Free Volume in Polymers.
Note I°: Theoretical Background

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Abstract : Free volume in polymers is defined as the difference of the specific volume and the volume which is not available for the particular molecular motion, which is responsible for the process that is considered. Relations between free volume and viscosity, free volume and diffusion coefficient are presented both in the case of simple low molecular weight liquids and in the case of polymers. Molecular models and free volume models are reminded starting from the equilibrium state equation of Simha and Somcynski. The non equilibrium situations of specific volume of glass polymers below T_g are shown introducing different relaxation volume equations, which involve different material's parameters and concept of the fictitious temperature. The diffusivity equations of Vrentas and Duda are introduced both for the glassy and rubbery states. The possibility of introducing time relaxation functions is also suggested. The importance of finding experimental evidences of the free volume is stressed. Highlights of the free volume measurement methods are given, in particular as to dilatometry, photocromy, fluorescence, electron spin resonance, small angle X-ray scattering, positron annihilation spectroscopy.

1. Free Volume Definition

The specific free volume (for unit mass) V_f can be defined as the difference between the specific volume $\left(\dfrac{1}{\rho} = V\right)$ and the "occupied" volume V_0 which is the characteristic volume (or co-volume) of the atoms or molecules, making up the materials, in the unit mass:

$$V_f = V - V_0. \tag{1}$$

V_0 is the volume not available for the molecular motion, which characterizes the process under investigation. However the question of what to use

for the magnitude of V_0 is quite a difficult one. Doolittle [1] for example suggested three possible definition of V_0:

  i) V_0 is calculated from the van der Waals atomic dimensions [2]
 ii) V_0 is the crystalline volume at 0° K
iii) V_0 is the volume of the liquid extrapolated, without change of phase, to 0° K [3]

Other definitions involve the volume swept – out by the gravity center of the molecules during thermal motions. It is important to remark that V_f allows the motions of polymeric groups and segments inside the material.

V_f rules therefore the rigidity and the mechanical

properties of polymers and also the penetrant diffusion coefficients, which are fundamental for the study of transport properties.

The transition from rubberlike (liquid) to glassy state of amorphous polymers is paralleled by marked changes in viscosity, specific heat, thermal expansion coefficient, elastic modulus, within a narrow temperature interval, centered about the so called glass transition temperature (T_g). According to Fox and Flory [4,5] this transition is not a thermodynamic phase change, but is due to the decrease of the free volume of the amorphous phase below some small characteristic value that does not allow the free movements of polymeric chains inside the material.

The evaluation of free volume below T_g is even nowadays subject of argument. In past times a critical discussion was presented by Boyer [6] with reference to the free volume at T_g. The results can be summarized in Fig. 1, where specific volume is plotted versus absolute temperature. Suggestions according to point iii) foresee the reaching at $T=0$ K° of a specific occupied volume $V_O=V_{OL}$ (no further compressible) obtained with a liquid like behavior during the cooling.

The free volume fraction at any temperature should be (with reference to V_{OL}):

$$f = (V_L-V_{OL})/V_{OL} = \alpha_L \, T$$

at T_g it should be $f_g = \alpha_L \, T_g$.

According to Boyer [6] this value should be equal to 0,16; however his proposal is not experimentally acceptable. Another proposal [7] is that, by cooling down to 0° K, the system volume goes reversibility down to V_{OL} and comes back on increasing temperature, as if the system's behavior were glassy, that is following a straight line having a slope $\alpha_g V_{OL}$ (Fig. 1, line b). In this case it is easy to show that the free volume should be at any $T < T_g$, $f=(\Delta \alpha)*T$. At T_g it should be $f_g=(\Delta \alpha)*T_g$, where $\Delta \alpha = \alpha_L - \alpha_g$. Following this procedure, f_g was estimated on the basis of experimental data to be 0,113 for most polymers [6]. However by plotting versus $1/T_g$ a linear behavior could roughly be observed, but with a large scatter
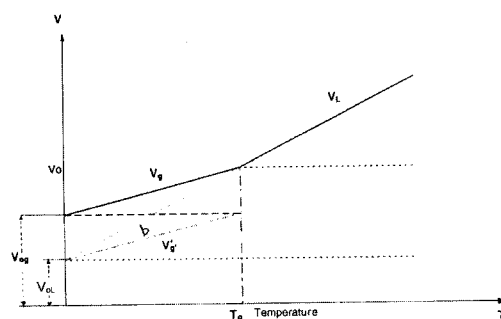

Fig. 1. Specific free volume vs. temperature according to Boyer [6].

of data.

Williams, Landel and Ferry [8] proposed a semiempirical equation relating f and T on the basis of the viscosity behavior of many amorphous polymers (see later), which is generally accepted above T_g. The WLF point of view supposes however that the free volume fraction is a constant below T_g, and equal to 0,025 for most polymers. This is a rough approximation indeed either indicated by Ferry [9] or found by many experimental evidences, such as mechanical dynamic tests.

What do we think about V_O? V_O should be recognized as the specific volume of the polymer inaccessible to the particular molecular motion that is interested by the considered mass transport mechanism. With this definition it is possible to cover, for example, viscous motions above T_g [f = $f_g+ \alpha_f \, \Delta T$ with $f_g = 0.025$], viscoelastic transitions below T_g, where mechanical dynamical transitions β, γ, δ can happen only if free volumes is higher than the size of the vibrating groups. As to diffusivity in membranes the choice of V_O is not easy to be defined mainly in the glassy state. We found by PAL that holes can exist much larger than the dimensions of the permeating gas; however in any case certain selectivity exists. We think that this behavior can be interpreted according to the solution-diffusion mechanism, considering a flux partition in series and parallel of the permeant so that the maximum resistance to the permeant is due to the membrane fraction, which is compact.

1.2. Free Volume in not Polymeric Substances

We start considering the studies of free volume in the case of small molecules. This is useful for basic considerations.

1.2.1. Free Volume and Viscosity

Is well known experimentally that both viscosity and specific volume V of liquids change with temperature and pressure [10]. Equation (1) shows that variations of specific volume and of free volume are of the same entity because the volume variation ΔV_0 is usually small: $\Delta V_f = \Delta V - \Delta V_0$.

Therefore density and viscosity, which depend on the molecular inter distance should be related to the free volume.

