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A first step towards a quantum mechanical description of surface energy and diffusivity in the bubble model of positronium annihilation

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ABSTRACT

In the bubble model of positronium annihilation in liquids, the inward contractile force on the bubble surface is described through classical surface tension of the liquids. In the present calculation, we adopted a simple quantum mechanical approach to describe the bubble surface energy in terms of the motion of a representative quasi-free electron outside the bubble. The bubble parameters (radius, potential, etc.) for different liquids obtained using the prescribed model are consistent with the results obtained using classical surface tension.

1. Introduction

The longer lifetime of ortho-positronium (o-Ps) atom in liquid helium is accounted by bubble model (Ferrell, 1957) where the o-Ps is considered as a quantum point particle self-trapped in a potential through the repulsive exchange interaction with the surrounding electrons of the medium having same spin and annihilates via *pick-off* process with the electrons with opposite spin. Ferrell's first proposition was that the self-trapping potential is of infinite sharp spherical type and o-Ps annihilates with the electron of the molecules of saturated vapor inside the cavity. However, the variance of experimental results with the theoretical prediction for different liquids, where the longer lifetimes of o-Ps were observed, led to consider the self-trapping potential to be finite sharp spherical type (Daniel and Stamp, 1959; Stewart and Brisco, 1967). However, Tao has proposed another model where he arrived at simpler equation for o-Ps *pick-off* annihilation using infinite spherical well with radius R_0 having an electron layer of thickness ΔR inside the wall of the well (Tao, 1972).

The above models were successfully applied for many liquids, however, the principal approximations and sources of errors in the standard bubble model were first identified by Beling et al. and subsequently, by Mukherjee et al. and were corrected with simple analytically solvable model (Beling and Smith, 1980; Nakanishi and Jean, 1988; Mukherjee et al., 1997a, 1997b). Their proposition was that the liquid-bubble surface should be smooth rather than having a sharp boundary and accordingly, they have chosen appropriate model bubble-potential. The reliability of the use of the particular model bubble-potential was examined by theoretical prediction of the non-trivial angular correlation parameter (FWHM) using that potential and by comparing the values of the parameters with the experimentally available data. Subsequently, different alternate forms of model potential were used by the authors and other collaborators for different polar, non-polar, and high surface tension liquids (Mukherjee et al., 1999; Dutta et al., 2002). They have also used the models successfully to account for Ps-complex formation reaction (Gangopadhyay et al., 2000). The dependence of o-Ps *pick-off* annihilation rate on the parachor of different liquids and liquid mixtures have been formulated much earlier by Lévay et al. (Lévay et al., 1973). However, in all the above mentioned models, whether sharp or smooth boundary, the inward (contractile) force by the outside liquid molecules has been considered due to the surface tension of the liquid, which balances the outward force on the bubble wall exerted by the zero-point kinetic motion of the Ps atom by minimizing the total energy i.e. $\frac{\partial E_{Ps}}{\partial R}+\frac{\partial E_S}{\partial R}=0$ where E_{Ps} is the Ps atom energy inside the bubble and E_S is the energy due to the bulk surface tension (σ) of the surrounding liquid ($E_S=4\pi R^2\sigma$, R being the bubble radius). However, the question has been raised for the use of the bulk surface tension for such a highly curved surface of very small radius (of 3–6 Å), which leads to the use of effective surface tension (σ_{eff}) rather than its bulk value (σ) and is given by $\sigma_{eff}=\sigma(r/r+\delta)$, '$\delta$' being the diffusivity parameter (also called 'Tolman Length') of the system (Tolman, 1949). The surface energy calculated from the effective surface tension was successfully applied to determine the bubble parameters using observed decay rate of o-Ps and the angular correlation parameters were predicted (Mukherjee et al., 1999). However, the question still

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remains unanswered about the validity of the use of classical surface tension to describe the tiny bubble (Radhakrishnan and Gubbins, 1999) which is formed due to quantum mechanical electron exchange interaction of Ps with surrounding atoms.

The concept of surface tension is mainly applicable when the liquid is treated as a continuum system. If the liquid is considered as composed of discrete molecules, then one finds the origin of surface tension as an attractive van der Waals force between atoms/molecules and surfaces (Israelachivli, 1991), which contracts the liquid surface to occupy the smallest area. The fact that a liquid surface contracts spontaneously, shows that there is "free energy" associated with it. This free energy is of fundamental importance and for simplicity in calculation it is usually substituted by a "hypothetical tension", which is equal to the free surface energy. Coming to the Ps-bubble system, as discussed before, classically this free energy is associated with the van der Waals interaction between Ps atom and the nearest molecules of the medium. Here we have treated the surroundings of the Ps-bubble in liquid medium as consisting of quasi-free molecular electrons and ions which are formed in the diffusive part of the terminal spur as discussed in the next section. It is to be noted that the *pick-off* annihilation takes place due to the interaction of the electron of the Ps atom with the quasi-free electron (of opposite spin) outside the bubble. To the best of our knowledge, there is no such calculation in bubble model which takes into account the motion of external electron near the bubble surface to describe the bubble parameters. Here we have developed a simple model quantum mechanical description of the motion of the quasi-free electron outside the bubble bound in the van der Walls-type potential and tried to find correlation with the surface energy of the bubble. Furthermore, in the earlier calculations, the diffusivity of the particles involved has been included through classical length parameter. Thus it is also essential to search for a quantum analogue of this parameter and to verify whether it is only a parameter or variable of the total system.

