Localization of a quantum-mechanical particle in classical simple fluids

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We present a self-consistent scheme to study the localization of a light particle obeying quantum mechanics immersed in classical simple fluids. The interparticle correlations between the particles of the host fluid are analyzed with the Percus-Yevick approximation using the Lennard-Jones potential. The interaction between the light particle and the fluid particles is represented by a contact potential. The Percus-Yevick approximation is also used to describe the density distribution of the fluid particles around the light particle. The effective potential acting on the light particle and the wave function of the light particle are self-consistently determined by the coupled Percus-Yevick and Schrödinger equations. The formalism was used to investigate ortho-positronium localization and annihilation in liquids He and Ne. The theory is found to be in fairly good agreement with existing experiments.

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I. INTRODUCTION

The problem of a light particle trapped in fluids has been extensively studied during the past three decades [1,2]. The light particle here refers to an electron, positron, or positronium which behaves quantum mechanically. When such a particle is injected into a fluid, it polarizes the host fluid to form a dilute cavity or a droplet of dense material around it depending on whether the interaction between them is repulsive or attractive. As a result of the polarization, the light particle may be in a localized state. Therefore the mobility of the light particle may be substantially reduced [3]. If a positron or a positronium happens to be localized in the fluid, its annihilation rate differs considerably from that when it is in a free state [4,5].

For theoretically treating the localization, the crucial quantity is the density distribution of the fluid particles which impose a potential on the light particle. For the case of a repulsive interaction, the most simple description for the fluid density distribution is the "bubble" model [6], according to which there are no fluid particles inside of the bubble while the density is uniformly distributed outside of it. Various improvements to this model have been developed. Most of the theoretical schemes are based on the density-functional approach [2,7-11]. In these schemes, one usually composes the grand thermodynamic potential which depends on the wave function of the light particle and the local fluid density. The equilibrium state is obtained by minimizing the grand thermodynamic potential with respect to these two functions. Moore, Cleveland, and Gersch provided a treatment of the localization in an ideal gas [8]. Iakubov and Khrapak took the correlation effects into account via van der Waals fluids [2]. The additional effects of interparticle correlations were considered by Stott and Zaremba [9] and by Ebner and Punyanitya [10]. Stott and Zaremba employed a trial wave function and an empirical equation of state for treating positron annihilation in helium, while

in Ebner and Punyanitya's work [10], they analyzed the interparticle correlations of the fluid through the Percus-Yevick (PY) equation [12,13] with a Lennard-Jones 6-12 potential. The density distribution of the fluid particles around the light particle was parametrized as a continuous function. Recently, Miller and Reese investigated the problem by adopting the local-density approximation in which the density distribution is determined by the equation of state of the fluid and the potential asserted by the light particle [14].

In this paper, we present a fully self-consistent treatment of the localization. The particles of the fluid are nonpolar and obey classical mechanics. For such a fluid, the interaction between its particles may be fairly characterized by the Lennard-Jones 6-12 potential, and the PY equation is found to provide a good description of the interparticle correlations [13]. We still use the conventional contact-potential approximation for the interaction between the light particle and the fluid particle because the localization scale is much larger than the interaction range [2]. Under this approximation, the effective potential acting on the fluid particles can be explicitly expressed in terms of the wave function of the light particle. We also use the PY equation to describe the density distribution around the localization center. This density distribution acts as an effective potential on the light particle. Thus the wave function of the light particle and the fluid density distribution can be self-consistently determined by the coupled Schrödinger and PY equations.

As an application, we will consider ortho-positronium (o-Ps) localization and annihilation in classical rare-gas fluids. For the fluid at low density, there is no localized state for the light particle. Experiments show that the pick-off annihilation rate increases linearly with density [1]. This linear dependence results from a sequence of independent collisions between o-Ps and the fluid particles. As the density increases further, the annihilation rate starts to drop from the linear dependence. By observing such behavior in ethane gas, Sharma, Eftekhari, and

McNutt [15] have suggested a semiempirical model which explains the reduction of the annihilation rate in terms of fluid density fluctuations. This model fails in higher density region, where the localization effects are expected to be predominant. The present theory is suitable for treating the problem of strong localization. It can give a better evaluation of the annihilation rate in strong localization cases.

