Intermolecular free volumes and intramolecular defects in \( n \)-alkanes

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Abstract. Ortho-positronium lifetime and intensity were measured as a function of temperature for a homologous series of normal alkanes. Free volume shape and concentration of defects are different for various phases. The lifetimes observed were compared with model predictions for an empty gap in the crystalline structure (at low temperatures), finite cylinder or cuboid (rotator phase) and sphere (liquid). The role of intramolecular defects (nonplanar conformers) was discussed. A distinct difference in temperature dependence of lifetime spectra when melting is preceded by the rotator phase or C phase was found. Attention was paid to equality of lifetimes in the rotator phase and in liquid in a broad range of carbon chain lengths.

1. Introduction

Positron annihilation lifetime spectroscopy (PALS) is a method of investigation of “free” volumes in condensed matter, basing on the effects of trapping positrons or positronium in such low electron density spaces. In metals, \( e^+ \) lifetime value serves to identify the structural imperfections, like vacancies, dislocations, vacancy clusters, etc. In insulators, trapped \( \text{ortho-Ps} \) lifetime allows to estimate the trap sizes. In 1972, Tao [1] proposed the relation between \( \text{ortho-Ps} \) lifetime \( \tau \) and the radius \( R \) of “bubble” forced by \( \text{Ps} \) in the liquid. Naturally, it was assumed that the geometry of free volume was spherical. The final form of that “spherical model” was given by Eldrup [2] and applied to the case of vacancies in plastic crystals. Such crystals are composed of molecules not too far from sphericity, thus accepting the Tao’s idea seems a good approximation. However, already in the series of papers by Eldrup et al. [3,4] the radius has no the meaning of a real sphere, but rather that of Wigner-Seitz, i.e. of an equivalent sphere with the volume equal to that of the elementary crystal cell divided by the number of molecules per cell. The Tao-Eldrup model found soon a wide application to free volumes in polymers, which certainly are neither spheres, nor prisms. In the Tao-Eldrup equation

\[
\tau = 0.5\text{ns} \left[ 1 - \frac{R}{R + \Delta} + \frac{1}{2\pi} \sin \frac{2\pi R}{R + \Delta} \right]^{-1}
\]

\( R \) is an equivalent radius of a sphere giving the same \( \text{ortho-Ps} \) lifetime as observed for real free volume (\( \Delta \) means the parameter describing penetration of \( \text{Ps} \) wave function into the bulk matter; \( \Delta = 0.166 \) nm). The \( \text{ortho-Ps} \) decay rate in the bulk in this equation and the next one is assumed 2 ns\(^{-1}\).

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In 1996, Jasińska et al. [5] published an equation similar to (1) assuming the geometry of a rectangular box, which seems to be useful in cases of long channels or gaps in the layered structures (one or two dimensions extending to infinity):

\[
\tau = 0.5\text{ns} \left[ 1 - \prod_{i=1}^{3} \left( \frac{a_i}{a_i + 2\Delta} + \frac{1}{\pi} \sin \frac{\pi a_i}{a_i + 2\Delta} \right) \right]^{-1},
\]

(2)

where \( a_i \) are the sides of a cuboid. Finally, we introduced the cylindrical geometry [6] and modified the equations to describe correctly the voids exceeding 1 nm in size, by taking into account the population by Ps some higher lying states in a potential well (Extended Tao-Eldrup model, ETE [6,7]):

\[
\tau = \left[ N \sum \lambda_i \exp(-E_i / kT) + \lambda_T \right]^{-1},
\]

(3)

where \( N \) is the normalizing factor, \( \lambda_i \) are the pick-off decay constants of \( o \)-Ps from various levels of energy \( E_i \) in the well, \( \lambda_T \) is the decay constant of intrinsic three quantum annihilation.

The present status of PALS enables to discuss not only the size (equivalent radius) but also the shape of free volumes. In the paper below, we would like to give some examples of positronium in free volumes of various shapes, which can be found in a homologous series of \( n \)-alkanes.

