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General trends of positronium pick-off annihilation in molecular substances

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Abstract

The characteristics of positronium (Ps) annihilation in molecular substances (ranging from organic liquids to molecular solids), manifested through the observed lifetimes (τ_p) for the ‘pick-off’ process and values of angular correlation ($\theta_{1/2}$) of decay gammas, can be shown to be simply related to the size (radius R) of the cavity which the Ps creates in a liquid or finds in a molecular solid. The measured τ_p and $\theta_{1/2}$ are in turn calculable from the wavefunction describing the Ps centre-of-mass motion, which is determined from the average potential experienced by it in the confining cavity. Thus the height of this repulsive barrier (U_0) at the wall of this vacant region corresponding to different materials (with varying R) can be obtained by fitting experimental observations, namely τ_p and $\theta_{1/2}$. The model we use is an improved version of the usual spherical well description of the cavity (where we take the walls to be diffuse). It is found that the values of U_0 and R , taking into account all available and relevant data for different molecular substances, fall on a universal curve. We attempt to explain the reason behind this ‘universality’ by relating the potential to the Ps work-function in materials. Finally, the fit provides us with a very convenient linear relationship between the size (R) of the cavity and the pick-off lifetime (τ_p).

1. Introduction

The positronium atom (Ps) (bound state of an electron and a positron) is formed in many solids, liquids and gases when positrons impinge on them and after losing energy are thermalized. This composite exists in two states, namely *ortho*-positronium (*o*-Ps) where the spins of the two particles are parallel (3S_1) and *para*-positronium (*p*-Ps) with spins anti-parallel (1S_0). Intrinsically (in vacuum) *p*-Ps annihilates ($\tau = 125$ ps) into two gammas, while *o*-Ps decays very slowly ($\tau = 140$ ns) into three gammas. However, in the presence of matter *o*-Ps can decay

into two gammas through a process known as pick-off annihilation, whereby the positron in *o*-Ps seeks out electrons with opposite spin in the surrounding medium and annihilates through the two-photon decay mode. This component of the positron annihilation spectrum (PAS) is of great utility since this enables its use as a microprobe in the study of condensed matter.

The rate for pick-off annihilation is observed to be considerably lower than what one would have anticipated if the atoms (or molecules) of the material were closely packed around the Ps. Furthermore, most of these substances seem to have a negative work-function for the Ps, a feature that is understandable from the repulsive electron exchange interaction between Ps and the atoms, as was first recognized by Ferrell [1]. This led to the visualization of the Ps as a 'digger and seeker of holes' in the words of Mogensen [2]. Thus in liquids the positronium, by virtue of the exchange repulsion, pushes away the surrounding atoms and occupies a self-trapped state in a cavity or bubble, which it supposedly creates around itself, while, on the other hand, in molecular solids the Ps soon finds itself in pre-existing vacant regions (or pores). In either case this leads to the observed increase in lifetime, as compared to what would be expected if the atoms were allowed to freely crowd around the Ps.

Clearly, given the setting described above, the characteristics of Ps pick-off annihilation in a given substance would require knowledge of the wavefunction for the Ps centre-of-mass motion $\psi_{\text{Ps}}(r)$ trapped in the cavity (be it the created bubble in a liquid or a pre-existing pore in a solid), r being reckoned from the centre of the cavity. Due to the exchange interaction the Ps experiences a repulsive barrier at the walls of the cavity and accordingly it is not unreasonable to obtain $\psi_{\text{Ps}}(r)$ from a model where the Ps is considered to be a point particle of mass $2m$ ($m =$ electron mass) moving in a spherical well (SW) with a barrier of height U_0 and range R , namely $U_{\text{SW}}(r) = U_0\Theta(r - R)$, Θ being the Heaviside step function which is zero for $r < R$ and unity for $r > R$. In view of the short-ranged nature of the exchange repulsion one may approximately consider the number density profile for the molecules to be close to the potential and adopt the functional form $\rho(r) = \rho_0\Theta(r - R)$, where ρ_0 is the number density of molecules in the bulk. Henceforth R shall be called the cavity radius (or size parameter). The normalized wavefunction for the Ps centre-of-mass motion in the given spherical cavity is