In Sec. II, we outline the self-consistent formalism. Section III gives the numerical technique for solving the coupled simultaneous equations. The PY equation can be solved by a simple iteration algorithm with very fast convergence and good precision. We apply the formalism derived in Sec. II to calculate the pick-off annihilation rate of o-Ps in fluid He and Ne. The numerical results and their comparison with experimental data are shown in Sec. IV. Conclusion and remarks are given in Sec. V.

II. FORMALISM

We consider a light particle immersed in a classical simple fluid with average number density n at temperature T. The fluid is assumed to be in the thermodynamic equilibrium state. By omitting the kinetic energy of the fluid particles, the Hamiltonian of the whole system is given as

$$H = p^2/2m + \int d\mathbf{R} v(\mathbf{r} - \mathbf{R}) n(\mathbf{R})$$
$$+ \tfrac{1}{2} \int d\mathbf{R} \int d\mathbf{R}' u(\mathbf{R} - \mathbf{R}') n(\mathbf{R}) n(\mathbf{R}') , \qquad (1)$$

where the first term on the right-hand side is the kinetic energy of the light particle with mass m, the second term is the interaction energy between the light particle (at position $\mathbf{r}$) and the fluid particles, and the third term comes from the interaction between the fluid particles whose density operator is denoted as $n(\mathbf{R})$. The potential $v(\mathbf{r})$ is usually approximated as [2]

$$v(\mathbf{r}) = (2\pi\hbar^2 L/m)\delta(\mathbf{r}) . \qquad (2)$$

where L is the scattering length. For the interaction between the fluid particles, we use the Lennard-Jones 6-12 potential [12]

$$u(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6] . \qquad (3)$$

For the pick-off annihilation, the available electron number from a fluid particle is denoted as Z_{eff}. The parameters ε and σ as well as the quantities L and Z_{eff} for the fluids under consideration are given in Table I.

Before we treat the problem, we need to study the correlations between the particles. To determine the

TABLE I. Parameters ε and σ used in the interparticle potentials of the fluids [12]. The scattering length L and the effective charge number Z_{eff} are the characteristic parameters for collisions between ortho-positronium and the fluid particles [2]. All the lengths are in the unit of Bohr's radius a_B.

Element	ε/k_B (K)	σ (units of a_B)	L (units of a_B)	Z_{eff}
He	10.2	4.832	1.5	0.125
Ne	35.6	5.197	1.65	0.235

correlation functions of the fluid, we use the PY equation and the Ornstern-Zernike (OZ) relation [13]

$$c(r) = \{\exp[-\beta u(r)] - 1\}[N(r) + 1] , \qquad (4a)$$

$$N(k) = nc^2(k)/[1 - nc(k)] , \qquad (4b)$$

where $\beta = 1/k_B T$, and $c(r)$ and $N(r)$ are the direct correlation function and the nodal function, respectively. Here the function in real space and its Fourier components are distinguished by their arguments r and k. For the correlation function, we have

$$h(r) = c(r) + N(r) . \qquad (5)$$

We notice Eq. (4a) is different from its conventional form. The advantage of writing it in such a form will be mentioned in Sec. III.

We now return to the Hamiltonian (1) and look for an effective interaction between the light particle and the fluid. In actual calculation, one frequently uses the mean-field approximation in many theoretical schemes. In taking the average, the contribution from the excited states of the light particle is neglected for the smallness of occupation probability. We here also confine ourselves to this approximation to see the ground-state localization. Using the mean-field approximation, we decompose the second term on the right-hand side of Eq. (1) as

$$\int d\mathbf{R} v(\mathbf{r} - \mathbf{R}) n(\mathbf{R})$$
$$\simeq \int d\mathbf{R} v(\mathbf{r} - \mathbf{R}) n_0(\mathbf{R})$$
$$+ \int d\mathbf{R} \int d\mathbf{r} |\psi(\mathbf{r})|^2 v(\mathbf{r} - \mathbf{R}) n(\mathbf{R})$$
$$- \int d\mathbf{R} \int d\mathbf{r} |\psi(\mathbf{r})|^2 v(\mathbf{r} - \mathbf{R}) n_0(\mathbf{R}) , \qquad (6)$$

where $n_0(\mathbf{R})$ is the averaged density distribution of the fluid particles in the field of light particle, and $\psi(\mathbf{r})$ is the wave function of the light particle [16]. The last term in Eq. (6) is a constant and will be dropped hereafter. The first term is just the effective potential acting on the light particle, while the second term is the averaged potential acting on the fluid. With the help of Eq. (2), the effective potentials acting on each particle can be written as

$$v_{\text{eff}}(r) = (2\pi\hbar^2 L/m)[n_0(r) - n] , \qquad (7)$$

$$v_0(r) = (2\pi\hbar^2 L/m)|\psi(r)|^2 , \qquad (8)$$

where we have subtracted a constant in $v_{\text{eff}}(r)$ and assumed that the origin is at the localization center.