2. Structure of \( n \)-alkanes
Normal-alkanes (\( n \)-alkanes, paraffins) are saturated hydrocarbons \( \text{C}_n\text{H}_{2n+2} \) (further “\( \text{C}_n \)” for shortness) in the form of carbon chains. The low temperature form of alkane molecules is a straight zigzag chain (all-trans). Alkane crystals have the lamellar structure; within the lamella the molecules are packed in parallel, perpendicularly (odd numbered chains), or obliquely (even numbered) to the lamella surface. In the range of carbon atoms \( 9 \leq n \leq 39 \) in odd numbered alkanes and \( 22 \leq n \leq 40 \) in even numbered ones, a “rotator phase” exists in the interval from 1 to 12 K before melting. In the rotator phase the translational symmetry of the crystal is preserved, yet the molecules can rotate around their long axes (orientational disorder). The reduction of ordering is accompanied by appearance of nonplanar conformers; their concentration rises with the chain length. For odd numbered chains with \( n \geq 25 \) and even ones with \( n \geq 34 \) next solid phases appear. They retain the lamellar structure although differ in lateral packing, tilt angle of carbon chains, stacking of lamellae etc.

3. Experimental
The PALS spectra were measured using a standard fast-slow delayed coincidence setup; the resolution time was about 250 ps. The spectra were assumed to consist of three exponential components (\( p \)-Ps decay, free annihilation, \( o \)-Ps decay) and were analysed using the LT programme [8]. Our object of interest was the lifetime \( \tau_3 \) and relative intensity \( I_3 \) of ortho-positive,ronium formed in the sample. The polycrystalline samples were from Sigma-Aldrich, 99% purity, and were used without further refinement. Liquid samples were degassed by the freeze-thaw technique in order to eliminate the ortho-para conversion in dissolved paramagnetic oxygen. The measurements were performed above the room temperature (if not stated otherwise), where the effect of excess electron trapping, distorting the Ps intensity, does not appear.

4. Low temperature phase
In the low-temperature phase (“rigid solid”), the ortho-positronium lifetime \( \tau_3 \) is 1.1 – 1.5 ns, depending mainly on temperature. Figure 1 shows the temperature dependence of \( o \)-Ps lifetime in some solid \( n \)-alkanes. In rigid solid, the lifetime rises slowly with temperature. It is visible that the experimental data lie on two parallel curves; these for odd-numbered alkanes are shifted, compared to even-numbered, by about 200 ps upwards. This odd-even difference is likely to indicate that positronium in this phase locates in the interlamellar gap. The width of gap in even numbered alkanes is \( d_0 = 0.125 \text{ nm} \), while in odd numbered ones \( 0.195 \text{ nm} \) [9]. Inside the lamella the molecules are tightly packed leaving no sufficient free space to accommodate the Ps atom (application of high pressure up to 1.4 GPa does not induce transitions to any other phase; above 500 MPa, the \( o \)-Ps
lifetime is almost constant [10]). Another argument in favour of Ps location in the gap is an increase in o-Ps lifetime in mixed alkanes, e.g. \( n \)-nonadecane with 20\% of \( n \)-heneicosane [11]. Longer \( n \)-heneicosane molecules protrude from the lamellae forcing increased separation of lamellae. Another example supporting the concept of Ps location in the interlamellar gaps is the behaviour of very long chain alkanes at relatively low temperatures (near the room temperature). The X-ray scattering measurements with \( n \)-hexatriacontane \( C_{36} \) prove the coexistence of two or three phases [12]. We have analyzed the PALS spectra at 303 K using the MELT routine [13]. The result is shown in figure 2. Two o-Ps peaks can be distinguished (thus belonging to two phases). The peak at about 1.2 ns is typical of the low-temperature rigid phase appearing in all solid alkanes. The other one is located at 1.8 ns; it is a very long lifetime as for the rigid phase (and low temperature), however X-ray measurements demonstrate that the interlamellar gap in one of these phases is \( d_0 = 0.36 \) nm [12]. It is more than twice of that in shorter even chain alkanes, and one can expect the respective lifetime elongation.