Doolittle [3] found this correspondence on the basis of experimental data in the case of hydrocarbon liquids, by using the empirical relation:

$$\frac{1}{\eta} = A \exp\left(-b\frac{v_0}{v_f}\right) \qquad (2)$$

where the free volume per molecule $v_f = v - v_0$ is the difference between the average volume per molecule and its van der Waals volume.

1.2.2. Diffusion Coefficient, Viscosity and Free Volume

Both viscosity and diffusion coefficient D were found related, also theoretically, in the case of simple liquid systems.

Stokes Einstein [11] equation: $D = \frac{kT}{3\pi a_0}\frac{1}{\eta}$, (where a_0 is the equivalent diameter of the molecule) gives the self-diffusion coefficient in a liquid made by simple spherical molecules. D is directly related to fluidity $(1/\eta)$.

Cohen and Turnbull [12] considered that molecular transport occurs in molecularly simple liquids by motions of molecules, envisioned as uniform hard spheres of volume v*, into voids characterized by a size equal or larger than the critical value v*. Each molecule (hard sphere) resides in a cage (volume v) bound by their neighbors. Fluctuation in density opens a hole, within a cage, large enough

($v \geq v*$) to allow the displacement of the molecule contained by it. Diffusion is verified when another molecule jumps into the hole left by the preceding molecule. Voids are simply formed by redistribution of the mean free volume. No energy is required for redistribution. The expression of the diffusion coefficient is expressed [12] by:

$$D = A \exp\left(-\frac{\gamma v^*}{v_f}\right) \qquad (3)$$

where $v_f = v - v*$, and γ is a numerical factor needed to correct for the overlap of free volume ($\frac{1}{2} \leq \gamma \leq 1$); $v_f = \frac{V_f}{N}$ is the mean free volume per molecule; factor A (A=g*a*u) is the product of a geometrical factor (g), the molecular diameter (approximately a), the gas kinetic velocity (u). D depends on temperature through u and through v_f; and depends on pressure through v_f.

Equation 3) has the form found empirically by Doolittle (eq. 2) for the fluidity $\frac{1}{\eta}$ of low molecular weight liquids.

1.3. Free Volume in Polymers

Williams Landel and Ferry [8] extended the Doolittle equation valid for simple liquids to polymers, proposing:

$$\eta = \tau E = A \exp\left(+\frac{B}{f}\right) \qquad (4)$$

where $f = V_f/V_g$ is the free volume fraction; with reference to the specific volume at T_g, A and B are constants; τ is the polymer relaxation time, E is the elastic modulus. The dependence of η on entanglements can reasonably be considered a structural factor included in A.

They propose for the free volume the expression (at constant pressure):

$$f = \frac{V_f}{V_g} = f_g + \alpha_f(T - T_g) \qquad (5)$$

which satisfies the experimental behavior of the amorphous polymers. V_g is the volume at the T_g ;

$\alpha_f = \alpha_L - \alpha_g$ is the difference between the thermal expansion coefficients of the rubber (liquid) and of the glass; f_g is the free volume fraction at T_g.

It is noteworthy to observe that W.L.F. formula relates the free volume to the relaxation time of the glass transition multiplied by the glass elastic modulus and therefore to the viscoelastic properties of the (amorphous) polymers. The reference temperature is the T_g; the W.L.F. equation can be used with confidence above the T_g. Notwithstanding this formula is semiempirical, it is very much used because it corresponds to the real behavior of most of the amorphous polymers above T_g. W.L.F. assume at T_g and at lower temperatures that $f_g = 0.025$ for amorphous polymers. If one substitutes eq. (5) into eq. (4) and applies the latter at the temperatures T and T_g, from the ratio between the two equations one obtains :

$$a_T = \frac{\eta}{\eta_g} = \frac{\tau}{\tau_g} = \exp\left[B\left(\frac{1}{f} - \frac{1}{f_g}\right)\right]$$

$$\log a_T = \frac{-C_1(T - T_g)}{1 + C_2(T - T_g)} \tag{6}$$

where $C_1 = B/(2.3\ f_g)$ and $C_2 = f_g/\alpha_f$.

The theoretical studies on diffusion, done using models of low molecular weight molecules assimilated to hard spheres, can be extended to systems made by macromolecules and by small amounts of small penetrant molecules mobile in the polymers, taking in consideration that their diffusion process is governed by the segmental motion of the polymer chains which opens the space needed for the diffusion jumps. Therefore it is justifiable to apply the results of studies concerning polymer segmental mobility (e.g. viscosity temperature relations) to the study of diffusion of small molecules in polymers.

This observation justifies the Fujita [13,14] expression of the mobility m_d of the diffusant relative to the polymer: $m_d = A_d \exp\left(-\dfrac{B_d}{f}\right)$. A_d and B_d are assumed independent of concentration and temperature. The thermodynamic diffusion coefficient is given by:

$$D_t = RT\ m_d = RTA_d \exp(-B_d/f) \tag{7}$$

The free volume fraction f is assumed as an additive function of the diffusant volume fraction Φ and of temperature, that is:

f(T, Φ)=f (T, 0)+ γ (T)$*\Phi$ where T is the temperature, Φ is the volume concentration of the penetrant, and γ is a factor which takes in consideration the swelling due to the interaction diffusant-polymer. This equation describes satisfactorily the concentration and temperature dependence of D_t for a number of polymers and organic penetrants above T_g, at atmospheric pressure and at a relatively low concentration ($\Phi < 0.15$). [15]

In the particular case $\Phi = 0$, equations (7) and (5) describe the diffusivity in pure polymers. In case pressure P is a variable we get:

$$f(T,P) = f_s + \alpha_f (T-T_s) - \beta (P-P_s) \tag{8}$$

where f_s is the free volume fraction in the reference conditions (generally $T_s = T_g$, $P_s = 1$ atm); α_f is the thermal dilatation coefficient of the free volume. β is the compressibility factor. Fujita equation is satisfactorily applicable when applied to large organic molecules in amorphous polymers but not when applied to small molecules as water in polar polymers. We found in the case of amorphous polyurethanes that eq. (7) can be used satisfactorily with different polymers and for low MW gases rather insoluble in the polymers: in this case equation (8) can be used above T_g to get the free volume fraction.