With the averaged potential, the wave function and the energy of the light particle are determined by Schrödinger equation

$$[p^2/2m + v_{\text{eff}}(r)]\psi(r) = E\psi(r) . \qquad (9)$$

The averaged density distribution $n_0(r)$ is involved in the averaged potential $v_{\text{eff}}(r)$. The deviation of $n_0(r)$ from n stems from the presence of the localized particle which polarizes the fluid. So such a localization is also called "self-trapping."

As for the correlations between the fluid particles, the PY equation may provide a good description for the den-

sity distribution, $n_0(r)$ in the effective potential $v_0(r)$, which is a short-range one. If we use subscript 0 to denote the various correlation functions between the localization center and the fluid particles, the corresponding PY equation can be written as

$$c_0(r) = \{\exp[-\beta v_0(r)] - 1\}[N_0(r) + 1] , \quad (10a)$$

$$N_0(k) = nc_0(k)h(k) , \quad (10b)$$

where $h(k)$ is the solution of Eqs. (4) for the host fluid. The averaged density distribution is given as

$$n_0(r) = n[1 + h_0(r)] , \quad (11)$$

where $h_0(r) = c_0(r) + N_0(r)$. Therefore the differential equation (9) and integral equations (10) compose the coupled simultaneous equations which self-consistently determine the state of the light particle.

III. NUMERICAL TECHNIQUE FOR COMPUTATION

In order to solve the coupled simultaneous equations, we have to look for a simple but efficient method. Many efforts have been devoted to solving the PY equation in its original form:

$$c(r) = \{1 - \exp[\beta u(r)]\}g(r) , \quad (12)$$

where $g(r) = 1 + h(r)$ is the radial distribution function. Near the triple point, one needs to order 1000 iterations to solve this equation [13]. The very slow convergence stems from the short-range part of the interaction $u(r)$, where the absolute value of the factor in Eq. (12) is larger than unity, $|1 - \exp[\beta u(r)]| \gg 1$. After a rearrangement of Eq. (12), one can get the form as given by Eq. (4a) in which the absolute value of the factor is less than unity in most of the r domain.

In order to see why such a form may lead to fast convergence, let us consider a very simple example: $x = ax + b$ where $a \neq 1$. If we solve this equation by the iteration, $x_n = ax_{n-1} + b$, the error in nth step is given as $\Delta x_n = a\Delta x_{n-1} = a^n \Delta_0$. Therefore the iteration procedure may converge or diverge depending on $|a| < 1$ or $|a| > 1$, respectively. Although the PY equation differs from this simple example, the philosophy of numerical technique is the same. In the present work, we have used a fast-converging iteration method developed by Ng for solving the hypernetted-chain equation [17], by which the solution of Eqs. (4) were obtained with typically 30 iterations. However, for attractive interactions, e.g., between a positron and rare-gas atoms, Eq. (12) is a suitable form.

The Schrödinger equation (9) can be solved with the Numerov algorithm, which is fast and precise [18]. It needs a proper initial input for the potential $v_{\text{eff}}(r)$. We have solved the coupled simultaneous equations for a number of combinations of fluid parameters n and T. The solution of $v_{\text{eff}}(r)$ at a point (n, T) was used as input for next calculation at another point near (n, T). After several iterations, we obtained an accuracy of

$$\left[\int dr [h_0^{(\text{in})}(r) - h_0^{(\text{out})}(r)]^2 \right]^{1/2} < 10^{-7} . \quad (13)$$

