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Energy dissipation and Ps bubble growth in liquids

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Abstract

Dissipative energy losses accompanying growth of the Ps bubble are calculated using the Navier–Stokes equation. This allows to demonstrate a fulfilling of the total energy balance in this process. It is in favor of the adopted approach.

Keywords: Positronium; Nanovoid; Bubble growth; Energy dissipation

1. Introduction

In view of rapid development of experimental methods of the positron spectroscopy sensitive to kinetics of the picosecond processes (first of all the age–momentum correlation technique), it becomes important for adequate description of positronium (Ps) formation to take into account all intratrack processes up to 1 ns. They are retardation of the energetic positron and knocked out electrons, thermalization, formation of primary radiolytic products and physico-chemical reactions between them. The blob model (Stepanov and Byakov, 2003) is aimed on the description of this stage of radiolysis including Ps formation. However, it allows to calculate formation probability of the quasi-free positronium (qf-Ps), which is a bound state of the $e^+ - e^-$ pair in unperturbed medium, before any rearrangement of the molecules caused by the presence of the pair. A further energy gain occurs on the bubble formation stage when qf-Ps localizes in a cavity (bubble) of a subnanometer size. Formation of such a free volume around Ps is due to the exchange repulsion among the positronium electron and surrounding molecular electrons (Ferrel, 1957).

It is usually assumed that the formation of the Ps bubble state in liquids takes a negligible time as compared to the positronium lifetime. This assumption is based on the rough dimensional assessment of the bubble formation time: $2R_{Ps}/v \sim 1$ ps, where R_{Ps} is the equilibrium radius of the Ps bubble and v is the speed of sound. The dynamics of growth of the Ps bubble has not been rigorously discussed yet. The work (Iakubov and Khrapak, 1982) only briefly touched this problem in liquid helium, and our previous paper (Mikhin et al., 2003) tackled growth of the bubble solving the Navier–Stokes (NS) equation.

Although application of the macroscopic hydrodynamics is not justified on a molecular level (for the description of the Ps bubble), it may serve as a rough simulation of the process. It would be an argument in favor of the used approximation, if we demonstrate a fulfilling of the total energy balance within the same approach. So this work is aimed on the calculation of the dissipative energy losses accompanying growth of the Ps bubble in the frameworks of the NS equation.

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2. Kinetics of the Ps bubble formation

Condition of incompressibility of the liquid and the continuity equation result in relationship $\mathrm{div}\,\mathbf{v} = 0$, which in case of centrosymmetrical growth of the bubble allows to represent velocity of the liquid in the following form: $v(r,t) = F(t)/r^2$ (here, $F(t)$ is an arbitrary function). Substituting this expression to the NS equation and integrating it over whole volume, one may come to equation on the radius, $R_\sigma(t)$, of the first molecular layer (FML) of the bubble (Mikhin et al., 2005):

$$\rho\left(R_\sigma\ddot{R}_\sigma + \frac{3}{2}\dot{R}_\sigma^2\right) = p_{\mathrm{FML}} - p_0\frac{R^2}{R_\sigma^2}, \quad R_\sigma = R + R_{\mathrm{WS}}. \tag{1}$$

R_σ is the radius of the sphere, passing through the centers of masses of molecules residing on FML, i.e. the radius of the bubble. R_{WS} is the radius of the Wigner–Seitz sphere of the given liquid ($4\pi R_{\mathrm{WS}}^3/3$ is the volume per one molecule). ρ is the density of the liquid. R is the free volume radius of the bubble. The difference $p_{\mathrm{FML}} - p_0R^2/R_\sigma^2$ in Eq. (1) appears from an integration of the term containing ∇p in the NS equation (see below). p_0 is the external pressure and p_{FML} is the pressure acting on the molecules on FML.

To improve description of motion of a liquid on a molecular scale with the aid of macroscopic hydrodynamics we shall make use of reasonable physical hypotheses, beyond the NS approach.

At $t \to \infty$, the right-hand part of Eq. (1) must vanish and reproduce the results of the static Ps bubble model (Stepanov et al., 2000). This requirement determines the appearance of the factor R^2/R_σ^2 in Eq. (1). Formally, it stems from the finite thickness of the bubble boundary in the present treatment, unlike an infinitely thin boundary in the standard derivation of the NS equation.

