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Localization in fluids: A comparison of competing theories and their application to positron annihilation

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This paper addresses two central issues in our understanding of self-trapping, or localization, of a light particle (e.g., electron, positron, or positronium atom) in a fluid. The first concerns the relationship between the mean-field calculations of localized states carried out from the mid-1950s until the present, and the direct calculation of light-particle (LP) properties from the adiabatic model. The second concerns the universality of the ring polymer representation of the LP, which has proved to be extremely useful for computing the properties of localized electrons. We first demonstrate that the mean-field theories of localization, which are derived from density functionals, can be obtained from the adiabatic model by employing a Gutzwiller type of approximation. We then study the application of the adiabatic model, via the polymer representation, to the annihilation of positrons and positronium atoms in a fluid. Expressions for the decay rate and its variance are derived in terms of the two- and three-point distribution functions for the polymer sites and positions of the atomic nuclei. The momentum distribution of the localized LP is shown to be proportional to the Fourier transform of the distribution function for the displacement between the ends of a broken polymer.

I. INTRODUCTION

A self-trapping system consists of a light particle (electron, positron, or positronium) and a dense fluid. If the mean de Broglie wavelength of the light particle (LP) is much greater than the mean spacing between fluid particles (FP's), the LP can simultaneously interact with many FP's. Therefore, in certain regions of temperature (T) and density (ρ) of the fluid, the LP can produce a region of altered fluid density in which it is localized. This phenomena is most significant near the liquid-vapor critical point where the isothermal compressibility of the gas is large.[1]

Experimental manifestations of self-trapping come in two broad categories. The range of electron mobility measured in fluids is extreme.[2] In a given fluid, the mobility depends sensitively on the mean density and pressure. Small values of the mobility are attributed to the presence of trapped states. Density and temperature dependence are also observed in various characteristics of the annihilation of positrons in fluids. Most notable is the pick-off decay rate of orthopositronium, λ_{PO}, in which a positron bound in orthopositronium annihilates with an electron associated with an atom or molecule of the host fluid.[1] Nonlinearity in plots of λ_{PO} vs ρ on isotherms is usually attributed to self-trapping (see Fig. 1). Related behavior is observed for the annihilation rate of positrons, but on a much shorter time scale.

In contrast with orthopositronium (o-Ps), parapositronium (p-Ps) has a short natural lifetime (1.23×10^{-10} sec for p-Ps vs 1.47×10^{-7} sec for o-Ps) and avoids the pick-off decay mode: The positron simply annihilates with its electron partner via a two-photon process. The momentum distribution of the positronium center of mass immediately before the annihilation can be experimentally accessed by measuring the angular distribution of the decay products. A signature of trapping is a mean positronium kinetic energy which exceeds $\frac{3}{2}kT$.[3]

Although the o-Ps decay rate and the p-Ps momentum distribution provide information about the LP environment, they are not equivalent. It will be shown below that the decay rate provides a measure of the local distortion of the fluid produced by the LP while, conversely, the momentum distribution provides a measure of the distortion of the LP due to the "pressure" exerted by the fluid molecules.

In order to simplify the role played by the atomic electrons, in theoretical studies of trapping it is popular to adopt a mesoscopic formulation which employs two effective potentials, one for the interaction between the FP's, u, and the other between the LP's and the FP's, v.

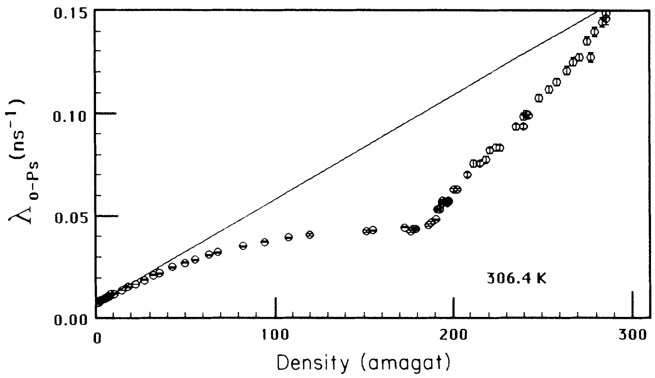

FIG. 1. Decay rate ($\lambda_{o\text{-Ps}}$) of orthopositronium vs density (D) in ethane at 306.4 K. The figure illustrates linear dependence at low density followed by a soft transition to a plateau in a broad region surrounding the critical point (from Ref. 19).