Initially, there is no such proper input available. We may start the calculation in a different way by writing $h_0(r)$ as

$$h_0(r) = \exp[-\beta v_0(r)] - 1 + f(r) , \quad (14)$$

with

$$f(r) = N_0(r)\exp[-\beta v_0(r)] . \quad (15)$$

Omitting $f(r)$ at the first step of iteration, a nonlinear Schrödinger equation is obtained, since $v_0(r)$ is given in terms of the wave function $\psi(r)$ which satisfies the necessary boundary and normalization conditions. This nonlinear Schrödinger equation can be solved with the Runge-Kutta method or the Adams-Bashfourth-Moulton schemes [19]. Having the potential $v_0(r)$ obtained from the wave function, we can solve the PY equation and get the function $f(r)$. This finishes the first step of iteration. With the function $f(r)$ as input, we can proceed to the consecutive steps of iteration. The procedure is continued until the self-consistent solution within the accuracy set by Eq. (13) is obtained.

IV. POSITRONIUM LOCALIZATION AND ANNIHILATION IN LIQUIDS He AND Ne

In this section, we apply the formalism derived in Sec. II to study the problems of o-Ps localization and annihilation in the classical liquid Ne and He. For the sake of description, we introduce some parameters characterizing the state of the liquids. The reduced temperature and density are defined as

$$T^* \equiv k_B T / \varepsilon \quad (16)$$

and

$$n^* \equiv n\sigma^3 , \quad (17)$$

respectively. For the length scale, we use the Wigner-Seitz radius

$$a \equiv (3/4\pi n)^{1/3} . \quad (18)$$

The coupled simultaneous equations have been solved for a number of combinations of T^* and n^*. In Fig. 1, we show the results for positronium in liquid Ne at
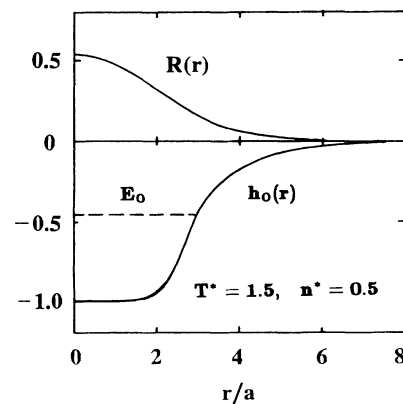

FIG. 1. Wave function $R(r)$, reduced potential $h_0(r)$, and energy E_0 of the localized positronium in fluid Ne at $T^* = 1.5$ and $n^* = 0.5$.

$T^* = 1.5$ and $n^* = 0.5$. The radial part of the Ps wave function, $R(r)$, satisfies the normalization condition,

$$\int_0^\infty dr\, r^2 R^2(r) = 1 \ . \tag{19}$$

The energy is scaled by constant g_0,

$$E = g_0 E_0 \ , \tag{20}$$

with

$$g_0 = 2\pi\hbar^2 Ln/m \ , \tag{21}$$

thus the correlation function $h_0(r)$ expresses the scaled potential in which the positronium moves. The form of the potential is different from a square well. The classical turning radius is about $3a$ within which a large part of the wave function is localized.

With the knowledge of the density distribution of the fluid particles and the Ps wave function, we can calculate the Ps annihilation rate λ. For the pick-off annihilation of o-Ps in liquids, λ is given as [2]

$$\lambda = \lambda_v + 4\pi r_0^2 c Z_{\text{eff}} n \left[1 + \int d\mathbf{r} |\psi(r)|^2 h_0(r) \right] \ , \tag{22}$$

where $\lambda_v = 0.704 \times 10^7$ s^{-1} is the annihilation rate in vacuum, r_0 is the electron classical radius, and c is the light velocity. The last term in Eq. (22) is due to collisions with the fluid particles. This term is also called the quenching rate. In Fig. 2, we exhibit this quenching rate through the normalized quantity

$$R = n^* \left[1 + \int d\mathbf{r} |\psi(r)|^2 h_0(r) \right] \tag{23}$$

as a function of n^* for o-Ps in liquid Ne at two temperatures. At these parameters, the quenching rate decreases above a certain density and after reaching a minimum it increases linearly with density. At the outset, with in-
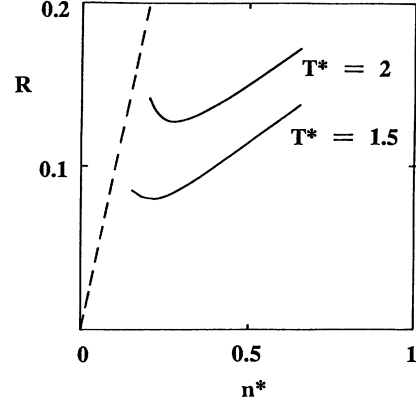