![Figure 1](image1.png)  
**Figure 1.** Temperature dependence of o-Ps lifetime in homologous series of \( n \)-alkanes (transition to liquid phase is not shown). Reddish colours are for even carbon chains, green-blue for odd ones. Solid and dashed lines are drawn at the transition rigid – rotator (no such transitions in \( C_{18} \) and \( C_{20} \)).

![Figure 2](image2.png)  
**Figure 2.** Distribution of positron lifetimes found by MELT routine in \( C_{36} \) at 303 K. The sample is obtained from the melt. The peaks, from left to right, belong to \( para \)-Ps, free \( e^- \) annihilation, and the two last components originate from \( ortho \)-Ps.
All these examples show a correlation between the interlamellar gap width and \( o\)-Ps lifetime. In such cases, the free volume seems to be a flat empty space with two dimensions tending to infinity, the third dimension is \( d_0 \). If so, one can apply equation (2) to get the ETE estimate of lifetime. The calculated \( \tau_3(d_0) \) dependence is shown in figure 3. The experimental values, at least for moderately long alkane chains, lie rather close to the model curve, the point for \( C_{36} \) is evidently too low. The source of disagreement could be the definition of gap width. The gap width, given in the papers about X-ray diffraction [14], is

\[
\begin{align*}
  d_0 &= D - 0.127(n-1) \sin \beta - w, \\
  \beta &= \text{the staggering angle of molecular chain,} \\
  w &= \text{small addition (\approx 0.12 nm) for methyl groups at the end of a molecule.}
\end{align*}
\]

where \( D \) is the spacing of lamellae (in nm), \( \beta \) is the staggering angle of molecular chain, \( w \) is small addition (\approx 0.12 nm) for methyl groups at the end of a molecule. It is not evident whether this definition can be used in positron lifetime experiments. It can rather serve as a rough estimate; by accounting the finite size of carbon atoms and neglecting the hydrogen atoms extending at the end groups \( \text{CH}_3 \) we obtain the value of \( d_0 \) similar to that given above. However, possible misestimate of that gap should be a constant, independent of chain length. If so, the model curve in figure 3 can be shifted to the left or right only, yet the experimental data indicate that we need the modification leading to lowering of the curve inclination. In our calculations, we have assumed that the interlamellar gap limits have the form of ideal planes extending to infinity whereas in real crystal the lamella surface is rough, due to the presence of longitudinal shifts of molecules. Thus, in fact, positronium is not delocalized in an unlimited interlamellar space, but trapped between local distortions of the structure. If this was the source of divergence between the ETE model and experiment seen in figure 3, the reduction of \( \tau_3 \) from 3 ns to 2 ns would mean Ps localization in the area of \( \approx 0.8 \) nm in size.

