$  and  $\eta(T)$  dependences (coefficients  $c_{1g}, c_{2g}$ ) and values calculated from our model [ $T_0, f(T_g), \alpha_0, B$ ] using these coefficients (second and third lines). There are also given values obtained from our model using data from PALS measurements, for comparison (first line).

Using the  $c_{1g}, c_{2g}$  coefficients from viscosity  $\eta(T)$  or temperature shift factor  $a_T(T)$  measurements we can reverse the process of computation in the model and obtain values of  $T_0, f(T_g), \alpha_0, \alpha_{F2}$  if we somehow choose the value of  $B$  [Eqs. (24)–(29)]. Table IV summarizes some of these values in dependence of  $B$ . Given interval of  $B$  values was chosen because of the negative values of  $\alpha_{F1}$  for smaller  $B$  and because of the negative values of  $\alpha_0$  for bigger  $B$ . Just for clarity, these calculations are totally independent of any PALS data.

As we can see in Table IV the only parameters which are directly comparable between PALS and  $\eta(T)$  respectively,  $a_T(T)$  are  $c_{2g}$  and  $T_0$ . In the case of  $\eta(T)$ , respectively,  $a_T(T)c_{2g}$  is directly obtained from fit by WLF equation [Eq. (22)] to experimental data, in the case of PALS  $c_{2g}$  is obtained from thermal expansion coefficient of free volume above  $T_g$   $\alpha_{F2}$  [Eq. (24)].  $T_0$  is directly connected with  $c_{2g}$  by Eq. (24) and with  $\alpha_{F2}$  by Eq. (26).

To compare also the values of  $f(T_g)$  and  $\alpha_0$  obtained from  $\eta(T)$ , respectively,  $a_T(T)$  and PALS measurements using our proposed model we treated two special cases (bottom part of Table IV). In the first case (I) the value of  $B$  was chosen in such a way that it gives the same value of  $f(T_g)$  as  $f(T_g)$  from PALS data. In the second case (II) such value of  $B$  was chosen that it gives the same value of  $\alpha_0$  as that  $\alpha_0$  from PALS data. For the first case [equality of  $f(T_g)$ ] we

TABLE IV. Fitted [ $c_{1g}, c_{2g}$  for  $\eta(T), a_T(T)$ ] and computed (all the rest) data for PIB from proposed model using viscosity or shift parameter or PALS data. The bottom part of the table (I and II) treats the cases of special chosen values of  $B$  (see discussion).

	$c_{1g}$	$c_{2g}$ [K]	$T_0$ [K]	$f(T_g)$ [%]	$\alpha_0$ [ $0.10^{-4} \text{ K}^{-1}$ ]	$B$
PALS	$(16.8 \pm 0.8) \cdot B$	$55.5 \pm 2.3$	$143.5 \pm 3.0$	$2.6 \pm 0.1$	$1.2 \pm 0.1$	
$\eta(T)$	$15.6 \pm 0.3$	$93.9 \pm 3.5$	$106.5 \pm 3.5$	$(4.2 - 5.7) \pm 0.1$	$(0.0 - 1.5) \pm 0.2$	1.53–2.03
$a_T(T)$	$13.8 \pm 0.4$	$60.6 \pm 3.8$	$139.8 \pm 3.8$	$(2.7 - 3.6) \pm 0.1$	$(0.0 - 1.4) \pm 0.4$	0.86–1.14
$\eta(T)$				$2.6 \pm 0.1$	$3.2 \pm 0.1$	0.92
(I) $a_T(T)$				$2.6 \pm 0.1$	$1.6 \pm 0.3$	0.82
$\eta(T)$				$4.4 \pm 0.1$	$1.2 \pm 0.2$	1.57
(II) $a_T(T)$				$2.8 \pm 0.1$	$1.2 \pm 0.3$	0.88

TABLE V. Fitted [ $c_{1x}, c_{2x}$  for  $a_T(T)/a_T(T_x)$ ] and computed (all the rest) data for cis-trans 1,4 PBD from proposed model using temperature shift parameter or PALS data. The bottom part of the table (I and II) treats the cases of special chosen values of  $B_g$  (see discussion).  $B_x$  where  $x=g, B, C$  is Doolittle's constant for different temperature regions.