$$\psi_{\text{SW}}(r) = \frac{1}{\sqrt{4\pi}} \sqrt{\frac{2\kappa_0}{1 + R\kappa_0}} \begin{cases} \frac{\sin k_0 r}{r} & \text{for } r < R, \\ \sin k_0 R \frac{e^{-\kappa_0(r-R)}}{r} & \text{for } r > R, \end{cases} \quad (1)$$

where $k_0 = \sqrt{4mE_0/\hbar^2}$ and $\kappa_0 = \sqrt{4m(U_0 - E_0)/\hbar^2}$, the energy E_0 being given by the eigenvalue condition

$$k_0 \cot k_0 R = -\kappa_0. \quad (2)$$

Since the pick-off annihilation involves the Ps and the electrons in the surrounding medium, the rate for the process is governed by the product of the probability of finding the Ps in the surrounding matter (outside the cavity in SW model) and the density of electrons in the medium. This factor is given in this model by

$$Z_{\text{eff}}\rho_0\mathcal{P}_0 = Z_{\text{eff}}\rho_0 4\pi \int_R^\infty |\psi_{\text{SW}}(r)|^2 r^2 dr, \quad (3)$$

where the factor \mathcal{P}_0 shall be referred to as the overlap integral and Z_{eff} is the effective number of electrons available per molecule for pick-off annihilation (in effect the number of valence electrons, since the Ps atom is unable to penetrate to the cores of the surrounding atoms). Multiplying this with the annihilation rate given by quantum electrodynamics, one arrives at the result

$$\lambda_{\text{pick-off}}^{(0)} \equiv \lambda_{\text{p}} = 4\pi r_0^2 c \rho_0 Z_{\text{eff}} \mathcal{P}_0, \quad (4)$$

for the pick-off rate, where $r_0 = e^2/mc^2$ is the classical electron radius, e being the electronic charge and c the velocity of light.

Apart from the influence of the cavity on the annihilation rate (and hence the lifetime), the bodily motion of the confined Ps implies, by the uncertainty principle (and by virtue of momentum conservation) a non-trivial angular correlation (not back-to-back as for Ps decay at rest) for the two photons emitted through the annihilation of Ps in the cavity. The angular correlation curve $N(\theta)$ is given by the momentum distribution $\mathcal{P}(p)$ of the Ps which in turn is given by the square-modulus of the Fourier transform of the wavefunction, namely,

$$\mathcal{P}(p) = 4\pi p^2 |\tilde{\psi}(p)|^2, \quad (5a)$$

with

$$\tilde{\psi}(p) = \left(\frac{1}{2\pi\hbar}\right)^{3/2} \int \psi(r) \exp\left(-i\frac{\vec{p}\cdot\vec{r}}{\hbar}\right) d^3\vec{r}, \quad (5b)$$

and

$$N(\theta) = \int_{mc\theta}^{\infty} \frac{1}{p} \mathcal{P}(p) dp. \quad (5c)$$

The experimentally measured quantity $\theta_{1/2}$, the full width at half maximum (FWHM) of the angular correlation, is readily determined from

$$N(\frac{1}{2}\theta) = \frac{1}{2}N(0). \quad (5d)$$

The same basic mechanism also gives rise to Doppler broadening (ΔE_γ) of the decay gammas which is easily seen to be

$$\Delta E_\gamma \simeq mc^2\theta_{1/2}. \quad (6)$$

The model described above has been extensively used for the interpretation of PAS data for liquids and molecular solids. In the case of liquids an additional piece of information becomes available from the mechanism of bubble formation. The zero-point motion of the Ps inside the bubble (in a localized state of energy E_0) exerts an outward ‘force’ on the wall given by $\frac{\partial E_0}{\partial R}$ which is balanced by the inward (contractile) force due to the surface tension (σ) of the surrounding liquid, thus minimizing the total energy of the Ps–bubble system

$$\frac{\partial}{\partial R} \left(E_0 + 4\pi R^2 \sigma + \frac{4}{3}\pi R^3 P_{\text{ex}} \right) = 0. \quad (7)$$

The effect due to the third term $\frac{4}{3}\pi R^3 P_{\text{ex}}$ (where P_{ex} is the vapour pressure of the liquid) is very small for most of the molecular liquids and hence neglected from further calculation.