5. Rotator phase

In the rotator phase, the \( o\)-Ps lifetime is evidently longer than in the rigid one. In rigid crystal, we have the molecules in all-trans configuration (\( t \)), in the rotator one, nonplanar conformers begin to play an important role [15]. The main type of such conformers is that containing the end-gauche modification, or gauche-trans-gauche (gtg) sequence (figure 4). The latter gives a kinked shape to the molecule. The fraction of “kinked” molecules at \( n = 17 \) is about 8\%, and at \( n = 29 \) approaches 70\% [14]. Mismatching the nonplanar conformers and all-trans ones leads to creation of the free volume inside the lamellae. The shape of such a volume can be expected to be elongated; the cuboid or cylinder with
the cross section independent on chain length seems to be most suitable to estimate the lifetime of o-Ps trapped in the vicinity of a kinked molecule. With an increase in chain length the lifetime rises, tending to the limiting value of about (3.1 – 3.2) ns. If we assume as rough estimate the value of 3.2 ns for an infinitely long channel, we obtain the square cross section of rectangular channel 0.56×0.56 nm, or the radius of cylindrical one 0.32 nm. The position of kink can move along the molecule, thus, the lifetime observed in the experiment is averaged over certain distribution. One can suppose that the average length of channel (in nm) is \( a = \left[ (n-1) \times 0.127 + w \right]/2 + d_0 \). Taking the experimental \( \tau \) value and assuming the section of channel as given above, the channel length \( a \) can be calculated [16]. The result for the whole set of alkanes is shown in figure 5a. If average location of gtg kink is in the middle of chain, we can expect \( a - d_0 = L/2 \), where \( L \) is the molecule length. It is seen that \((a-d_0)/L\) approaches 1/2 for the longest chains only. For the chains shorter than \( n = 20 \) the value \((a-d_0)\) stabilizes at 0.2 \( L \). This value of \((a-d_0)\) is hardly acceptable. Thus, instead of fixing the channel cross section, we fix the channel length as \( L/2 + d_0 \) and calculate the cross section (assumed square). The result is shown in figure 5b. The cross section \( S \) rises from ≈0.18 nm\(^2\) for the shortest chains up to about 0.3 nm\(^2\) for chains with \( n > 25 \). This \( S \) dependence on chain length is easier to explain. In short alkanes the concentration of molecules containing (gtg) defect is very low, thus the kinked molecule is surrounded by all-trans ones. A part (half) of defected molecule is displaced sideways and the free volume is the one left after displacement. As a rough approximation one can assume the cross section of free volume the same as the cross section of a crystal cell per one molecule (cross section of a column occupied by all-trans molecule). This section is almost constant in a broad range of \( n \) [14] and amounts 0.196 to 0.198 nm\(^2\), which is close to \( S \) calculated from our experimental data for \( C_{11} - C_{17} \). With the chain length extending, the concentration of kinked molecules rises and for \( n > 30 \) almost all molecules are distorted. The empty volume near them is now a cluster of channels running along the molecules and the effective section increases up to a certain maximal value, found here as \( S = 0.30 - 0.31 \) nm\(^2\). Note that experimental points in figure 5 are given for both even and odd numbered chains, having different \( d_0 \).

**Figure 5.** a) The ratio of empty channel length found using equation (2) to the molecule length for a set of alkanes. The channel is assumed rectangular with sides 0.56 × 0.56 nm. b) Channel cross section found using equation (2) assuming the channel length \( L/2 + d_0 \). Lower and upper end of bar on both drawings relate to beginning and end of the rotator phase range.

Naturally, there is a certain distribution of free volumes depending on kink location and on mutual orientation of kinked molecules (if in large concentration). This should be reflected in the distribution of lifetimes, which is confirmed by LT analysis [8] of high statistics spectra.
In fact, there are five versions of the rotator phase. In some alkanes, depending on temperature, one observes phases RI and RII for $22 \leq n \leq 26$, and phases RIII, RIV for $27 \leq n \leq 30$. The transitions from one rotator phase to the other are not visible in PALS measurements. The change of $\tau_3$ lifetime (or $I_3$ intensity) is related to the structure modification; more radical rebuilding of the structure should result in more distinct changes in $\tau_3$. A certain measure of structural modification can be the enthalpy of transition. The enthalpy of alkane melting is of the order from 60 kJ/mol for C$_{25}$ to 144 kJ/mol for C$_{40}$, of the transition rotator-rigid crystal from 28 kJ/mol to 47 kJ/mol, while e.g. for transition RI-RII in C$_{25}$ it is only 0.2 kJ/mol.

An interesting feature of the rotator phase is weak dependence of positronium formation intensity on the molecule length. The values of $I_3$ for the whole range of existence of the rotator phase are drawn in figure 6, in which the dashed line divides the regions of rotator RI and rotator RIV phases. It seems that in phase RIV the $I_3$ value is constant, while in RI it slightly decreases with shortening of the carbon atom chain. However, it may have nothing in common with the crystalline structure, being the result of very high concentrations of non-planar conformers. In one of our early papers [17], we have shown that the addition of spatially mismatched molecules (e.g. anthracene to p-terphenyl host) in the amount of 1% is enough to obtain maximal (saturation) $I_3$ intensity. The fraction of “kinked” molecules in cases of large $n$ is much higher than 1% [14], thus at such concentrations $I_3$ should be maximal possible.