The Hamiltonian of this system is given by

$$H=\hat{\mathbf{p}}^2/2m+\sum_i v(\mathbf{x}-\mathbf{R}_i)+\tfrac{1}{2}\sum_{\substack{i,j\\ i\neq j}} u(\mathbf{R}_i-\mathbf{R}_j)+\sum_i P_i^2/2M\,, \tag{1}$$

where the first term is the kinetic energy of the LP; the second, $V(\mathbf{x},\mathbf{R})$, is the total LP-FP interaction energy; and the third, $U(\mathbf{R})$, and fourth are the total FP internal potential energy and kinetic energy, respectively. Because $M \gg m$, the LP has to be treated quantum mechanically while FP's are usually treated classically. In this work we shall adopt this view. Therefore the last term in (1) is decoupled and can be dropped for most studies of self-trapping.

This model has been studied since about 1950 by many investigators.[1] Most of them employed some version of macroscopic mean-field theory in which the free energy of the system is considered as a function (or functional) of an average LP wave function $\psi(\mathbf{x})$ and the average local fluid density $\rho(\mathbf{x})$. By nullifying the functional derivative with respect to variations in $\psi(\mathbf{x})$ and $\rho(\mathbf{x})$, one obtains a nonlinear Schrödinger equation [Eq. (10) in this paper] for the optimal $\psi(\mathbf{x})$.[4,5] Alternatively, one can use a trial wave function to minimize the free energy.[6] These models exhibit many of the qualitative features one expects of localized states. However, they all have a common weak point. In certain regions of T and ρ, localized LP states exist, but in regions with high T or low ρ, or both, no localized state can be found. Consequently, all physical quantities predicted by these models have a discontinuity. This feature does not agree with experiments, which indicate that the system properties change smoothly.

In an effort to solve this problem, Siili, Tuomisaari, and Niemenen[7] and Fan and Miller[8] extended different versions of the mean-field models to include the effect of additional LP states by taking into account the contribution of local fluctuations. Siili *et al.*[7] argue that the LP experiences various density profiles with probabilities determined by the corresponding Gibbs factors. By choosing a specific function family for the density profiles and evaluating the response of the LP wave function they calculated the positronium decay rate on some isotherms. Their results do not show the discontinuity and fit the experimental data fairly well in limited (T,ρ) regions. Fan and Miller[8] employed the same idea in the opposite direction by choosing a particular family of LP wave functions and computing the FP density response. They obtained results similar to those in Ref. 7, but with a quantitative improvement.

In all of these works,[4-8] various further approximations—more or less reasonable—have to be used. A common artifact is that they have to artificially break the translational invariance of the system. All of the wave functions and densities previously considered have spherical symmetry, but the center can be anywhere. After assigning the center to an arbitrary fixed point, the contribution of the self-trapped state(s) to the entropy is reduced.[9,10] This problem becomes very serious when the system favors an extended LP state more than an *individual* localized state. The problem of determining the relative degeneracy of trapped and extended states has not been resolved for the density-functional models. A possible solution is to employ a microscopic description which maintains the translational invariance of the real system.

A good candidate is provided by the path-integral approach proposed by Feynman,[11] which can be used to establish an isomorphism between the partition function of the hybrid system and a purely classical model of a ring polymer. Here, following Feynman's approach for a single-particle Hamiltonian, the trace of the LP part of the density operator is modeled by the imaginary-time path integral. There is one important difference: In Feynman's treatment, the external potential experienced by the particle is fixed and independent of the time. Here, the potential experienced by the LP depends on the positions of the FP's, which are treated classically. Averages over the LP states are constructed by taking the usual quantum trace in which the FP coordinates are *fixed,* and then weighting each FP configuration with the Gibbs factor of classical statistical mechanics. This hybrid construction is frequently referred to as the adiabatic model. Variations of the ring-polymer isomorphism (RPI) have been used to investigate quantum corrections in fluids since the mid-1960s.[12] An "industry" for computing the properties of solvated electrons in different systems has developed around this isomorphism during the last decade.[13]

Important questions concern the relationship between the mean-field approximations and the adiabatic model. In particular, it would be useful to know to what extent they are equivalent, or if one follows from the other by a systematic sequence of approximations. In this paper we establish the relationships among all of these models. We then show that the difficulty which occurs in the mean-field theories due to the lack of translational invariance can be naturally removed. We exploit the polymer isomorphism to provide explicit formal expressions for the experimentally observed decay rate and its variance. Last, we derive an expression for the momentum distribution of the localized LP. We demonstrate that it is proportional to the Fourier transform of the distribution in displacement between the ends of a broken polymer.