However, though the predictions of the model are in general agreement with experiment [3–9] it has been shown [10–13] that there are systematic discrepancies. That apart it is difficult to accept a picture which

- (a) treats the Ps as a point particle,
- (b) considers the interface of the cavity as a sharp discontinuity (an assumption at variance with the atomicity of matter) and
- (c) neglects, in the case of liquids, the curvature dependence of the effective surface tension by replacing its magnitude for such micro-bubbles by its bulk value.

These shortcomings of the prevalent model could in principle be overcome by introducing length parameters describing the diffusivity of the wall, its roughness and corrections due to finite Ps size. However, this would be too elaborate for the present purpose and we shall introduce these effects through a lumped parameter Δ with the dimension of length.

We take a more realistic density profile which smoothly interpolates between the value zero at the centre of the cavity ($r = 0$) and the bulk density ρ_0 as r becomes large:

$$\rho(r) = \rho_0 \left[1 - \frac{1 + e^{-R/\Delta}}{1 + e^{(r-R)/\Delta}} \right] \quad (8)$$

with $\Delta \rightarrow 0$, $\rho(r) \rightarrow \rho(0)\Theta(r - R)$ so that for small Δ/R the density profile is basically a spherical cavity with a little diffusivity in the boundary. Again we adopt the self-trapping potential to be of the same shape as $\rho(r)$, namely,

$$U_{\text{WS}} = U_0 \left[1 - \frac{1 + e^{-R/\Delta}}{1 + e^{(r-R)/\Delta}} \right], \quad (9)$$

which is the Woods–Saxon (WS) potential [14] widely used by nuclear physicists. Since Δ/R is expected (and in fact found) to be rather small we may treat the diffuseness as a perturbation on the SW. The shift in energy from the SW value is then given by

$$\delta E = E_{\text{WS}} - E_{\text{SW}} \simeq E_0 \frac{2\pi^2 \Delta^2 \kappa_0^2}{3(1 + \kappa_0 R)}. \quad (10)$$

To the same order of accuracy the perturbed wavefunction has the form of the unperturbed solution (equation (1)) except that k_0 and κ_0 are replaced by k and κ which solve the modified eigenvalue condition

$$k \cot kR = -\kappa \left[1 + \frac{\pi^2 \Delta^2 (k^2 + \kappa^2)}{3} \right]. \quad (11)$$

The introduction of diffusivity in the bubble surface enables us to incorporate in a natural manner the influence of the radius of curvature on the surface energy leading to the notion of an effective surface tension (σ_{eff}) in place of the bulk value (σ), via a formula put forward by Tolman [15] and Koenig [16],

$$\sigma_{\text{eff}}(r) = \sigma \frac{r}{r + \Delta}, \quad (12)$$

and accordingly the surface energy of the bubble, instead of being $4\pi R^2 \sigma$ (see equation (7)), will now be

$$E_s = \int_0^R \frac{2\sigma_{\text{eff}}(r)}{r} 4\pi r^2 dr = 4\pi R^2 \sigma \left[1 - \frac{2\Delta}{R} + \frac{2\Delta^2}{R} \ln \left(\frac{R + \Delta}{\Delta} \right) \right]. \quad (13)$$

While the possible importance of the effect was emphasized long ago by Nakanishi *et al* [17], and also by Byakov and Petuchov [6], they introduced the diffusivity by hand as a freely adjustable parameter. In the present version, however, the total energy depends (see equation (10)) both on R and Δ and as a consequence it must be minimized with respect to each, and hence the single condition (equation (7)) is now replaced by two (in the case of liquids), namely

$$\frac{\partial E_t}{\partial R} = \frac{\partial}{\partial R} (E_0 + \delta E + E_s) = 0, \quad (14a)$$

$$\frac{\partial E_t}{\partial \Delta} = \frac{\partial}{\partial \Delta} (E_0 + \delta E + E_s) = 0. \quad (14b)$$

Therefore, even though a new parameter Δ has been introduced, at least for liquids, we have an additional minimizing condition so that we have no more free parameters than the primitive model which we have corrected.

The model described above even with the improvements we have introduced is rather crude and is at best a phenomenological description which enables us to capture the essence of the

experimental data in a simple manner. A more basic approach would be to adopt a molecular-level picture of the liquid and the cavity [18] or to take recourse to numerical simulation using molecular dynamics [19, 20] or to employ the density functional methods [21]. However, since the objective of the present study is to search for common features of the process in different substances the use of a simple and adequate model is appropriate for the purpose.

