Journal of Physics: Conference Series **443** (2013) 012003 doi:10.1088/1742-6596/443/1/012003

A simple shape-free model for pore-size estimation with positron annihilation lifetime spectroscopy

Ken Wada and Toshio Hyodo

Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan

E-mail: ken.wada@kek.jp

Abstract. Positron annihilation lifetime spectroscopy is one of the methods for estimating pore size in insulating materials. We present a shape-free model to be used conveniently for such analysis. A basic model in classical picture is modified by introducing a parameter corresponding to an effective size of the positronium (Ps). This parameter is adjusted so that its Ps-lifetime to pore-size relation merges smoothly with that of the well-established Tao-Eldrup model (with modification involving the intrinsic Ps annihilation rate) applicable to very small pores. The combined model, *i.e.*, modified Tao-Eldrup model for smaller pores and the modified classical model for larger pores, agrees surprisingly well with the quantum-mechanics based extended Tao-Eldrup model, which deals with Ps trapped in and thermally equilibrium with a rectangular pore.

1. Introduction

The positron annihilation lifetime spectroscopy (PALS) is used for estimating size of pores in insulating materials. The lifetime of the spin-triplet Ps, *o*-Ps, trapped in pores (defects, voids or free spaces) is shorter than the value in vacuum owing to its quenching through the annihilation with an electron on the pore surface (pick-off annihilation). Thus on assumption that the pickoff annihilation rate is practically independent of the material comprising the pore wall, the size of the pore can be deduced from the measured lifetime. The above assumption of the insensitivity of the pick-off annihilation rate to the material species is supported by a recent observation that the probabilities of the pick-off quenching of the thermalized *o*-Ps per collision with all the atoms and molecules in gas phase observed so far are almost constant [1].

2. Models for estimation of pore sizes by PALS analysis

2.1. Models based on quantum mechanics

The original model for pore-size estimation with PALS analysis, the Tao-Eldrup (TE) model [2–4], is applicable to size estimation of very small pores ($<\sim 1\,\mathrm{nm}$). The TE model regards the *o*-Ps in the pore as a single particle with a mass twice as large as the electron mass in the ground state in a spherical potential well with radius R (pore radius). To simplify the picture of the penetration of the Ps wave function into the wall, the pore is modeled by an infinitely deep well of radius $R + \Delta R$ with the position of the abrupt potential step recessed inside the wall. It is assumed that the fraction of the Ps wave function within the thickness ΔR contributes to the pick-off annihilation with the rate of the spin-averaged Ps annihilation

in vacuum, $\lambda_{\rm A} = (\lambda_{\rm S} + 3\lambda_{\rm T})/4 = 2\,{\rm ns}^{-1}$; here $\lambda_{\rm S}$ and $\lambda_{\rm T}$ are the intrinsic annihilation rates in vacuum for spin-singlet Ps (p-Ps) and o-Ps, respectively. A straightforward calculation of the overlap gives the annihilation rate of the trapped o-Ps as

$$\lambda_{\rm TE}(R) = \lambda_{\rm A}\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right] \quad . \tag{1}$$

The parameter ΔR has been empirically determined to be 0.165 nm by fitting to data acquired in variety of well-characterized small-pore materials.

In figure 1, the relation between o-Ps lifetime to the mean free length of the pore is plotted (relation between the mean free length and the pore radius is described in the next section).

The TE-model is insufficient, however, for pores larger than $\sim 1\,{\rm nm}$. Several attempts to modify this model for larger pores have been reported [5–10]. It is trivial to add the vacuum annahilation rate of o-Ps [6], as

$$\lambda_{\rm MTE}(R) = \lambda_{\rm TE}(R) + \lambda_{\rm T} \tag{2}$$

which we call modified Tao-Eldrup (MTE) model in the present paper. In addition, inclusion of the (translational) excited states in the pores is considered [5]; the separations between energy levels become narrower as the pore size increases, resulting in larger fraction of the Ps atoms annihilated from the excited states. Gidley *et al.* employed a model of rectangular pore geometry [7,8] to avoid calculation difficulty for a spherical pore [5]. This extended Tao-Eldrup (ETE) model gives the annihilation rate of o-Ps trapped in and thermally equilibrium with a rectangular well with sides a, b, c at temperature T as