In Eq. (1) we have attributed p_{FML} with the sphere $r = R_\sigma$, passing through FML. Intermolecular forces responsible for appearance of the surface tension act between FML molecules at $r = R_\sigma$. Viscous friction also becomes operative in this area ($r \gtrsim R_\sigma$). Despite that the viscosity-containing term disappears from NS equation in case of spherically symmetric expansion of the bubble, viscosity, η, affects its growth dynamics via boundary condition or, in other words, through the pressure at the bubble–liquid interface:

$$p_{\mathrm{FML}} = -p_\sigma + p_{\mathrm{Ps}} + \Pi_{\mathrm{rr}}. \tag{2}$$

Here, the quantity Π_{rr} is the jump of the radial component of the viscous-stress tensor

$$\Pi_{\mathrm{rr}} = 2\eta\frac{\partial v(r,t)}{\partial r}\bigg|_{\mathrm{FML}} = -4\eta\frac{\dot{R}_\sigma}{R_\sigma}. \tag{3}$$

Let us consider the first two terms in p_{FML}. If the surface energy E_σ is meant as the number of broken intermolecular bonds proportional to the area of the surface formed, it turns out that $E_\sigma = 4\pi R^2\sigma$ (Stepanov et al., 2000). A particular expression of the Laplace pressure p_σ depends on the choice of the position of the surface of tension. As we have mentioned above, it seems natural to draw the surface of tension through the centers of masses of FML molecules, i.e. to identify it with a sphere having radius R_σ. Then the Laplace pressure may be defined as follows:

$$4\pi\sigma_\infty R^2 = \int_{R_{\mathrm{WS}}}^{R+R_{\mathrm{WS}}} p_\sigma(r)\,\mathrm{d}^3r,$$

in which the integration domain is limited by the position of the surface of tension. Differentiating the latter equality over R, we obtain

$$p_\sigma = \frac{2\tilde{\sigma}(R_\sigma)}{R_\sigma}, \quad \tilde{\sigma}(R_\sigma) = \frac{\sigma_\infty}{1 + R_{\mathrm{WS}}/R}.$$

Here, $\tilde{\sigma}$ is the curvature-dependent surface tension. Of course, this expression is qualitative, but numerical values of p_σ can be refined ensuring the best fit of the positron spectroscopy data. For this purpose, $\tilde{\sigma}$ is rewritten in the Tolman-like form $\tilde{\sigma}(r) = \sigma_\infty/(1 + 2\Delta/r)$, where 2Δ is considered as an adjustable parameter. Its numerical values are given in Stepanov et al. (2000).

The last quantity has to be defined is the pressure exerted by Ps on the FML molecules. As we have mentioned, the cavity in the liquid presents a potential trap for Ps because of exchange interaction. We shall simulate it by a spherically symmetric rectangular potential well of the depth U and radius R_U. These parameters as well as penetration depth δ of the molecular electrons into the bubble ($\delta = R_U - R \approx 1.1-1.2$ Å) may be unambiguously obtained from the ortho-Ps lifetime and the width of the narrow (para-Ps) component of the ACAR spectrum (Stepanov et al., 2000). Then it is easy to find energy E_{Ps} of the ground state of Ps in the bubble and pressure p_{Ps} that repels molecules of the liquid outwards:

$$p_{\mathrm{Ps}} = -\frac{\mathrm{d}E_{\mathrm{Ps}}(U,R_U)}{\mathrm{d}V_\sigma} = -\frac{\mathrm{d}E_{\mathrm{Ps}}}{\mathrm{d}R_U}\frac{1}{4\pi R_\sigma^2} > 0, \tag{4}$$

$$E_{\mathrm{Ps}} = \frac{\hbar^2k_U^2}{4m}, \quad \frac{\mathrm{d}E_{\mathrm{Ps}}}{\mathrm{d}R_U} = \frac{2k_UE_{\mathrm{Ps}}}{\tan(k_UR_U) - k_UR_U},$$

$$U = \frac{\hbar^2k_U^2}{2m_{\mathrm{Ps}}\sin^2 k_UR_U} = \frac{\pi^2\hbar^2}{8m_{\mathrm{Ps}}\delta^2}. \tag{5}$$

The last relationship, which relates U and δ, implies that in the absence of the free volume ($R = 0$) Ps energy level disappears ($E_{\mathrm{Ps}} = U$). Collecting all pressure terms