2. Search for universality and discussion of the result

Armed with the model for pick-off annihilation of the Ps described in the previous section in terms of a spherical cavity with diffuse boundaries we search for a universal and generic description for the phenomena in various media, namely liquids and molecular solids. We adopt the strategy of first fitting the data for different liquids, as also for some liquids at different temperatures. The reason for taking this approach is that in the case of liquids the two additional conditions, equations (14a) and (14b), together with one of the two data (say the lifetime τ_p) is enough to fix the three parameters of the model (namely the barrier height at the walls U_0 , the size parameter of the cavity R and the diffusivity and roughness of the surface described through Δ). This enables one to predict $\theta_{1/2}$ and compare with experiment thereby verifying the consistency of the model. The lifetime data on different liquids taken from Nakanishi and Jean [5], and for *n*-hexane [22] and neo-pentane [23] for different temperatures can be fitted to the modified bubble model. The lifetimes versus the resulting values of the cavity radius R are found to lie very closely on a straight line (figure 1) and an extremely simple relationship results, namely

$$\tau_p = 1.88R - 5.07, \quad (15)$$

where τ_p is expressed in ns and R is in Å.

A similar quest for a simple relation between τ_p and R was made much earlier by Eldrup *et al* [24] through the introduction of a model where the Ps is taken to be trapped by an SW potential with infinite walls. However such a totally confined Ps does not penetrate the walls of the cavity and thus is unable to indulge in pick-off annihilation. To amend this unrealistic situation a virtual electron layer of thickness $\Delta R (= R - R_0)$ was added to the inside wall of the well and the overlap of the Ps wavefunction with this electron layer of density ρ_0 was taken to parametrize the pick-off decay of the trapped *o*-Ps. The resulting formula becomes

$$\lambda_{po} \text{ (ns}^{-1}\text{)} = \lambda_0 \left[1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R_0}\right) \right], \quad (16)$$

where $\lambda_0 = \pi r_0^2 c \rho_0$, the decay rate in this virtual electron layer, was somewhat arbitrarily set equal to 2 ns^{-1} . This relation due to Eldrup is often used to determine the cavity size R from observed lifetimes. It may be claimed that the simpler relation (equation (15)) found by us is also based on a model which is not only more realistic but also fits simultaneously the lifetime and angular correlation data. Furthermore, it is encouraging to note that the data on solids are also consistent with our proposed linear relationship (equation (15)).

Again considering all the data on liquids we are able to find the dependence of the barrier height (U_0) at the wall on the radius (R) of the cavity. This is shown in figure 2 and the fit is of the form

$$U_0(R) = A + B \exp[-(R - R')/a_0], \quad (17)$$

with $A = 0.40 \text{ eV}$, $B = 1.25 \text{ eV}$, $R' = 3.44 \text{ Å}$ and $a_0 = 2.09 \text{ Å}$.

We wish to consider this relationship as pivotal and advance the hypothesis that it is universal and that it reflects the average of the basic Ps–atom interaction. If this were indeed

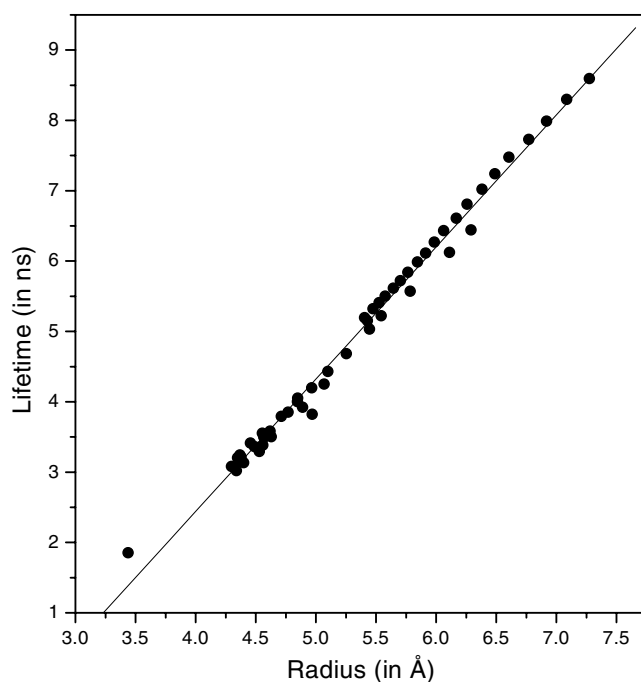


Figure 1. Bubble radius (R) obtained by diffuse square well model versus pick-off lifetime (τ_p) for different liquids, n -hexane and neo-pentane, at different temperatures.