II. RELATIONSHIP AMONG MODELS

We start by considering the expectation value of an operator O in the adiabatic model. The operator may depend on both the LP and FP coordinates, but not the FP momenta. The trace refers to both the quantum part and the classical part, which consists of the integral $\int d\mathbf{R}_1 \cdots d\mathbf{R}_N \equiv \int d\tilde{\mathbf{R}}$ weighted by $\exp(-\beta U)$. We simply assume that the expectation does not depend on their order. The result reads

$$\langle O\rangle=(1/Z)\int d\tilde{\mathbf{R}}\sum_\alpha \langle\alpha|O|\alpha\rangle \exp[-\beta U(\mathbf{R})-\beta E_\alpha(\tilde{\mathbf{R}})]\,, \tag{2}$$

where $|\alpha\rangle \equiv |\alpha(\tilde{\mathbf{R}})\rangle$ is the eigenstate of $H'=\hat{\mathbf{p}}^2/2m+V(\mathbf{x},\mathbf{R})$, $E_\alpha(\tilde{\mathbf{R}})$ is the corresponding eigenvalue, and the partition function Z is obtained from the numerator by letting $O=1$.

Now let us look at a different expectation value,

$$\langle O\rangle' = (1/Z')\int D_\psi \delta(\langle\psi|\psi\rangle - 1) \times \int d\tilde{\mathbf{R}} \langle\psi| O \exp[-\beta H'(\mathbf{x},\tilde{\mathbf{R}})] |\psi\rangle \times \exp[-\beta U(\tilde{\mathbf{R}})] . \tag{3}$$

In Eq. (3), $\int D_\psi$ is defined by[8]

$$\int D_\psi \equiv \int \prod_\alpha dC_\alpha dC_\alpha^* \equiv \int d\tilde{\mathbf{C}} , \tag{4}$$

where C_α are the coefficients of a complete set and Z' is the appropriate partition function. The δ function ensures that only normalized states contribute to the sum. Apparently, (2) and (3) are two different quantities because, in (3), the sum is performed over the complete Hilbert space. Under the assumption that the order of $\int D_\psi$ and $\int d\tilde{\mathbf{R}}$ can be interchanged, we can prove their equivalence. Suppose we choose the eigenstates of $H'(\tilde{\mathbf{R}})$ as the complete set and perform $\int D_\psi$ first. Then, the $\tilde{\mathbf{R}}$-dependent average is proportional to

$$\int D_\psi \delta(\langle\psi|\psi\rangle - 1)\langle\psi| O \exp[-\beta H'(\mathbf{x},\tilde{\mathbf{R}})] |\psi\rangle = \int d\tilde{\mathbf{C}}\, \delta\left[\sum_\alpha |C_\alpha|^2 - 1\right] \left[\sum_{\alpha',\alpha''} O_{\alpha'\alpha''} C_{\alpha'}^* C_{\alpha''} \exp[-\beta E_{\alpha''}(\tilde{\mathbf{R}})]\right] , \tag{5}$$

where $O_{\alpha'\alpha} = \langle\alpha'|O|\alpha\rangle$. It is easy to see that the terms with $\alpha \neq \alpha'$ in the double summation vanish because the $\tilde{\mathbf{C}}$ dependence is even in the rest of the integrand. Therefore (5) becomes

$$\int d\tilde{\mathbf{C}}\, \delta\left[\sum_{\alpha'} |C_{\alpha'}|^2 - 1\right] \left[\sum_\alpha O_{\alpha\alpha} |C_\alpha|^2 \exp[-\beta E_\alpha(\tilde{\mathbf{R}})]\right] = \sum_\alpha O_{\alpha\alpha} \exp[-\beta E_\alpha(\tilde{\mathbf{R}})] \left\{ \int d\tilde{\mathbf{C}}\, \delta\left[\sum_{\alpha'} |C_{\alpha'}|^2 - 1\right] |C_\alpha|^2 \right\} . \tag{6}$$