$$\lambda_{\rm RTE}(a,b,c) = \lambda_{\rm A} - \frac{\lambda_{\rm S}-\lambda_{\rm T}}{4}F(a,\delta,T)F(b,\delta,T)F(c,\delta,T)\,, \tag{3}$$

where

$$F(x,\delta,T) = 1 - \frac{2\delta}{x+2\delta} + \frac{\sum_{i=1}^{\infty}\frac{1}{i\pi}\sin\left(\frac{2i\pi\delta}{x+2\delta}\right)\exp\left\{-\beta i^2/\left(x+2\delta\right)^2 kT\right\}}{\sum_{i=1}^{\infty}\exp\left\{-\beta i^2/\left(x+2\delta\right)^2 kT\right\}}\,. \tag{4}$$

Here, $\beta = h^2/16m = 0.188\,{\rm eV\,nm}^2$ and m is the electron mass (the Ps mass is $2m$). The value of the adjustable parameter δ has been determined by fitting to experimental data as 0.18 nm. Note that the pore dimension in the original RTE model was $(a-2\delta)(b-2\delta)(c-2\delta)$ [7,8], but we have redefined it as abc and the potential wall dimension as $(a+2\delta)(b+2\delta)(c+2\delta)$ to be consistent with the picture of the traditional TE model.

2.2. Models based on classical mechanics

Classical models are applicable where the Ps mean free path between collisions, $\overline{L}_{\rm Ps}$, is much larger than the thermal Ps de Broglie wavelength $\lambda_{\rm dB}$ ($= h/\sqrt{4\pi mkT} = 3.05\,{\rm nm}$ at room temperature). The pick-off quenching rate of o-Ps is given by the product of pick-off annihilation probability per collision with the cavity wall, $P_{\rm A}$, and the collision frequency, $v_{\rm th}/\overline{L}_{\rm Ps}$; the total annihilation rate of o-Ps is described as [7]

$$\lambda_{\rm CM} = \frac{v_{\rm th}P_{\rm A}}{\overline{L}_{\rm Ps}} + \lambda_{\rm T}\,, \tag{5}$$

where $v_{\rm th}$ is the thermal velocity of the Ps. Gidley et. al deduced the product of $v_{\rm th}P_{\rm A}$ at room temperature to be $0.021 \pm 0.002\,{\rm nm/ns}$ for silica powders of two different grain sizes for which $\overline{L}_{\rm Ps}$ was systematically varied by controlling the packing from 35 nm to 600 nm [11]. This model

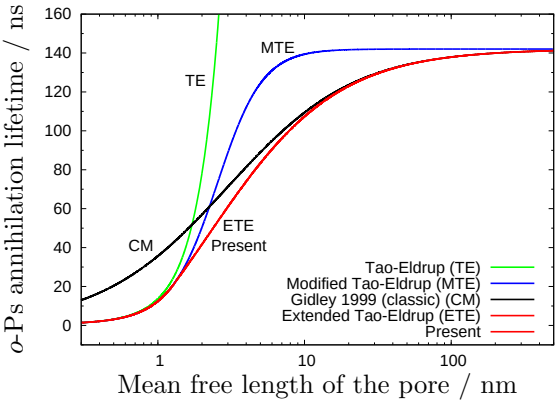

Figure 1. Models for pore-size estimation with PALS analysis. The curves of the present model and ETE model are indistinguishable.

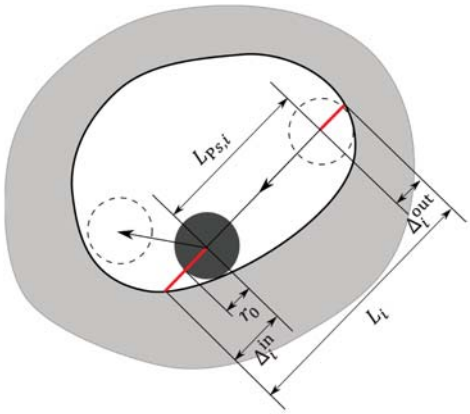

Figure 2. The difference between flight length of the Ps and that of an infinitely small particle

successfully relates the *o*-Ps annihilation rate and the mean free length for free spaces larger than several tens nm but fails for smaller; at ~ 1 nm, this model predicts annihilation rate about an order of magnitude lower than (lifetime longer than) the MTE model (figure 1).