1.3.1. Diffusion Interpretation

Diffusion models are very important to study one of the main factors influencing permeability, that is diffusivity. The other one is solubility. Models of diffusion can be divided in two main classes: molecular models and free volume models. The first ones stress the importance of the detailed microscopic specific interaction polymer-penetrant and the change in the matrix due to this interaction. For each jump of length Λ moving a given molecule of a section area σ^2 in a polymer an energy must be given. For example as suggested

by Meares [16] $E_D = \sigma^2 \cdot \Lambda \cdot CED$, where CED is the cohesive energy density and E_D is the activation energy for diffusion. The hole of volume $\sigma^2\Lambda$ must be created (but it is recovered when the hole is closed after the jump). The energy of activation was found to increase linearly with the penetrant volume in a copolymer polyvinylchloride-vinyl acetate in the range from 7 to 17 kcal/mole corresponding to H_2 and CO_2 permeation [17]. By using the Meares equation however, too high values of jump distance are obtained (e.g. $\Lambda(CO_2) = 84\text{Å}$). In the reality the jump length should be controlled by the segment mobility of the polymer, which depends from the rigidity factor C_∞ of the chain [18]. However in the rigid system bisphenol A-polycarbonate the activation energy is low and changes only from 5 to 8 kcal/mol when using respectively N_2 and CO_2 as penetrants.

Other remarkable molecular models are that due to Di Benedetto and Paul [19] and that due to Brandt [20].

The diffusion activation energy is postulated to be the energy needed for causing a volume increment of the hole to reach the volume needed to allow the passage of the molecule. One of the most interesting molecular model is the Pace and Datyner model [21] which incorporates features of references [19] and [20]. The transition through the Tg is supposed to increase only the hole dimensions but not the number of cavities.

1.3.2. Free Volume Modeling

Free volume models are based on phenomenological equations [22]. On the basis of the specific volume behavior of polymeric amorphous materials versus temperature and of their mechanical properties (pioneered by Kovacs [23] and Struik [24]) it is possible to say that at $T>T_g$ the equilibrium state, in terms of PVT variables, is easily and promptly reached, while at $T<T_g$ the physical variables of the polymers are function of time; T_g itself is a function of time.

Fig. 2 illustrates the previous considerations: for $T<Tg$ the specific equilibrium volume V is lower than the experimental volume determined on laboratory short time scale. By leaving the sample
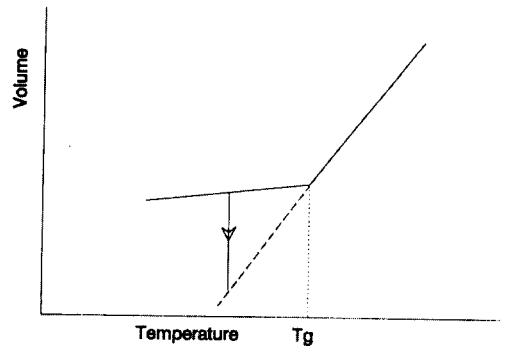

Fig. 2. Specific volume of amorphous polymer vs. T_g.

for a long time the experimental volume decreases going towards the equilibrium value.

Various attempts were done to express the specific volume and the free volume at equilibrium as a function of temperature and pressure.

A very good equation of state for polymers was proposed by Simha and Somcymsky [25]. They applied the statistical mechanical theory on a cell model in the solid-like approximation. P. Flory [26], Sanchez and Lacombe [27], Di Benedetto and Paul [19] also proposed other equations of state.

The Simha-Somcynsky state equation which is valid both above and below Tg is:

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \left[1 - y(\sqrt{2}y\tilde{V})^{-\frac{1}{3}}\right]^{-1}$$
$$+ \frac{y}{\tilde{T}}[2,002(y\tilde{V})^{-4} - 2.409(y\tilde{V})^{-2}]$$

$$(9)$$

$$\tilde{P} = \frac{P}{P^*} \; ; \; \tilde{V} = \frac{V}{V^*} \; ; \; \tilde{T} = \frac{T}{T^*}$$

$\tilde{V} \; \tilde{P} \; \tilde{T}$ are the reduced variables.

$P^* \; V^* \; T^*$ are the characteristic scaling parameters for each polymeric material: they are usually deduced by fitting P, V, T data; y is the fractional occupancy of the cells: $y=v_o/v$.

The fractional free volume is $f=(v-v_o)/v=1-y$; f is the excess free volume fraction., and v is the volume per segment of the polymer.

Since at equilibrium free energy F is minimum, by minimizing the free energy another independent
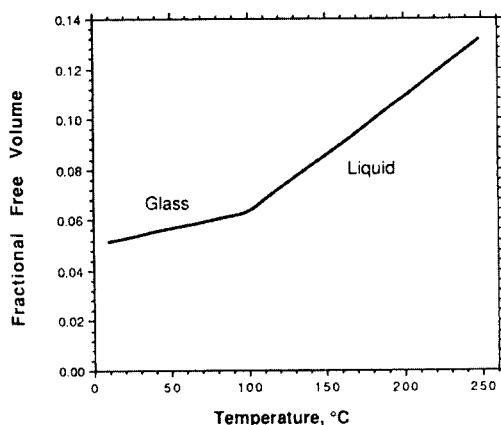
Fig. 3. Free volume for polystyrene at 1 bar pressure computed according to Simha-Somcynsky [22]. The free volume has been computed for both liquid state (above 373 K) and for the glassy state. Note that the free volume of the glass is not independent of temperature.

Fig. 4. Distribution curves of free volume evaluated according to Simha at different temperature [22].

equation involving the variables y, V, is obtained [28] that is:

$$\left(\frac{\delta F}{\delta y} \right)_{T,V} = 0 \qquad (10)$$

For given values of P and T the two previous equations can be solved for y and V.

The solution procedure is reported in Fortran language [28].

Simha has shown that for polymers not far away from equilibrium the previous procedure gives an approximate value for y not far from the true value [29].

For system not at equilibrium equation (10) does not hold; in this case a good approximate value of y can be obtained from equation (9) provided experimental values of V at constant P are used.

For quenched glasses as a first approximation it is possible to calculate V approximately by using the following equation:

$$V = V_g[1 + \alpha_g(T - T_g)]$$
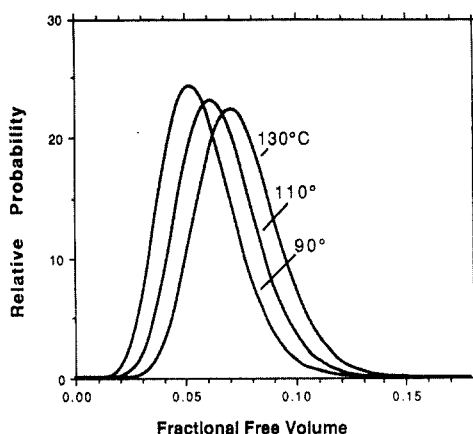
where α_g is the thermal expansion coefficient for

polymer glassy state (Fig. 2).