The range of rotator phase narrows with increasing of the chain length. In C$_{38}$ it is still visible in the $I_3(T)$ curve as a knee less than 1 K wide, in C$_{40}$ it cannot be found (at least by the PALS method [18]).

![Figure 6](image.png)

**Figure 6.** Intensity of o-Ps component in the rotator phase as a function of carbon chain length. Vertical dashed line separates the regions of RII and RIV phases.

### 6. High temperature solid phases

When the chain contains over 25 carbon atoms, new solid phases, preceding the rotator phase, appear. In odd numbered alkanes with $n \geq 25$, there are two phases, usually denoted as IV and V. Phase IV is clearly visible as the range where $\tau_3$ is increased by about 0.2 ns. An example of $\tau_3(T)$ dependence in C$_{27}$ is shown in figure 7. The region of phase IV extends from 320.5 to 325.5 K. An increase in $\tau_3$ in that phase is due to increased concentration of end-gauche defects, shortening slightly the molecules. Phase V is not seen by the PALS method. Similarly to different rotator phases, the enthalpy of transition from low-temperature phase I to phase V is only 0.3 kJ/mol.

In even numbered alkanes, new phases appear from $n = 36$ upwards. In such alkanes, the structure is much more complex than in shorter ones. The crystalline phase depends on the way of sample preparation. Different phases are obtained when the sample is crystallized from the solution, different when obtained from the melt. The phase transition points given in literature are inconsistent [19].
concerns not only the high temperature phases, but also the structure at low temperatures. In the meltgrown samples of C\textsubscript{36} up to three phases coexist at room temperature \[20\]; an example of the room temperature structure consisting of two phases was already mentioned in section 4.

If the sample is obtained by crystallization from the solution, the PALS method allows to observe the transition from the low-temperature monoclinic structure to the (also monoclinic) phase called C\textsuperscript{[21]} or M\textsubscript{101} for \(n\) longer than 36. In such positron measurements, the spectra in the region near that transition and in the range of phase C look differently than those in shorter chain paraffins. Up to C\textsubscript{34}, the transitions rigid \(\rightarrow\) rotator and rotator \(\rightarrow\) liquid are sharp, step-wise, while between the transition points the spectrum parameters are constant, as shown for C\textsubscript{32} in figure 8. In C\textsubscript{38} and next homologues, where the rotator phase is substituted by phase C, the lifetime begins to rise already below the transition point, the step in \(I_3\) values extends over several degrees. In phase C, the \(\tau_3(T)\) curve has a high slope; the transition to C phase is visible in \(\tau_3\) as a change of slope only. Such a smooth change of sample properties was seen by Kim et al. \[22\] in the temperature dependence of gauche bond density, i.e. the number of such bonds per one molecule, \(m(g)\), for alkanes longer than C\textsubscript{36}. For these longest chains, the step in \(m(g)\) at the phase transition point is entirely lost and described by the authors as “premelting”. This term seems to be exaggerated; in PALS spectra, the transition point is still well observable (moreover, melting looks more sharp than rigid \(\rightarrow\) C transition).

Contrary to the rotator phase, in which the \(\alpha\)-Ps lifetime is the same as in liquid, this lifetime in phase C is shorter, changing with temperature, and the next phase transition, i.e. melting, is well marked by a stepwise rise of \(\tau_3\) by about 0.2 ns, i.e. to the value observed in all shorter chain structures. Figure 8 shows the \(\tau_3(T)\) dependence for C\textsubscript{40}; similar dependences can be seen in other even alkanes in C phase, C\textsubscript{38}, C\textsubscript{44}. In PALS measurements, an increase in \(\alpha\)-Ps lifetime is usually a signal of growing disorder. In long chain alkanes we expect that the number of defects rises with chain length. Relatively shorter lifetime in phase C suggests rather a reverse effect, which is confirmed by the results of Kim et al.; their estimate of \(m(g)\) for C\textsubscript{36} is 0.7, whereas for C\textsubscript{50} it reduces surprisingly to about 0.4.