Another classical-mechanics based model, specific for PALS measurement in air, has also been reported [10].

3. A new model based on a classical picture

The failure of the classical model in the smaller mean free length region may be removed by taking into account the effect of the size of Ps atom.

A free flight length of the Ps before the i-th collision with wall surface, $L_{\mathrm{Ps},i}$, is schematically shown in figure 2, or $L_{\mathrm{Ps},i} = L_i - \left(\Delta_i^{\mathrm{out}} + \Delta_i^{\mathrm{in}}\right)$, where L_i is the free flight length of the infinitely small particle in the same trajectory, and $\Delta_i^{\mathrm{out}} + \Delta_i^{\mathrm{in}}$ represents the effect of the finite size. The average length $\overline{L}_{\mathrm{Ps},i}$ is written as

$$\overline{L}_{\mathrm{Ps},i} = \sum_{i=1}^{n} \frac{L_i - \left(\Delta_i^{\mathrm{out}} + \Delta_i^{\mathrm{in}}\right)}{n} = \overline{L} - 2\overline{\Delta}\,. \tag{6}$$

Here, $\overline{L}$, represents the mean free length of the pore. Substituting $\overline{L}_{\mathrm{Ps}}$ in (5) with the right-hand side of eq. (6), the *o*-Ps annihilation rate in this modified classical model (MCM), λ_{MCM}, is given as

$$\lambda_{\mathrm{MCM}}(\overline{L}) = \frac{v_{\mathrm{th}} P_{\mathrm{A}}}{\overline{L} - 2\overline{\Delta}} + \lambda_{\mathrm{T}}\,. \tag{7}$$

The adjustable parameter $\overline{\Delta}$ is set so that the *o*-Ps-lifetime to cavity-size relation merges smoothly with that of the MTE model. Since the MTE model is described as a function of radius R of the spherical pore, we transformed R into $\overline{L}$ with a procedure using the general relation, $\overline{L} = 4V/A$ [12] for a cavity of volume V with surface area A, giving $\overline{L} = 4R/3$. Two functions touch at $\overline{L} = 1.28\,\mathrm{nm}$ when $2\overline{\Delta} = 0.76\,\mathrm{nm}$. A combined model is practical: MTE model for pores less than $\overline{L} = 1.28\,\mathrm{nm}$ or measured *o*-Ps lifetime less than 21.1ns, and MCM for pores greater than $\overline{L} = 1.28\,\mathrm{nm}$ or lifetime longer than 21.1 ns, i.e.,

$$\lambda_{o-\mathrm{Ps}}^{\overline{L}} = \begin{cases} \lambda_{\mathrm{MTE}}(R = 3\overline{L}/4) & (\overline{L} < 1.28\,\mathrm{nm} \ \text{ or } \ 1/\lambda_{o\text{-Ps}} < 21.1\,\mathrm{ns}) \\ \lambda_{\mathrm{MCM}}(\overline{L}) & (\overline{L} \geq 1.28\,\mathrm{nm} \ \text{ or } \ 1/\lambda_{o\text{-Ps}} \geq 21.1\,\mathrm{ns}) \end{cases}, \tag{8}$$

where $v_{\rm th}P = 0.021 \pm 0.002\,{\rm nm/ns}$ and $2\overline{\Delta} = 0.76\,{\rm nm}$. When pores are assumed to be spherical with radius R, the following expression where $\overline{L}$ is transformed into R is used:

$$\lambda^{R}_{o\text{-Ps}} = \begin{cases} \lambda_{\rm MTE}(R) & (R < 0.96\,{\rm nm} \ \text{ or } \ 1/\lambda_{o\text{-Ps}} < 21.1\,{\rm ns}) \\ \dfrac{3}{4}\dfrac{v_{\rm th}P}{R - r_0} + \lambda_{\rm T} & (R \geq 0.96\,{\rm nm} \ \text{ or } \ 1/\lambda_{o\text{-Ps}} \geq 21.1\,{\rm ns}) \end{cases}, \tag{9}$$

where $2r_0 = 3\overline{\Delta} = 1.14\,{\rm nm}$, which corresponds to an effective size of the Ps. This value is one order of magnitude larger than the diameter of the Ps (quantum mechanically expected value for the electron-positron distance in Ps), 1.058 nm, and about one thirds of the thermal de Broglie wave length of the Ps at room temperature, $\lambda_{\rm dB} = 3.05\,{\rm nm}$.