Fig. 3 shows [28] the free volume fraction at 1 bar of polystyrene (PS) both in the liquid and the glassy state evaluated from Simhas' model. According to this model, but also with the experimental data, the free volume of the glassy state depends on temperature. This is better than the assumption of the W.L.F theory of free volume, which considers the free volume as constant below the glassy state. Simha equation can also be used to calculate the thermal fluctuations of the mean free volume at different temperatures (Fig. 4).

2. Non Equilibrium Processes in Polymers

State equations cannot be used in studying the evolution of free volume with time: they can be used indeed only to obtain the equilibrium values (or ∞ time limit values).

A priori molecular dynamic calculations of the kinetics of a given physical processes evolution (as : volume-time, enthalpy-time and so on) are not presently available.

Free volume time evolution can be used semi-empirically to compute the kinetic of a process, by relating free volume variation and relaxation rate of the studied property (e. g. viscosity or elastic

modulus or even diffusivity).

Relaxation time is related to viscosity, specific volume and free volume changes.

Kovacs first [30] has found that after cooling a polymer from $T_o > T_g$ to $T_1 < T_g$, the isothermal volume v contraction with time t can be followed according to the following empirical relation:

$$v = f[\log(t)]$$

Different isotherms can be shifted and superposed simply by abscissa translation; the shift factor a_T is essentially the same as that deduced from viscoelastic studies that relate elastic modulus with time at different T [31]. This suggests that similar molecular processes are involved both in stress relaxation and in isothermal volume contraction of glasses.

The relaxation rate (or reciprocal of the relaxation time) for viscoelastic measurements can be written, according to W.L.F., equation (6) as:

$$\tau^{-1} = \tau_g^{-1} \exp\left[2.3 C_1 \frac{T - T_g}{C_2 + (T - T_g)}\right] \qquad (11)$$

where C_1 and C_2 are universal constants for all amorphous polymers.

Since the Simha free volume f changes practically linearly with temperature (see Fig. 3), $T - T_g$ in the previous equation may be replaced by $f - f_g$; a good approximation [32] is:

$$T - T_g = \frac{f - f_g}{f^*} T^*$$

where f^* is the reference free volume at $T*$. The straight-line slope of $f[T]$ (Fig. 3) is assumed as $f*/T*$.

The preceding equation (11) after simple replacement, becomes:

$$[\tau(f)]^{-1} = \tau_g^{-1} \exp\left[2.3 C_1 \frac{(f - f_g)}{C_2 \dfrac{f^*}{T^*} + (f - f_g)}\right]$$

This equation is a general relationship between

relaxation rate of viscoelastic properties and other related properties and free volume; it is assumed to relate average relaxation time and average free volume, some authors say irrespectively of whether or not the material is in equilibrium. In the study of glassy polymers it is important to find a model describing how free volume changes with time. Non-exponentiality (because of relaxation time distribution) and non-linearity with time characterize the glass transition kinetic. Kovacs multiparameter model [33] was the first to be proposed: it is non-linear and non-exponential, but other models are often used today. For example Moynihan [34] model is phenomenological and expresses the volume variation with time according to:

$$\phi(t - t_1, t) = \frac{V - V_1}{V_\infty - V_1} = \exp\left[-\left(\int_{t_1}^{t} \frac{dt}{\tau_0}\right)^\beta\right]$$

$$\qquad (12)$$

This function is said relaxation function and describes well the behavior of volume after a sudden step in temperature. Index 1 is referred to the beginning of the relaxation; τ_0 is the relaxation time and depends on the activation energy Δh needed for the mobility of the polymer segments:

$$\tau_0 = A \exp\left[\frac{x \Delta h}{RT} + \frac{(1 - x)\Delta h}{RT_f}\right] \qquad (13)$$

The coefficient β depends on the distribution of τ_0; x is the fraction of the activation energy depending on T and (1-x) is the activation energy fraction depending on structure.

The fictitious temperature T_f, which appears in equation (13) represents structure (due to chain conformation), and it is determined by solving the integer differential equation:

$$\int_T^{T_o} \frac{\delta(V - V_g)}{\delta T} dT = \int_{T_f}^{T_o} \frac{\delta(V_e - V_g)}{\delta T} dT$$

where V_e is the volume at equilibrium.

One starts from the experimental data $\phi(t')$ (eq. 12) and using equation (11) and (13), one finds by optimization [35] the parameters x, Δh, A. The
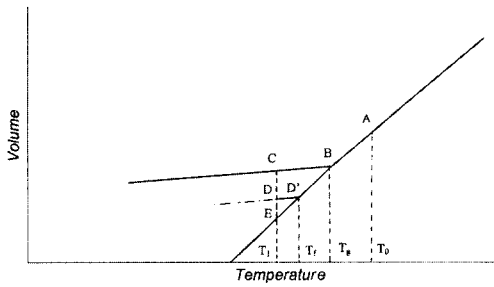
Fig. 5. Evaluation of glassy polymer structure evolution during aging by means of the fictitious temperature T_f.

product $(1-x)$ Δh is a direct measure of the physical structural aging [35].

T_f is the temperature (see Fig. 5) which describes the evolution of the polymer structure during aging. For example cooling down an amorphous polymer from T_o to T_1, volume changes, passing through point A, B (T_g) and C where cooling stops and relaxation begins at time t_1, and goes on in a isothermal way (at T_1). At time t the relaxation function ϕ has a certain experimental value while the instantaneous volume V (t) is, e.g., at point D. V_D is the same which should be generated by an hypothetical (fictitious) cooling down through the way A, B, D'. D' is the last point along this way characterized by equilibrium conditions: its abscissa is T_f. T_f is changing from T_g to T_1 during the isothermal volume variation (from C to E). In conclusion T_f describes univocally the fictitious equilibrium state of the glass, while relaxation time goes on.