so then given the radius R of the cavity (whether induced as in liquids or intrinsic as in molecular solids) one could find the barrier height U_0 at the wall and hence the Ps centre-of-mass wavefunction ψ_{Ps} is determinable, and therefrom the pick-off rate λ_p and angular correlation $\theta_{1/2}$ (or Doppler broadening) can be obtained.

In order to test the applicability of equation (17) to molecular solids we follow a methodology which was put forward by Yu *et al* [25] and subsequently employed by Dauwe and co-workers [26], which they named ‘scaling of the bubble model’. We introduce a scaled pick-off lifetime η , where

$$\eta = 4\pi r_0^2 c \rho_0 Z_{\text{eff}} \tau_p. \quad (18)$$

By comparison with equation (4) it is clear that the dimensionless quantity η is nothing but the inverse of the overlap integral, a quantity characteristic of the mean potential felt by the Ps. Similarly consider a scaled radius R/R^* where

$$R^* = \sqrt{\frac{\hbar^2}{4mU_0}}. \quad (19)$$

All the data in liquids have been fitted to our modified bubble model (with diffuse boundaries) and the plot of η against R/R^* is displayed in figure 3.

We first assume that the dependence of τ_p on R (figure 1), of U_0 on R (figure 2) and of η on R/R^* (figure 3) also apply to solids [27]. Knowing the experimental value of τ_p for a solid sample we use figure 1 to find R ; the value of R is employed to determine U_0 from figure 2. The value of U_0 may be used to find R^* and hence R/R^* ; the scaled radius and figure 3 would then furnish us with the magnitude of η the inverse of the overlap integral. On the other hand the overlap integral can be directly obtained from equation (4) knowing Z_{eff} and ρ_0 . When

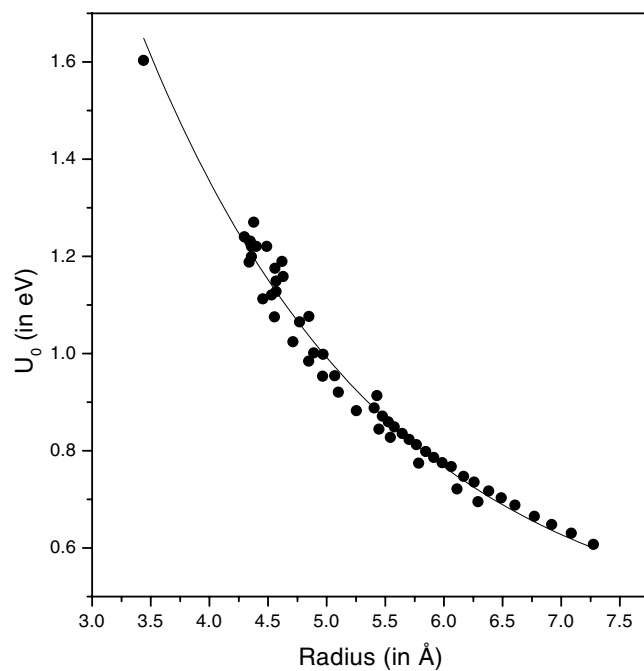


Figure 2. Barrier height (U_0) versus bubble radius (R) as calculated applying the diffuse square well model for the substances in figure 1.