$T_x$	$c_{1x}$	$c_{2x}$ [K]	$T_0$ [K]	$f(T_x)$ [%]	$\alpha_0(T_x)$ [ $0.10^{-4} \text{ K}^{-1}$ ]	$B_x$
PALS: $V_d(T)$ dependence						
$T_g = 176 \pm 1$	$(12.3 \pm 0.6) \cdot B_g$	$49.7 \pm 1.8$	$126.3 \pm 2.0$	$3.5 \pm 0.2$	$0.7 \pm 0.1$	
$T_B = 207 \pm 2$	$(7.6 \pm 1.7) \cdot B_B$	$55.8 \pm 1.3$	$151.2 \pm 2.4$	$5.7 \pm 1.3$	$0.7 \pm 1.6$	
$T_C = 266 \pm 1$	$(3.4 \pm 0.3) \cdot B_C$	$1290.3 \pm 126.5$		$11.6 \pm 0.9$	$0.7 \pm 0.2$	
$a_T(T)/a_T(T_x)$ dependence						
$T_g = 178.0 \pm 0.1$	$8.4 \pm 0.4$	$17.0 \pm 1.5$	$161.0 \pm 1.5$	$(1.0-1.3) \pm 0.1$	$(0.0-2.0) \pm 0.7$	$0.19-0.25$
$T_B = 213.4 \pm 0.2$	$5.5 \pm 0.2$	$55.8 \pm 3.5$	$157.2 \pm 3.5$			
$T_C = 271.1 \pm 0.2$	$2.5 \pm 0.4$	$83.1 \pm 15.3$				
$T_g = 178.0 \pm 0.1$				$3.5 \pm 0.2$	$-13.0 \pm 2.1$	$0.66$
$T_B = 213.4 \pm 0.2$						
(I)						
$T_g = 178.0 \pm 0.1$				$1.2 \pm 0.1$	$0.7 \pm 0.7$	$0.23$
(II)						
$T_B = 213.4 \pm 0.2$				$3.6 \pm 0.3$	$0.7$	$0.45$

can see that the values of  $\alpha_0$  are too high, resulting in negative temperature expansion coefficient of free volume below  $T_g$  ( $\alpha_{F1}$ , not shown in the table). A physically more acceptable picture is the second one (equality of  $\alpha_0$ ) resulting in a higher free volume fraction in  $T_g$ . So if we choose such values of  $B$  that we receive equal values of  $\alpha_0$  for PALS and  $\eta(T), a_T(T)$  data [ $B = 1.57$  for  $\eta(T), B = 0.88$  for  $a_T(T)$ ] we get higher values of  $f(T_g)$  for  $\eta(T), a_T(T)$  than that for PALS. But in the case of  $a_T(T)$  this difference is small and in the range of experimental error. We must remind the reader here that the samples had different  $\bar{M}_w$  which probably influenced these results. Another fact is that there were nine temperature points in  $a_T(T)$  dependence in  $\langle T_g; T_B \rangle$  region in comparison with seven temperature points in  $\eta(T)$  dependence and the  $a_T(T)$  points were better “spread” over this region. A better comparison of these two measurements from the point of view of the above made analysis would require measurement in the same temperature points.

Anyway the similarity of results obtained from such different kinds of measurements as microscopic positron annihilation and macroscopic temperature shift parameter is remarkable [ $f(T_g) = 2.6 \pm 0.1\%$  from PALS,  $f(T_g) = 2.8 \pm 0.1\%$  from  $a_T(T)$ ]. Also the expansion of total free volume above  $T_g$  in the case of PALS and  $a_T(T)$  measurements is very similar as expressed by the value of the  $c_{2g}$  coefficient [Eq. (24)],  $c_{2g} = 55.5 \pm 2.3$  for PALS, and  $c_{2g} = 60.6 \pm 3.8$  for  $a_T(T)$ . That means that these two measurements “feel” similar free volume and it allows us to estimate also the Doolittle constant  $B$  ( $B = 0.88$ ) for these processes in this polymer.

For cis-trans 1,4 PBD we used data of temperature shift parameter  $a_T(T)/a_T(T_g)$  provided by Zorn,<sup>20</sup> made fits by WLF equation in different temperature regions (for  $T > T_x$ ) and obtained coefficients  $c_{1x}, c_{2x}$ . Temperature points  $T_x$  for  $a_T(T)/a_T(T_x)$  dependence were chosen to be closest to  $T_x$  values from PALS  $V_d(T)$  dependence. The sample was of the same type of PBD as our sample. The temperature inter-

val of  $a_T$  measurement was quite large— $\langle 172.9; 298.5 \text{ K} \rangle$  and this fact allowed us to compare our PALS results with that from  $a_T$  measurement in different temperature regions what we could not do for PIB.

The thermal expansion coefficient of total volume used for this calculations are given in Table I, comparison of values computed from model using PALS or  $a_T(T)$  data is given in Table V. Looking at the data from PALS  $V_d(T)$  dependence we can see very high value of  $c_{2x}$  for  $T > T_C$ . This value is connected with a small change of  $V_d(T)$  above  $T_C$ . As it was said before in this temperature region the  $V_d(T)$  dependence does not reflect the change of  $F(T)$  any more and the effect of a small temperature change of  $V_d(T)$  is probably connected with the creation of free volume holes by positronium atoms themselves.