V_D must be measured experimentally. However as a first approximation due to the rapid cooling in the range T_g–T_1, the volume V_D can be calculated simply by equation:

$$V_D = V_{D'}[1 - \alpha_g(T_g - T_1)]$$

where the relaxation effects have been omitted. When $V_{D'}$ is known the state equation of Simha Somcynski can be used to calculate any V_D values and the corresponding occupancy y and the corresponding excess free volume f=(1−y).

3. Diffusion and Free Volume

Vrentas and Dudas proposed a complex formulation of the free volume theory based on Cohen and Turnbul and Fujita models, completed with the relation between the mutual diffusion coefficients and the friction coefficient and with the Flory thermodynamic and the Bueche entanglement theory [36]. Duda's theory gives an overall global perspective and describes diffusion both above and below T_g through the presumption that transport is controlled by the availability of free volume within the system.

In this presentation other models, such for instance those based on statistical mechanics and which give a local perspective as the Pace and Datyner model [21], will not be considered.

3.1. Above T_g

Wrentas and Duda proposed for the self diffusion coefficient of the penetrant the following expression:

$$D_1 = D_{01}\exp\left[\frac{-\gamma(\omega_1\widehat{V}_1^* + \omega_2\widehat{V}_2^*\xi)}{\widehat{V}_{FH}}\right] \quad (14)$$

where: γ is a numerical factor (between 0.5 and 1) that has been introduced to account for the overlapping among neighboring free volume elements (i.e. volume shared by neighboring molecules) ; ω_1 and ω_2 are the weight fractions of the penetrant and polymer respectively; $\widehat{V}_1^*$ and $\widehat{V}_2^*$ are the minimum specific free volume needed for a diffusive jump of the penetrant (component 1) and of the polymer (component 2); $\xi = V_1^*/V_2^*$ is the ratio between the critical molar free volume required for a jumping unit of the two species: the penetrant (1) and polymer units (2); $\widehat{V}_{FH}$ is the free volume per gram of all individual jumping units in the solution. The number of parameters needed for calculations of D_1 is very high (it is ten after grouping).

At the limit of a trace amount of penetrant, after some transformations, one obtains:

$$D_1 = D_{01}\exp\left[\frac{-2.303C_1C_2\xi}{C_2 + (T - T_g)}\right] \quad (15)$$
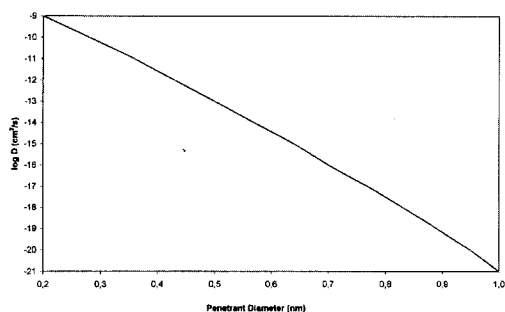
Fig. 6. Diffusion coefficient of various gases in PVDC amorphous polymer at 298K as a function of gas permeant diameter according to Vrentas and Duda.

where C_1 and C_2 are the universal constant of the W.L.F. equation; D_{01} and ξ are in this case the only two adjustable parameters. Equation (14) is independent from time because the system is, above T_g, always in equilibrium. Fig. 6 shows the diffusion coefficients, calculated according to equation (15), of various gases, having different diameters, in completely amorphous PVDC at 298° K: parameter ξ is an indicator of the size of the penetrant because V_2^* is similar for all the polymers.

3.2. Below T_g

The glassy state is a non-equilibrium state. As amorphous rubberlike polymers are cooled down and pass through T_g, polymer segments do not maintain sufficient mobility to reach equilibrium within the ordinary time scale. An extra free volume is generated which is continuously reduced over time until the minimum energy is reached. Duda assumes that diffusivity is again expressed by eq (14), but correcting the available free volume with a factor Q (eq. 16) which accounts for the concentration dependence of the penetrant, and with the substitution of $\hat{V}_{FH}$ with the term $\hat{V}^g_{FH}$ (which specifies the glassy state and is the hole free volume of the mixture). Therefore:

$$\hat{V}^g_{FH} = \omega_1 \hat{V}_{FH1} + \omega_2 \hat{V}^g_{FH2}$$

The term V^g_{FH2} is the sum of the excess free volume V^{ex}_{FH2} of the polymer and of the free

volume at the equilibrium V_{FH2}. The excess free volume is expressed by:

$$\hat{V}^{ex}_{FH2} = \hat{V}^0_2(\alpha_g - \alpha_r)(T - T_g)$$

where $\hat{V}^0_2$ is the specific volume of the equilibrium polymer at T_g, while $(\alpha_g - \alpha_r)$ is the difference between the polymer thermal expansion coefficients of the glass and rubberlike states, the first one in the real (not equilibrium) conditions, the second one at the equilibrium because rubber state equilibrium is easily reached, due to the high mobility of the segments. Introducing in $\hat{V}^g_{FH}$ the contributes due to $\hat{V}_{FH2}$ and $\hat{V}^{ex}_{FH2}$, the Vrentas Duda equation becomes:

$$D_1 = D_{01} \exp \left[\frac{-\gamma(\omega_1 \hat{V}_1^* + \omega_2 \xi \hat{V}_2^*)}{(\omega_1 \hat{V}_{FH1} + \omega_2 \hat{V}_{FH2}) + \omega_2 \hat{V}^0_2(\alpha_g - \alpha_r)(T - T_g)} \right] Q$$

(16)

This expression introduces two more parameters (Q and $\hat{V}^{ex}_{FH2}$) which can be estimated, in our opinion, only by optimization: in the reality these parameters are function of the relaxation time of the compaction process and of the time of aging. Until now only a few not systematic studies were done on diffusivity or permeability dependence on aging time of glassy polymer so no conclusion can be given about the predictive power of the Vrentas and Duda equation, which, at this time, appears one of the most complete diffusivity approaches. Numerous studies on the contrary were done on other properties, such as specific heat [35] and compliance [23,24]. Only numerical calculations [37] and rigorous experiments will allow to verify the models of diffusivity.

We believe that a connection could be done with aging time introducing in (16) the relaxation function:

$$\phi(t) = \frac{\hat{V}_2(t) - \hat{V}^0_2(t=0)}{\hat{V}_{2e} - \hat{V}^0_2(t=0)} = \exp\left[-\left(\int_0^t \frac{dt}{\tau} \right)^\beta \right]$$

where τ is the relaxation time and β is a factor, which takes account for the relaxation time distribution.

This suggestion could give some help for introducing the relaxation effects also in the diffusivity studies.