Hexatriacontane C\textsubscript{36} is an intermediate case, still containing the rotator phase, with phase C already appearing (both in the range about 2.5 K wide).
The intensity $I_3$ in phase C is rather low, resembling that in the low-temperature rigid phase. The step at the rigid→C transition diminishes with chain length; that intensity increase $\Delta I_3$ in $C_{36}$ amounts 4.4 %, in $C_{44}$ 1.5 %, and in $C_{50}$ it disappears. All the data about lifetime and intensity indicate that phase C, appearing at higher temperatures and in the case of chains longer than in the range of existence of the rotator phase, is better ordered than the last one. This supposed (partial) restoration of order needs confirmation by independent methods.

The transition temperature rigid→C is weakly depending on the chain length and locates at about 75°C, thus the range of phase C stretches with increasing chain length; in $C_{44}$, it amounts about 11 K.

The existence of a next phase at cooling the melt was reported recently [23,24,25]. This is the effect of surface freezing, extending up to 3 K above the bulk solid-liquid transition. Such a monolayer structure cannot be visible in the measurements using positrons from $\beta^+$ decay, due to deep penetration of energetic positrons, which interact with the bulk and not with the surface. Moreover, the enthalpy of transition liquid – frozen surface is extremely small ($\approx 0.01 \text{ kJ/mol}$).

6. Liquid

$ortho$-Ps lifetime in liquid $n$-alkanes, near the melting point is almost independent on chain length (except for the shortest ones) and is found to be $(3.1–3.2)$ ns. The positronium bubble is naturally spherical, and according to (1) its radius is 0.38 nm.

To date, it has been commonly assumed that the mechanism of Ps formation is entirely different for solid and liquid phases. In the former, Ps is a “seeker”, which forms in free volumes existing $a$ $priori$, their dimensions are determined by the imperfect structure of solid. In the liquid, Ps is a “digger”, producing the free volume by itself, owing to the pressure exerted by zero-point motion of the confined Ps particle. However, according to our experimental data, the lifetime for $25 \leq n \leq 38$ on both sides of the melting point is the same (figure 8)! If in the rotator phase the free volume is given in
advance, and in the liquid the size of bubble is determined mainly by surface tension, such an identity of lifetimes cannot be a random effect in such a broad range of chain lengths.

The rotator phase contains certain elements of disorder, however, incomparable to the structure of liquids. The disorder in solid is introduced by gauche bonds. Kim et al. [22] estimate that in the rotator phase of C$_{36}$ m(g) is about 0.7 only; in the closest vicinity of melting point that number rises to about 2, thus in the middle of rotator phase range, an average linear trans segment contains more than 18 C-C bonds. Raman spectroscopic investigations of liquid alkanes by Brambilla and Zerbi [26] demonstrate the length of trans-planar sequences, which can appear (almost independently on chain length) as about 5 C-C bonds (0.625 nm), i.e. comparable to the “bubble” size. Thus, in the rotator phase the molecules retain a roughly linear form and long range order; in liquid alkanes, the ordering can be neglected (even if close to the melting point certain bundling of trans fragments can exist [26]).

In the same sample, where o-Ps lifetime $\tau_3$ does not feel the transition from rotator to liquid, the intensity $I_3$ changes substantially at transition, in a stepwise form. In the melting point the intensity $I_3$ rises by about 10%. An increase in intensity at melting the phase C is even larger. The o-Ps lifetime is determined by the molecular structure around the bubble surface, while the intensity is related to the radiochemical processes in the bulk. A question arises whether the molecular structure surrounding the bubble is the same as that in the unperturbed bulk medium.

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