From (6) one can see that the order between O and $\exp[-\beta H(\tilde{\mathbf{R}})]$ is irrelevant to the result. The quantity inside the curly brackets is an α- and $\tilde{\mathbf{R}}$-independent constant. This constant is well defined in a finite-dimensional space. If a total of υ quantum states were included in the sum, the constant would take on the value $\pi^\upsilon/\upsilon!$. Consequently, in Hilbert space ($\upsilon \rightarrow \infty$) it vanishes. However, the same factor also appears in Z', the denominator of (3), which is obtained from the numerator by replacing $O_{\alpha\alpha}$ with unity. Thus, for any finite basis set, the equivalence of (2) and (3) is established. Here we neglect mathematical rigor and assume that this factor cancels out in Hilbert space. In general, the transformation between two arbitrary complete sets will also produce a constant functional Jacobian determinant.[14] This factor is also canceled in the denominator. Thus we arrive at the same expression as (2).

Miller proposed another model similar to (4).[5,15] In his model each system is represented by an element of the tensor product of the phase space (for the FP's) and Hilbert space (for the LP) in which each element carries the statistical weight $\exp[-\beta\langle\psi|H(\tilde{\mathbf{R}})|\psi\rangle]$. The partition function then takes the form

$$Z = \int D_\psi \delta(\langle\psi|\psi\rangle - 1) \exp(-\beta\langle\psi|\hat{\mathbf{p}}^2/2m|\psi\rangle) \times \left\{ \int d\tilde{\mathbf{R}} \exp[-\beta(\langle\psi|V|\psi\rangle + U)] \right\} . \tag{7}$$

The quantity in the curly brackets is equivalent to the configurational partition function of N classical particles under an "external potential,"

$$V_\psi(\mathbf{x}) = \langle\psi| v(\mathbf{x}-\mathbf{x}') |\psi\rangle = \int d\mathbf{x}' v(\mathbf{x}-\mathbf{x}') |\psi(x')|^2 , \tag{8}$$

where, in the second step, $\mathbf{x}'$ is an operator. We can formally carry out the integral $\int d\tilde{\mathbf{R}}$ in (7) and obtain

$$Z = \int D\psi \delta(\langle\psi|\psi\rangle - 1) \times \exp\{-\beta(\langle\psi|\hat{\mathbf{p}}^2/2m|\psi\rangle + F[\psi])\} , \tag{9}$$

where F is the configurational free energy of N *classical* particles experiencing the external potential and is, in general, a functional of ψ. By minimizing $\langle\psi|\hat{\mathbf{p}}^2/2m|\psi\rangle + F$ with respect to variations in ψ, Miller naturally obtained the nonlinear Schrödinger equation for the optimal state without resorting to a local-density approximation for F:[15,5]

$$-(\hbar^2/2m)\Delta\psi(\mathbf{x}) + \psi(\mathbf{x}) \int d\mathbf{x}' v(\mathbf{x}-\mathbf{x}') \rho(\psi(\mathbf{x}')) = E\psi(\mathbf{x}) . \tag{10}$$

In Eq. (10), $\rho = \rho(\psi)$ is the conditionally averaged local FP density and is, in general, also a functional of ψ. Thus, the usual density-functional descriptions of trapping are the mean-field solutions for ψ and ρ obtained from Miller's path integral. Alternative versions of the mean-field theory employed by different investigators arise from the degree of approximation used in the representation of F,[1,4-6] which is used to close (10) by providing a second relation between ψ and $\rho(\psi)$. To recognize the relation between the adiabatic model, as represented in (3), and Miller's model, (7), we introduce the following approximation:

$$\begin{aligned} &\langle\psi|H^n|\psi\rangle = \langle\psi|H|\psi\rangle^n , \\ &\langle\psi|OH^n|\psi\rangle = \langle\psi|O|\psi\rangle\langle\psi|H|\psi\rangle^n , \\ &\qquad \text{for } n = 0, 1, \ldots . \end{aligned} \tag{11}$$

This is just the Gutzwiller approximation[16] in the representation of Ogawa, Kanda, and Matsubara.[17] By expanding $\exp[-\beta H(\tilde{\mathbf{R}})]$ in (3) in a Taylor series and using (11), we can arrive at (7). Thus, we are forced to conclude that density-functional formulations can be extracted from the adiabatic model only following serious approximation.