Duda's model, even in its simplified form which does not consider time dependency, differs from the well known dual mode theory of gas sorption and transport (Barrer, Vieth [38]), based on the existence of two distinct solute populations within the polymer, one dissolved according to the Henry solution mechanism, the other one residing in pre-existing voids in the glassy polymer. The solubility of the sorbed molecules is given (cc STP/ cc polymer) by:

$$C = k_d P + C'_H \frac{bP}{1 - bP}$$

where C'_H is the saturation limit, b is the hole affinity constant (atm^{-1}) k_d is the Henry dissolution constant (cc STP/ cc polymer atm). Paul has developed [39] an expression for the time lag based on the dual sorption model.

$$\theta_L = \frac{l^2}{6D}[1 + Rf(y)] \qquad (17)$$

where l=thickness, R=C'$_H$ b/k$_d$, y=bP$_1$.

P$_1$ is the upstream pressure; (downstream pressure P$_2$=0)

The expression of f(y) is :

$$f(y) = 6y^{-3}[0.5y^2 + y - (1 + y)\ln(1 + y)]$$

f(0)=1; f(∞)=0.

Calculation of θ_L can be done by measuring the slope of Q$_r$, the permeate volume under steady state, versus time at different pressures. C'$_H$, b and k$_d$ are calculated from equilibrium sorption data. The diffusion coefficient can be calculated according to equation (17).

4. Other Considerations on Free Volume

Some author defines the f.v. as not localized:

mobile holes should exist inside the condensed matter: viscosity of liquids is well interpreted by this model.

For an amorphous polymer Kaelbe's [40] definition is an "interstitial free volume" or a free volume uniformly distributed inside the polymer, not useful for molecular transport, and a "hole free volume" or a discontinuous distribution of f.v. which consists of holes in the polymer; only this f.v. seems to be involved in the molecular transport. Bueche [41] suggested that the number of holes in a polymer is a constant, at constant temperature and pressure, and moreover that their position changes with time, owing to the anharmonic oscillation of polymer chains; that is, the holes can move freely inside the bulk polymer as no energy changes are required for their redistribution.

When a hole opens near a molecule of a penetrating gas, and is as large as, or larger than, the molecule, this may move into the new hole. However a molecule may move into a hole of smaller size if it has a sufficient energy to distort the polymer segments, enlarging the hole to its own volume.

In the first case, the diffusion process should be determined only by the probabilities that a hole of sufficient dimension opens next to the diffusant molecule and that the molecule moves in the direction of the hole. In the second case, there is a further consideration: whether the molecule has a sufficient energy to enlarge the hole to its own volume.

The previous analysis allows one to say that a diffusion model in a polymer, based on the f.v. hole model, must consider the energy distribution function of the penetrating molecules and the distribution function of hole volumes in the polymer. Moreover the question of the shape of the holes is still unsolved. All the theoretical models assume spherical holes with unimodal distribution. Actually, there are several possibilities: are the holes, particularly in glassy polymers, isolated or interconnected with a system of channels, like the cages in zeolites? To what extent is the spherical model effective in describing the shape of the holes? And basically do the holes have a physical reality?

As mentioned above, William, Landel, and Ferry [8] proposed their well-known W.L.F. equation for the evaluation of the f.v. fraction for polymers in a rubber state, that is, at a temperature higher than that of glass transition. Their approach cannot be used to demonstrate hole existence. It is based on the difference between the expansion coefficient of the polymer in the rubber and in the glassy state. Simha-Somcynsky [25] developed a f.v. theory based on the lattice-cell model. They proposed an equation of state for the polymers and evaluated the "fractional free volume" as "excess free volume" and determined the mean f.v. in polymers. Litt [42] defined the f.v. in polymers above T_g on the basis of "passive motion", "activation", and "activated diffusion". He proposed an equation of state for rubbery polymers that can be used to obtain the gaseous diffusion coefficient in a polymer, in terms of molecular diameter of the permeating gas and of the polymer microscopic bulk modulus. From the correlation of the self-diffusion coefficient, Litt estimated the values of the mean effective size of the holes in polyethylene and poly (vinyl acetate) for different penetrants. It is important at this moment to try to describe the physical existence of the "holes", their size and their distribution by experimental techniques.

As far as the direct experimental determination of the free volume is concerned positron annihilation spectroscopy (PAS) is a relatively simple experimental technique that has given results consistent with theoretical evaluation (see cages in zeolites). Since the 1980s, PAS has been proposed as a suit-able technique for the investigation of the f.v. hole size and hole volume distribution in polymeric materials [43].

5. Highlight of the Free Volume Experimental Techniques

Many, and quite different, techniques have been proposed to estimate the free volume of polymers. Indeed one can measure the total free volume, the cage volume, and the distribution function of the cage volume.

Each technique investigates specific properties of the matter such for instance the density variation with temperature, the mobility of probe molecules introduced or bound to the polymers, the stimulated rotational motion of probe molecules, the density distribution function of electrons, the life time of positron, etc. The techniques are complementary in every respect.

5.1. Dilatometric Technique

The specific volume of polymers changes vs. temperature. This change is different either the polymer is in an equilibrium state, liquid or rubbery state, or in a quasi equilibrium solid state (glassy state). At the glass transition temperature there is no change in volume but only an abrupt (discontinuous) change of the slope of the volume vs. temperature. This change in slope is strictly bounded to the free volume variation owing to glass transition. (Fig. 1).

The apparatus that studies the dimensional change of a sample is the dilatometer. [44]

There are two basic types of dilatometers: linear dilatometers, used when it may be assumed that the shape of the test sample remains unchanged, such as rigid solids, glassy or semicrystalline polymers etc., and volume dilatometers, used without limitation.

It is possible to measure linear thermal expansion coefficient of the order of 10^{-4} (K^{-1}); the accuracy of volumetric dilatometers is 3×10^{-4} ml^3/g.

With this techniques it is possible to determine the total free volume and its variation with temperature if the occupied volume is known (equation 1).