FIG. 2. Reduced quenching rate R as a function of n^* for ortho-positronium annihilation in fluid Ne at the reduced temperatures $T^* = 1.5$ and 2.

creasing density, the potential well is deepened and so the localization is stronger. But for still higher density, the width of potential well is squeezed, which decrease the extent of localization. This explains the behavior of the quenching rate. At a given temperature outside of the above density regime, the potential well is too shallow (at low density), or its width is too narrow (at high density), to sustain a localized state. The dashed line in Fig. 2 denotes the low-density behavior of R when the o-Ps is in the extended state. For the case of liquid He, the behavior of R is the same as in Fig. 2.

There have been many experimental results for positronium annihilation in liquids. We pick here three available sets of data [5] for λ_{exp} which can be directly compared with our theory:

$\lambda_{\text{exp}} = 5.2 \times 10^7$ s^{-1}, $\lambda_{\text{theor}} = 4.37 \times 10^7$ s^{-1} for Ne at $T = 45$ K, $n = 0.88$ g/cm^3 ,

$\lambda_{\text{exp}} = 4.5 \times 10^7$ s^{-1}, $\lambda_{\text{theor}} = 4.11 \times 10^7$ s^{-1} for Ne at $T = 46$ K, $n = 0.79$ g/cm^3 ,

$\lambda_{\text{exp}} = 1.66 \times 10^7$ s^{-1}, $\lambda_{\text{theor}} = 1.36 \times 10^7$ s^{-1} for He at $T = 13$ K, $n = 0.03$ g/cm^3 .

It can be seen that the theoretical values are in fairly good agreement with the experimental ones.

V. CONCLUSION AND REMARKS

We have developed a fully self-consistent formalism for studying localization of a light particle in classical simple fluids; the wave function of the light particle and the potential are determined through the coupled Schrödinger and PY equations. The theory is applicable for investigating strong localization.

However, the property of translational invariance is still broken in the present theory as well as in others. The contributions of excited states including other bound states besides the ground one and the free states should be taken into account in a more sophisticated theory. Such a theory is still lacking. On the other hand, by Feynman's path-integral approach, this quantum problem can be transformed to a classical counterpart [20] and computer-simulation algorithms taking account of these effects are available.

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[16] In form of the second quantization, Hamiltonian (1) can be formally written as

$$H = \int d\mathbf{r}\, \phi^\dagger(\mathbf{r}) p^2/2m\, \phi(\mathbf{r})$$
$$+ \int d\mathbf{r} \int d\mathbf{R}\, v(\mathbf{r}-\mathbf{R})\phi^\dagger(\mathbf{r})\phi(\mathbf{r})n(\mathbf{R}) + V_f , \quad (1')$$

where $\phi^\dagger(\mathbf{r})$ and $\phi(\mathbf{r})$ are the creation and annihilation operators of the light particle, respectively, and V_f stands for the last term in Eq. (1). According to the mean-field approximation [e.g., A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971)], we have

$$\phi^\dagger(\mathbf{r})\phi(\mathbf{r})n(\mathbf{R}) \simeq \phi^\dagger(\mathbf{r})\phi(\mathbf{r})\langle n(\mathbf{R})\rangle + \langle \phi^\dagger(\mathbf{r})\phi(\mathbf{r})\rangle n(\mathbf{R})$$
$$- \langle \phi^\dagger(\mathbf{r})\phi(\mathbf{r})\rangle\langle n(\mathbf{R})\rangle . \quad (R1)$$

Following the notations in the text, these averages in Eq. (R1) are $\langle n(\mathbf{R})\rangle = n_0(\mathbf{R})$ and $\langle \phi^\dagger(\mathbf{r})\phi(\mathbf{r})\rangle = |\psi(\mathbf{r})|^2$ under our consideration that the light particle is localized in ground state. Substituting Eq. (R1) into Eq. (1') and rewriting the Hamiltonian in the coordinate space, we would obtain an effective Hamiltonian with approximation given by Eq. (6).

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