2. The present work

It is well known that there are two models to describe the phenomenon of Ps atom formation, one is spur model (Mogensen, 1974) and another is Ore model (Ore, 1949). Usually, the Ore model is applicable in gaseous system whereas, in molecular solids and liquids, most experimental data appears to be explained by spur model. According to the spur model, the positron, injected into a substance at high energy is slowed down by successive ionization and excitation processes by depositing several hundred eV of energy to the substances at each several hundred nanometer. The microscopic spatial region, where the energy is deposited is called spur. A spur can be defined as a group of 'reactive intermediates' which are so close together that there is a significant probability of their reacting with each other before diffusing into bulk medium. The spur model of Ps formation assumes that the positron stops in the terminal spur that is created by transferring its last energy and that the positron combines with one of the 'excess electrons' in the spur to form Ps. Although, inside the terminal spur there is every possibility of recombination of the created electron-ion pairs to form stable molecule (Byokov and Stepanov, 1993; Mukherjee et al., 1997a, 1997b), however, there are some recombined species (electron-ion pair) inside the terminal spur which are in a transient state where the electron is loosely bound to the molecular-ion. This transient electron-ion pair provides the necessary electron for *pick-off* annihilation. This loosely bound electron may be termed as quasi-free 'molecular electron'.

Outside the Ps potential barrier there are medium molecules, both in transient and stable states, surrounding the bubble. The interaction of these molecules with Ps atom results in the Lennard–Jones-like potential, which consists of both attractive and repulsive part, near the bubble surface. Usually, the long range attractive part is stronger than the repulsive part. Therefore, the molecules nearest to the bubble are attracted towards the bubble surface. The *ab-initio* calculations of energy of those molecules using molecular dynamics are difficult to simulate. Therefore, instead of calculating the 'energy of the molecules' we have considered the motion of the quasi-free electron only. The nuclei of the molecular-ion are considered as static due to their heavier mass, which is nearly equivalent to the adiabatic approach to perform the calculations involving the slow and fast variable. The quasi-free electrons move inside the layer of the Lennard–Jones-type potential formed by the interactions of Ps with the nuclei and core electrons of the molecular-ion. The Lennard–Jones potential consists of a 'soft' repulsive part with a long range attractive part. However, when compared to the experiments it is found that a hard sphere potential is a reasonable assumption to predict contact energies (Israelachivli, 1991). Therefore, to make the calculation simple, here we have considered that the potential layer outside the bubble is a hard spherical square well type of radius R_e. The stable Ps-bubble-electron configuration has been achieved by minimizing the energies of centre of mass motion of Ps atom and the quasi-free electron with respect to the bubble radius (R) and R_e, respectively. The calculated energy of quasi-free electron is then correlated with the surface energy of the bubble and hence surface tension (defined as surface energy required to increase unit area) associated with the bubble surface and computed it along with the diffusivity parameters. Finally, the calculated values of surface tension for different liquids were observed to be much close to the values obtained experimentally. In the following section we have described the basic theoretical developments to calculate the variables.

3. Basic theory

We have considered Ps atom trapped in a sharp spherical potential of finite depth. The bubble-potential function is defined as, $V_{Ps}=0$ for $r_{Ps}<R$, $V_{Ps}=V_{0Ps}$ for $r_{Ps}\geq R$, where V_{0Ps} is the height of the bubble potential, R is the bubble radius and r_{Ps} is the Ps radial coordinate measured from the bubble centre. Solutions of the Schrödinger equations in these two regions (inside and outside the bubble) give the ground state wave functions ($l=0$) of the Ps atom and are given by the following expressions (Nakanishi and Jean, 1988)

$$\Psi_{Ps}(r_{Ps})=\begin{cases}\dfrac{A\sin(k_{Ps}r_{Ps})}{r_{Ps}}, & 0\leq r_{Ps}\leq R\\ B\dfrac{e^{-\alpha r_{Ps}}}{r_{Ps}}, & r_{Ps}>R\end{cases} \quad (1)$$

where A and B are normalization constants, $k_{Ps}=\sqrt{(4mE_{Ps}/\hbar^2)}$ and $\alpha=\sqrt{\left(4m(V_{0Ps}-E_{Ps})/\hbar^2\right)}$ m being the rest mass of the electron and E_{Ps} is the total energy of o-Ps inside the bubble.

The ground state energy of Ps is given by

$$E_{Ps}=V_{0Ps}\sin^2(k_{Ps}R) \quad (2)$$

In the prevalent bubble model, only the Ps motion is considered, where Ps is self-trapped due to exchange repulsion with the surrounding electron. However, the dynamical motion of the quasi-free electron of the medium outside the bubble was not taken into account. Here we have adopted a model to describe the motion of a representative quasi-free electron described above in