5.2. Photocromic Technique

It is based on the reversible photochemically induced trans-cis isomerization of a chromophore present in a molecule used as label or probe. The trans and cis species have different absorption spectra and the change may be observed by UV-Vis spectroscopy. The absorption of the light over a range of wavelengths induces in the chromophore a trans-cis isomerization only if there is in the ambient where the chromophore is situated a

Table 1. Photocromic Probes, Appropriate Wavelength λ, and Estimated Isomerization Volume

Probe name	Symbol	λ (nm)	trans. vol. (A^3)	isomer. vol. (A^3)
azobenzene	AZB	320	144	127
p-azotoluene	PAZT	336	170	193
stilbene	SB	311	151	224
4,4´-dinitrostilbene	DNS	358	187	285
4,4´-diphenylazobenzene	DPA	362		356
4,4´-diphenylstilbene	DPS	340	270	575

sufficient free volume, and critical volume, which allows the isomerisation. So there is a strictly relation between the size of the chomophore and the volume cage inside the polymer. The most commonly used photochromic molecules are azobenzene derivatives [45-47].

By using photochromic molecule of different sizes, it is possible to estimate the distribution of free volume fraction in glassy polymers.

The fraction of cis isomer present at the photostationary state, Y, is related to the absorbance A, at an appropriate wavelength λ (see Table I), and to the molar absorptivity ε_{cis} and ε_{trans} at the same wavelength by the equation:

$$Y = \frac{1 - A/A_{trans}}{1 - \varepsilon_{cis}/\varepsilon_{trans}}$$

A_{trans} is the initial absorbance before irradiation.

If Y_S and Y_F are the extent of isomerization at photostationary state in the model solvent and in the polymer material, respectively, then the fraction of local free volume in polymer material, Φ, large enough for isomerizing the probe can be defined as:

$$\Phi = Y_F/Y_S$$

This implies that the difference between solvent and polymer in isomerizing ability is due to the local free-volume restriction present in the polymer.

The methods for calculating the volume required by probe for isomerizing have been presented in [48]. It has to be pointed out the evaluation of this volume is one of the critical point of the method.

The volume required for probe isomerization is the hard volume calculated according to van der Waals radii, as tabulated by Bondi [49] or other authors, plus an extra volume needed for the rotation. Indeed the volume required for isomerization consists of two components: the volume twist and the volume swept by the van der Waals area of the molecule; a good approximation for the extra volume evaluation is to sum this two contribution even if there is probably some overlap.

With this technique it is possible to determine the local free volume fraction and, by using probes with different volume, the cumulative distribution of local free volume fractions.

5.3. Fluorescent Spectroscopic Technique

This technique uses, as probe, a suitable fluorescent molecule which on absorbing light is excited from its ground state to an high energy state. Two pathways are available to the probe for releasing the adsorbed energy and to return to its ground state:

a) A thermal, or non-radiative, mechanism in which the excess energy is redistributed to various degrees of freedom of the molecules and from this to the near neighboring molecules.

b) A radiative mechanism involving photon emission and fluorescence.

If the probe has no degree of freedom since rotational motion is hindered by a lack of molecular mobility, the thermal pathway is not allowed and therefore the radiant mechanism becomes dominant.

Loutfy [50] for the first time observed a sharp

rise in the fluorescence as viscosity increases during the polymerization of PMMA: the fluorescence of the probes ([p-(N,N-dialkylammine) benzylidene]malonitriles) increases gradually (1.5 times) as the conversion increases to 60%; a further increase in conversion causes a sharp increase in fluorescence (20-40 times) A sudden increase in the fluorescence occurs when the polymerized monomer approaches to the glassy state. Since during this process there is a strong increase in the viscosity and therefore a reduction in the total free volume and in the size of the free volume holes, a decrease in molecular mobility has to be expected and consequently an increase of the fluorescence.

For the intensity I of the emitted fluorescence radiation holds the following relation:

$$I = K \, I^{\circ} \, C \, \varepsilon \, \xi$$

K is a proportionality constant; I° the intensity of the incident beam; C the concentration of the probe in the sample; ε the molar absorption coefficient; ξ the quantum yield.

Usually in a sample both the thermal and radiative mechanism occurs with different rates. Let k_r and k_{nr} the radiative and non-radiative decay rate constants, respectively. The fluorescence yield, κ_F, may be defined as:

$$\kappa_F = k_r / (k_r + k_{nr})$$

The fluorescence yield approaches unity in rigid system, such as polymer at low temperature. The radiative rate constant, k_r, may be calculated from the integration of the absorption spectra; moreover this value is related to I/I°.

The non radiative decay rate, k_{nr}, may be evaluated from the previous equation:

$$k_{nr} = k_r \, (1/k_F - 1) \qquad (18)$$

The importance of free volume v_f and free volume cage ν_f in molecular relaxation processes of excited probe is well known. Therefore it is possible to relate k_{nr} to the hindered rotation movements and excited state conformation to the free

hole volume by the following relation:

$$k_{nr} = k_{nr}^{\circ} \, \exp(-\nu^{\circ}/b \, \nu_f) \qquad (19)$$

where k_{nr}° is the intrinsic rate of molecular relaxation; ν° the van der Waals volume of the probe; b is a scale constant to change the van der Waals volume to the effective volume needed by the probe to perform internal movements. From equation (18) and (19) one gets:

$$\frac{k_F}{1 - k_F} = \frac{k_r}{k_{nr}^{\circ}} \exp\left(\frac{b\nu_f}{\nu^{\circ}}\right)$$

Loutfy plotted $\log(k_F)$ vs. $1/v_f$ for a mixture polymer/monomer (polymethylmethacrilate (PMMA)/ methylmethacrilate (MMA)) and obtained a good linear relationship. The free volume v_f was obtained according to the general expression of Bueche [51]. For certain aspects this technique can be considered similar to photocromic technique and gives similar results. Different studies on physical aging associated with free volume change with aging time were done in case of many glassy polymers [52].

5.4. Electron Spin Resonance Spectroscopy (ESR)

ESR, also known as electron paramagnetic resonance (EPR) spectroscopy, studies the spin resonance of unpaired electrons present in organic or inorganic free radicals. The resonance condition of an unpaired electron in an ESR experiment is:

$$\Delta E = h \nu = g \beta B$$

Where ΔE is the separation of the spin resonant energy levels produced by the application of the external magnetic field B, β is the Bohr magneton and g is called nuclear factor. Most of ESR operate at a fixed frequency and record an ESR spectrum by sweeping the external field B.

The interaction of the external magnetic field with the magnetic field arising from nuclei with a magnetic spin gives rise to a local magnetic field B_{loc} which splits the individual resonance lines into

their components, according to an hyperfine coupl-ing constant **a** (G). Therefore instead of a single line the spectrum shows two or more lines (2I +1 lines where I is the nuclei spin) each one separated by the coupling constant **a** and centered on the field determined by g.