III. AN APPROACH WITH TRANSLATIONAL INVARIANCE

The path-integral representation formulated in (7) naturally leads to a free-energy functional for describing the localized LP. To date, all computations based on this functional have encountered serious difficulties due to lack of translational invariance. In order to carry out computations with the functional, it was necessary to break the invariance by asserting a fixed center for the LP. The results obtained from mean-field theory always imply that in certain regions of (T,ρ) in a disordered fluid, LP states of infinite extent are more probable than trapped states. In the two approaches which went beyond mean-field theory,[7,8] and included a fluctuating wave function or density field, the extended state was always dominant at all (T,ρ) above T_c. All of these difficulties are artificial and can be avoided by employing the adiabatic formulation directly.

Earlier we described how the annihilation rate of positrons and orthopositronium, and the momentum distribution of parapositronium, are the best experimental signatures of trapping. Here we use the adiabatic model to construct practical expressions for these quantities which do not suffer from this "extended state dominance." We show that this defect can be naturally removed if we start with (2) or, equivalently, (3). We first define the decay rate operator,

$$\hat{\lambda}=\int d\mathbf{x}\,|\mathbf{x}\rangle\int d\mathbf{x}' f(\mathbf{x}-\mathbf{x}')\hat{\rho}(\mathbf{x}')\langle\mathbf{x}|\,, \tag{12}$$

where $f(\mathbf{x}-\mathbf{x}')$ is the electron distribution around the atomic nucleus located at $\mathbf{x}'$, which we assume to be rigid, and

$$\hat{\rho}(\mathbf{x}')=\sum\delta(\mathbf{x}'-\mathbf{R}_l) \tag{13}$$

is the microscopic fluid, or nuclear, density operator. [Alternatively, $\hat{\lambda}$ may be expressed in the simpler, but less suggestive, form $\sum_j f(\mathbf{x}-R_j)$.] An overall numerical factor has been dropped in (12) which is proportional to the effective number of atomic or molecular electrons that are available for annihilation.[1] By taking the average of $\hat{\lambda}$ in an LP state $|\psi\rangle$, we find the familiar expression for the decay rate,[1]

$$\lambda(\psi,\tilde{\mathbf{R}})=\int d\mathbf{x}\int d\mathbf{x}'\,|\psi(\mathbf{x})|^2 f(\mathbf{x}-\mathbf{x}')\hat{\rho}(\mathbf{x}')\,. \tag{14}$$

The meaning of both (12) and (14) is intuitive. For computational reasons, all mean-field calculations have to assume that the electronic charge distribution is a δ function. The *ensemble* average of $\hat{\lambda}$ is obtained by replacing O with (12) in (2) and then choosing $|\mathbf{x}\rangle$ as the complete set for all configurations $\{\tilde{\mathbf{R}}\}$:

$$\lambda=(N/Z)\int d\mathbf{x}\int d\tilde{\mathbf{R}}\,f(\mathbf{x}-\mathbf{R}_1)\langle\mathbf{x}|\exp[-\beta H'(\mathbf{x},\tilde{\mathbf{R}})]|\mathbf{x}\rangle \times\exp[-\beta U(\tilde{\mathbf{R}})]\,. \tag{15}$$

The isomorphism between the adiabatic model and a classical system consisting of a ring polymer with p sites in equilibrium with the fluid is constructed by following Feynman's imaginary-time path-integral representation for the electron briefly sketched below.[11] In his classic text on statistical mechanics,[11] Feynman first notes that

$$\langle\mathbf{x}|\exp[-\beta H'(\mathbf{x},\tilde{\mathbf{R}})]|\mathbf{x}\rangle=\prod_{2\le l\le p}\int d\mathbf{x}_l\prod_{1\le j\le p}\langle\mathbf{x}_j|\exp[-(\beta/p)H'(\mathbf{x},\tilde{\mathbf{R}})]|\mathbf{x}_{j+1}\rangle\,, \tag{16}$$

where $\mathbf{x}_{p+1}=\mathbf{x}_1=\mathbf{x}$. He then uses perturbation theory to derive