In the case of  $a_T(T)/a_T(T_x)$  dependence we were able to compute intervals of  $f(T_x), \alpha_0(T_x)$  values in dependence on  $B$  just for the region above  $T_g$  not for higher temperature regions because of not having the values of thermal expansion coefficients of total volume for these regions. In bottom part of Table V (similar as in Table IV) special cases of  $B$  are treated to be able to compare  $f(T_x), \alpha_0(T_x)$  values from PALS and  $a_T(T)$  measurements. In the first case (I) the value of  $B$  was chosen in such a way that it gives the same value of  $f(T_x)$  for  $a_T(T)$  as that  $f(T_x)$  in PALS, in the second case (II) the value of  $B$  ensures the same value of  $\alpha_0(T_x)$  for  $a_T(T)$  as that  $\alpha_0(T_x)$  in PALS. We can see that for the temperature region just above  $T_g$  the correspondence between  $a_T$  and PALS results is not very good. The value of  $B = 0.66$  which leads to equal  $f(T_g)$  for  $a_T(T)$  a PALS produces physically nonacceptable value of  $\alpha_0 = -13.0 \times 10^{-4} \text{ K}^{-1}$ . The case of equal  $\alpha_0$  is again physically more acceptable which gives  $B = 0.23$  and smaller  $f(T_g) = 1.2\%$  from  $a_T$  than  $f(T_g) = 3.5\%$  from PALS data.

For the next temperature region  $T > T_B$  for  $a_T(T)/a_T(T_x)$  dependence we took determined value of  $\alpha_0$ , calculated value of  $f(T_g)$  and using Eqs. (27)–(29) and Eq. (17) we

calculated  $f(T_B) = 3.6 \pm 0.3\%$  and  $B_B = 0.45$  ( $B_B \equiv B$  for  $T > T_B$ ). Again the value of  $f(T_B)$  is lower than  $f(T_B) = 5.7 \pm 0.3\%$  determined from PALS.

As this comparison shows the agreement between PALS and  $a_T(T)/a_T(T_x)$  is not very good for the case of cis-trans 1,4 PBD. This is caused by different value of  $c_{2g}$  for  $T > T_g$  for PALS and  $a_T$ . It seems that in this 30 K temperature interval (up to  $T_B$ ) both processes “feel” different free volume. For  $T > T_B$  the value of  $c_{2x}$  is the same for both processes indicating the same thermal expansion coefficient of free volume characterizing transport and dynamic processes in polymers.

It is also possible to make others computations and comparisons with all these coefficients, to “play around with the data” but the main purpose of this article is just to point out the possibility to obtain important parameters of free volume theory characterizing polymers, as a fraction of free volume, thermal expansion coefficients of free and occupied volume, from combination of PALS (respectively, viscosity) and dilatometric measurements.

## V. CONCLUSION

In this paper we presented the model for direct computation of the temperature dependence of fraction of free volume  $f(T)$ , expansion coefficient of occupied volume  $\alpha_0$ , Vogel temperature  $T_0$ , and the WLF coefficients  $c_{2g}, c_{1g}/B$  from temperature dependence of  $V_d(T)$  obtained from  $o$ -Ps lifetime  $\tau_3(T)$  dependence measurements.

The model is based on the assumption that the expansion of holes of free volume  $V_d$  as seen by positrons reflects the expansion of total free volume of material. The model as it's input parameters also uses thermal expansion coefficients of total volume just below ( $\alpha_1$ ) and above ( $\alpha_2$ )  $T_g$  and is able to compute the expansion coefficients of total volume for regions different from that stated above.

Results obtained from the proposed model for six different polymers (Table II) show values of  $f(T_g)$  from 2.0 up to 4.4%,  $c_{2g}$  from 31.4 up to 75.4 K,  $c_{1g}/B$  from 9.8 up to 21.9,  $\alpha_0$  from 0.70 up to  $1.39 \times 10^{-4} \text{ K}^{-1}$ , and they are of the same magnitude as coefficients obtained from the  $a_T(T)$

measurement<sup>18</sup>  $f(T_g)/B = 1.3 - 7.1\%$ ,  $c_{2g} = 17.6 - 129.4 \text{ K}$ ,  $c_{1g} = 6.1 - 32.2$ .

Table III gives us the fraction of free volume at different temperatures  $T_x$  together with calculated expansion coefficients of total volume for several temperature regions for PIB and cis-trans 1,4 PBD. Finally, Tables IV and V shows comparison of parameters computed from PALS data and  $a_T(T), \eta(T)$  data for PIB and cis-trans 1,4 PBD, respectively. In the case of PIB we reached very good agreement for  $a_T(T)$  and PALS data, in the case of cis-trans 1,4 PBD we received higher fraction of free volume around  $T_g$  from PALS as that from  $a_T(T)/a_T(T_x)$  data but agreement in thermal expansion coefficients of free volume at higher temperature region.

These results suggest that positrons in polymers reflect the same basic mechanism as other processes such as viscosity or relaxation processes. As positrons are governed by free volume, the abovementioned processes are influenced mainly by free volume. So, PALS measurements can be used to obtain information on dynamic processes in polymers and to predict the behavior of polymer materials at different temperature ranges. A more thorough investigation of temperature dependence of fraction of free volume in polymers would require measurements of temperature dependence of total volume, PALS measurements, and, for example, viscosity on the same polymer samples. A combination of these methods could bring more complex information about behavior of free volume in polymers and dynamics connected with this free volume. Moreover, the combination of PALS and dilatometric techniques gives direct access to the occupied volume ( $\alpha_0$ ) and it allows testing of the models proposed for this last and never subjected to experimental investigations.

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