Crystalline or molecular solids are structurally anisotropic systems therefore also the local magnetic field is anisotropic and hence the g-factor depends on the orientation of the sample relative to the direction of B.

The hyperfine structure of an ESR spectrum is a kind of fingerprint of a radical and its environment since the splitting depends on the magnetic nuclei present in the vicinities.

Radical molecules added, as label or probe, to polymer solids and melts behave as a sensor of the local motion of polymer segments. By means of ESR technique it is possible to study the molecular relaxation, in the frequency range 10^6-10^{12} Hz and to get information, from the movement free-doms of labels or probes, on molecular dynamics and microstructure of polymers.

Even if any kind of stable radical may be used as label or probe, the complexity of time-dependent contributions to linewidths of ESR spectra makes unpractical the use of most radicals and only the nitroxide have been employed widely and success-fully for their extraordinary stability, the solubility in polar and non polar media, the wide diversity of molecular structure. The nitroxide radicals may be covalently bonded, as label, to polymer chains or dispersed into the polymer matrix, as a probe. Ni-troxide free radicals give rise to an easily iden-tifiable three line pattern and they have a rotational correlation time (τ_R) in the range 10^6-10^{11} (s). Really the development of ESR technique based on labels or probes is strictly bounded to the use of nitroxides.

The analysis of the ESR spectra of label or probe samples give information on their rotatory and translatory mobilities, and from this motional freedoms it is possible to get information on their environment and microstructure of the polymer. [53-59]

5.5. Small Angle-X Ray Scattering (SAXS)

An incident X-ray beam at very small angles, typically less than 2°, is scattered by the electron "clouds" surrounding the atoms in the matter. This scattering occurs with a wavelength of CuK of 1.542 Å. That scattering is due to the variation in electron density from one point to another in the material. It has to point out that this small angle scattering has no relation on the inhomogeneities of atomic dimension that give rise to wide-angle diffraction. Indeed only the fluctuation of electron densities, in a range 30-1000 Å, determines the nature of the small-angle scattering. Therefore from the standpoint of small-angle the electron concentration in a crystal structure may be consi-dered as a continuous distribution of electrons.

The theory of the scattering due to density fluc-tuations in an ensemble of identical particle states that the scattered intensity extrapolated towards zero scattering angles is proportional to the fluc-tuation of the particle density [60-61].

The density fluctuation is defined as the ratio of the variance to the mean:

$$\Psi(v) = \frac{\langle (N - \langle N \rangle)^2 \rangle}{\langle N \rangle}$$

where N are the number of particle in a reference volume v, of a certain size and shape. As v increases ($v \rightarrow \infty$) the function $\Psi(v)$ converges to a finite value $\Psi(\infty)$, that is called thermodynamic limit.

By considering an X-rays incident beam and the electrons as the scattering media, the scattering intensity I (in electron unity) is bounded to the electron density fluctuation, by the following equa-tion:

$$\lim_{\vartheta \to 0} \frac{I}{N} = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \Psi_{el}$$

Where N is the number of electrons in the irradiated volume v. Function Ψ_{el} can be measured through the intensity of X rays scattered by the unit volume [66].

If the sample is composed of N_M identical par-

ticles (molecules) with Z_M electron per particle, the particle density fluctuation Ψ_M is given by:

$$\Psi_M = \frac{\Psi_{el}}{Z_M}$$

The particle density fluctuation Ψ_M, in the case of one component fluid, is related to the isothermal compressibility χ_T :

$$\Psi_M = \rho_M k_B T \chi_T$$

where ρ_M is the particle density, k_B the Boltzmann constant, T the absolute temperature. It has been shown [62] that Ψ_M is composed of two terms: the first one due to pressure fluctuations, and proportional to the adiabatic compressibility χ_S, and the second one due to the entropy fluctuations, and it is proportional to ($\chi_T - \chi_S$).

For crystalline solid, if harmonic approximation is valid, the total density fluctuation is entirely due to lattice vibrations.

In the case of non-equilibrium state, e.g. a super-cooled liquid, the value of Ψ_{el} depend on how the average value <N> of the particles (electrons or atoms) has been calculated, that is if <N> is an average value with respect to time or to space. If the reference volume is fixed in the space and the number of the particle inside it changes with time, for time $t \rightarrow \infty$ it is possible to define a time average value $<N>_t$; on the other end if the reference volume v is moved around in the sample and the number N of particles falling within the volume fluctuates, it is possible to evaluate a space average value $<N>_S$. While in equilibrium conditions the time and space average are equivalent (ergodic theorem) in non equilibrium conditions the fluctuations in time of the particle density is smaller than the fluctuations of the particle density in space (at a given time).

In the case of X-ray diffraction the average is basically a space average.

For material in glassy state, a disordered frozen-in state, the time average would be zero, at least for an interval time corresponding to a normal experimental run, while the space average is different

from zero [63-67]. SAXS is useful to follow the physical aging and pressure densification in polymers. Curro and Roe [67] have shown that Ψ (v) is related to the weight average volume of an hole $<f_w>$, by the expression :

$$\Psi(v) = \rho_E \cdot \langle f_w \rangle \frac{\phi}{(1-\phi)^2}$$

where ρ_e is the overall electron density, and ϕ is the volume fraction of the holes.

5.6. Positron Annhilation Spectroscopy (PAS)

A positron (e^-) injected into a non-metallic solid from a radioactive source, after a fast slowing-down requiring some p-second at most [43] becomes thermalized and may interact with the electrons of the medium. Owing this interaction the pair e^+e^- annihilates with production of two- or, much more rarely, three-photons. However, before this last event, the positron can be involved in a short although complex history: for instance, it can be annihilated into microscopic domains characterized by different electron densities (amorphous and crystalline regions, different kind of defects, etc.). Moreover, it can form, with an electron of the medium, a bound system that is called positronium (Ps). The result is a positron annihilation spectrum with different components, whose study is potentially useful to obtain information on the structure of the host medium. In the case of the lifetime spectroscopy (PALS), the most common positron technique, a timing spectrum is typically formed by three components, corresponding to annihilations from *ortho-Ps,* from free positrons and from *para-Ps* (in order of decreasing lifetime). Details of this technique will be given in the second part.

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