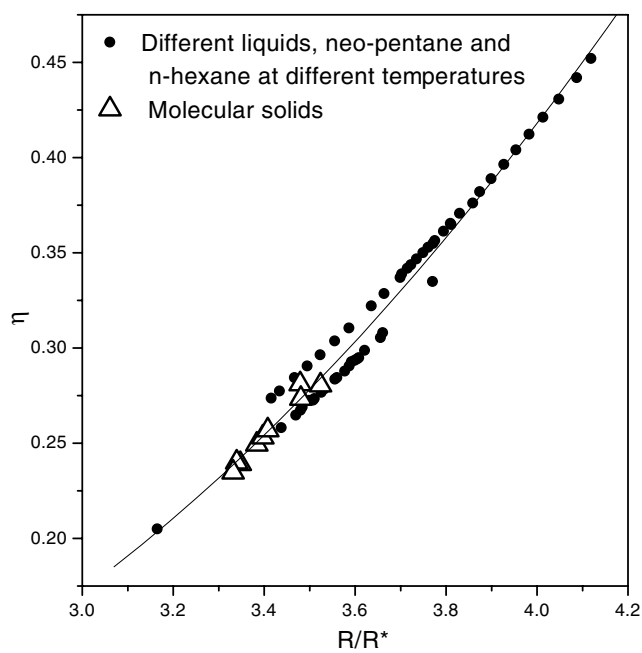


Figure 3. Relation between the scaled radius R/R^* and scaled pick-off lifetime η .

we compare the overlap integral thus obtained with that determined through the curves in figures 1–3 we find that the values are very close indeed, confirming the consistency of our ansatz, provided one adopts a modified bubble model which correctly reproduces both lifetime and angular correlation data in liquids. We thus have a model which can also describe faithfully Ps annihilation characteristics in molecular solids corresponding to the pick-off mode.

Some caution, however, must be exercised in determining the applicability of the model. Thus, for example, there are samples where more than one long-lived component is discernible [28, 29]. For instance, positrons injected into polymers have a complicated history and a consequent complex lifetime spectrum. With a high instrumental resolution one is able to distinguish these lifetime components in several cases, but a critical problem lies with the assignment of each component to a particular state from which the annihilation occurs. A common feature here is a component of lifetime ~ 1 ns and intensity $\sim 10\%$ whose origin has been debated for a long time. Studies using response to electrostatic fields [30], scrutiny of the narrow peak sensitive region of the angular correlation curves [31] and positron-age-momentum correlation measurements [32] seem to indicate that such components may not result from the annihilation of *o*-Ps. Similarly external magnetic field dependent lifetime quenching measurements are quite revealing as the *ortho-para*-Ps states are therein mixed and the superposition amplitude depends on the hyperfine splitting between the two states which in turn permits an estimation of $|\Psi(0)|^2$ (the square modulus of the electron positron wavefunction at zero separation). Departure of this from the value expected for *o*-Ps is indicative of a different decay mechanism. Thus, Bertolaccini *et al* [33] in some cases found no magnetic quenching while they obtained a small effect in others. Consolati and Quasso [34] studied magnetic quenching in five polymers and concluded that the intermediate 1 ns component comes from the decay of a positron–electron bound system (Ps-like) different from that associated with the longest lived component. Similar considerations led to the introduction of the notion of ‘swollen Ps’ by Goldanskii [35]. Eldrup [36], however, ascribes the ~ 1 ns component in molecular crystals to entrapment of the *o*-Ps in a densely packed region. On the basis of the arguments thus set forth we shall not consider data from samples where the lifetimes are shorter than 1 ns in view of the ambiguity concerning the very origin of the annihilation mode. On the other hand, cases where the lifetimes are very large (≥ 10 ns) may be left out of our purview, since these correspond to situations where the cavities are very large and there the pick-off annihilation is perhaps better described through the picture adopted by Fox and Canter [37]. They described the annihilation of *o*-Ps by adding the three gamma rate (which is not negligible in such a case) to the effect of collision with the wall leading to penetration of the potential barrier and hence the consequent annihilation declines. Thus to emphasize, the pick-off events we have considered correspond to lifetimes in the range 2–10 ns where our model is applicable. For exactly the same reason we have omitted from our consideration liquified gases such as liquid helium for which the lifetime is far too long and bubble radius too large to fall within the scope of our present model. This was in fact recognized by Ferrell [1] at the very inception of the bubble model and later commented on by Roellig [9].