When applied to cubic pores, the present model (MTE model + MCM) agrees surprisingly well with the RTE model throughout entire region. These are indistinguishable in figure 1.

Figure 3 shows the present model applied to spherical pores (9) and experimental data cited in ref. [6, 8] and those reported in references [10, 13]. The function (9) in the region $R < 0.96\,{\rm nm}$ and $R \geq 0.96\,{\rm nm}$ is plotted with blue and red lines, respectively. The sets of data in refs. [10] and [14] which was obtained in the normal atmosphere have been corrected for the spin-conversion quenching of o-Ps with a rate of $0.0048 \pm 0.004\,{\rm ns}^{-1}$ [15, 16] by O_2 in the air and shown with uncertainties. The data from ref. [11] is converted from $\overline{L}$ into R. Other data reported without measurement conditions specified are plotted at the values of "R" stated in the references.

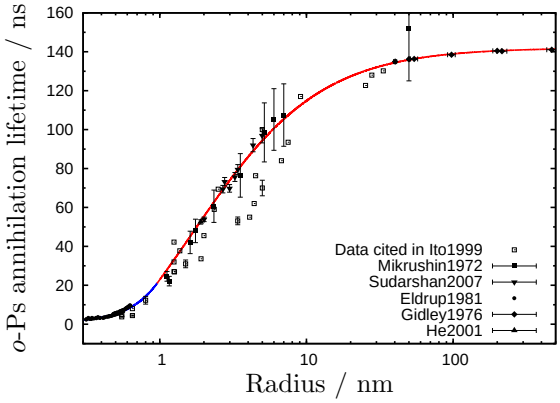

Figure 3. The present model applied to spherical pores, (9), and experimental data

As an application of the present shape-free model, we have measured the o-Ps annihilation rates in several silica aerogels having very complex open-pore structures. The mean free lengths obtained are consistent with other physical dimensions [17].

References

[1] Wada K, Saito F, Shinohara N and Hyodo T 2012 *Eur. Phys. J.* D **66** 108.
[2] Tao S J 1972 *J. Chem. Phys.* **56** 5499.
[3] Eldrup M, Lightbody D and Sherwood J N 1981 *Chem. Phys.* **63** 51.
[4] Wang Y Y, Nakanishi Y, Jean Y C *et al.* 1990 *J. Polym. Sci., Part B: Polym. Phys.* **28** 1431.
[5] Goworek T, Ciesielski K, Jasinska B *et al.* 1998 *Chem. Phys.* **230** 305.
[6] Ito K, Nakanishi H and Ujihira Y 1999 *J. Phys. Chem.* B **103** 4555.
[7] Gidley D W, Frieze W E, Dull T L *et al.* 1999 *Phys. Rev.* B **60** 8. The pore dimension was taken to be the position of the infinite potential step in this paper. It has been corrected on the web page of the lab (url: http://positrons.physics.lsa.umich.edu/current/nanopos/conversion/index.html) and the discrepancy in the physical picture with the other works does not exist anymore.
[8] Dull T L, Frieze W E, Gidley D W *et al.* 2001 *J. Phys. Chem.* B **105** 4657.
[9] Dutta D, Ganguly B N, Gangopedhyay D *et al.* 2004 *J. Phys. Chem.* B **108** 8947.
[10] Sudarshan K, Dutta D, Sharma S K *et al.* 2007 *J. Phys.: Condens. Matter* **19** 386204.
[11] Gidley D W, Marko K A and Rich A 1976 *Phys. Rev. Lett.* **36** 395.
[12] Kosten C W, 1960 *Acustica* **10** 245.
[13] He Y, Zhang H, Chen Y *et al.* 2001 *J. Phys.: Condens. Matter* **13** 2467.
[14] Mikrushin A D, Levin B M, Goldanskii V I *et al.* 1972 *Russ. J. Phys. Chem.* **46** 368.
[15] Goldanskii V, Mokrushin A, Tatur A *et al.* 1975 *Appl. Phys* **5** 379.
[16] Shinohara N, Suzuki N, Chang T *et al.* 2001 *Phys. Rev.* A **64** 042702.
[17] Paper in preparation