It remains for us to show that the dependence of the barrier height (U_0) on the cavity size (R) is consistent with the Ps–atom repulsive interaction, which is a short ranged exchange potential and may be taken to be of strength v for a range d . Thus the Ps at a distance \vec{r} from the centre of the bubble of radius R feels the repulsion of all atoms situated at \vec{q} with respect to it provided $q \leq d$ or located at polar angle θ ($\cos \theta = \hat{R} \cdot \hat{r}$) in the range

$$1 \geq \cos \theta \geq \frac{R^2 + r^2 - d^2}{2Rr}. \quad (20)$$

On performing the integral and considering the fact that the area occupied by each atom on the surface is r_{WS}^2 (modulo geometric factors) where r_{WS} is the Wigner–Seitz radius we arrive

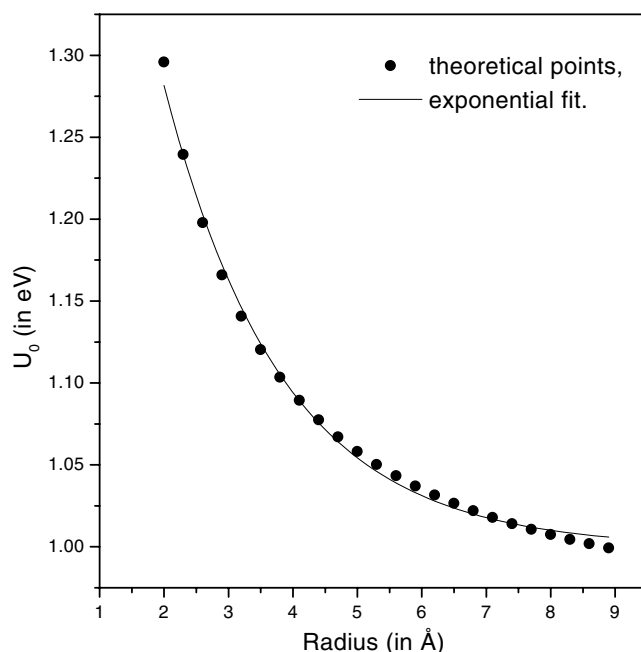


Figure 4. Dependence of potential U_0 on bubble radius R as obtained from equation (21) (considering $r_{WS} = 3 \text{ \AA}$, $d = 1 \text{ \AA}$ and $v_0 = 1 \text{ eV}$) showing a general dependence similar to that depicted in figure 2.

at the dependence of U_0 on R , namely

$$U_0 \sim \pi v_0 \left(\frac{R}{r_{WS}} \right)^2 \left(\frac{d}{R} \right)^2 \left[\frac{8 - 3(d/R)}{3 - 3(d/R) + (d/R)^2} \right]. \quad (21)$$

As shown in figure 4 with appropriate choice of v_0 and d the empirically determined curve is very well fitted by the form obtained by us from basic principles. Of course it must be recognized that d is a lumped parameter and includes, apart from the range of the Ps–atom interaction, the roughness of the surface and its diffusivity and contribution from the finite Ps size.

3. Conclusion

Summarizing, the paper rests on the picture that Ps interaction with any molecular substance is essentially due to the short range exchange potential involving the electrons of the atomic core with that of Ps and it is this repulsion that guarantees a moderately long pick-off annihilation rate. Be it liquid or solid, the root cause lies with this negative work-function, by virtue of which the Ps is designated as ‘digger and seeker’ of holes or void spaces in any molecular substance. This property is in turn utilized to calibrate the bubble size or void spaces in molecular matter.

In our efforts to do away with the shortcomings of the sharp boundary square well model we have introduced a diffusivity in the walls of the cavity, and arrive eventually at an extremely simple formula (equation (15)) relating the pick-off lifetime to the cavity radius. We find a basic description applicable to both molecular liquids and solids in terms of the average potential experienced by the Ps in the cavity. The universal curve for the dependence of this barrier

height (U_0) at the walls on the radius of the cavity (R) is also found to be explicable in terms of the short ranged repulsion between the Ps and surrounding atoms.

To gain a deeper physical meaning of the confining potential it is worthwhile comparing our findings with those of Fox and Canter [37] who estimate the potential barrier U_0 faced by Ps at silica grain surfaces (~ 0.8 eV) which in turn has been related to the peak in the energy distribution of p -Ps atoms emitted from silica surfaces via AMOC measurements by Hyodo [38]. This may be interpreted as the Ps work-function. Accordingly we suggest that the dependence of U_0 on R is describable as the curvature dependence of the Ps work-function in micro-cavities.

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