$$\langle\mathbf{x}_j|\exp[-(\beta/p)H'(\mathbf{x},\tilde{\mathbf{R}})]|\mathbf{x}_{j+1}\rangle\approx\exp[-\beta\Phi(\mathbf{x}_j,\mathbf{x}_{j+1},\tilde{\mathbf{R}})]\,, \tag{17}$$

$$\Phi\equiv(2mp/\beta^2\hbar^2)\,|\mathbf{x}_{j+1}-\mathbf{x}_j|^2+(1/2p)[V(\mathbf{x}_j,\tilde{\mathbf{R}})+V(\mathbf{x}_{j+1},\tilde{\mathbf{R}})]\,, \tag{18}$$

when $p\gg 1$. By letting $p\to\infty$ the approximation becomes rigorous and Feynman obtains the imaginary-time path integral

$$\langle\mathbf{x}|\exp[-\beta H'(\mathbf{x},\tilde{\mathbf{R}})]\mathbf{x}\rangle=\int D_{\mathbf{r}(t)}\int_0^{\beta\hbar}dt\,\exp\{-[(m/2)\mathbf{r}(t)^2+V(\mathbf{r},\tilde{\mathbf{R}})]\}\,, \tag{19}$$

where $\mathbf{r}(0)=\mathbf{r}(\beta\hbar)=\mathbf{x}$. Thus $\langle\mathbf{x}|\exp[-\beta H'(\mathbf{x},\tilde{\mathbf{R}})]|\mathbf{x}\rangle$ can be thought of as the classical configurational partition function of a large ring polymer consisting of a linear harmonic chain of nearest-neighbor interacting sites, each of which experiences the external potential $(1/p)V(\mathbf{x},\tilde{\mathbf{R}})$. The interaction potential acting between sites is simply $(p\hbar^2/2m)\times|\mathbf{x}_{j+1}-\mathbf{x}_j|^2$. The configurational partition function in the polymer representation takes the form

$$Z=\int d\tilde{\mathbf{R}}\exp[-\beta U(\tilde{\mathbf{R}})]\prod_{1\le j\le p}\int d\mathbf{x}_j\exp\{-(2mp/\beta\hbar^2)\,|\mathbf{x}_{j+1}-\mathbf{x}_j|^2+(\beta/p)V(\mathbf{x}_j,\mathbf{R})\}\,. \tag{20}$$

Because all of the labeled sites of the ring polymer are equivalent, we may express the mean annihilation rate as

$$\begin{aligned}\lambda&=\Big\langle\sum_{1\le j\le N}f(\mathbf{x}-\mathbf{R}_j)\Big\rangle=\Big\langle(1/p)\sum_{1\le a\le p}\sum_{1\le j\le N}f(\mathbf{x}_a-\mathbf{R}_j)\Big\rangle\\&=(1/p)\int d\mathbf{x}\int d\mathbf{R}\,f(\mathbf{x}-\mathbf{R})n_{LF}^{(2)}(\mathbf{x}-\mathbf{R})=\rho\int d\mathbf{r}\,f(\mathbf{r})g_{LF}(\mathbf{r})\,,\end{aligned} \tag{21}$$

where, in (21),

$$n_{LF}^{(2)}(\mathbf{x}-\mathbf{R})=\Big\langle\sum_{1\le a\le p}\sum_{1\le j\le N}\delta(\mathbf{x}-\mathbf{x}_a)\delta(\mathbf{R}-\mathbf{R}_j)\Big\rangle=\rho\rho_{\mathrm{pol}}g_{LF}(\mathbf{x}-\mathbf{R}) \tag{22}$$

is the two-point LP-FP distribution function and ρ_{pol} is the mean site density of the polymer.[13,18] Finally, by expressing the radial distribution in terms of the pair-correlation function, $g_{LF}(r)=1+h_{LF}(r)$, we arrive at

$$\lambda=\rho\int d\mathbf{r}\,f(\mathbf{r})[1+h_{LF}(\mathbf{r})]\,. \tag{23}$$

This simple looking result supports our expectation that, in the absence of correlations, the mean decay rate is simply proportional to the average fluid density. All of the difficulties in predicting λ arise in the computation of the pair-correlation function between polymer sites and the elements of the fluid.

An important related quantity is the variance of the annihilation rate, $\langle(\hat{\lambda}-\langle\lambda\rangle)^2\rangle$. If each positron, or positronium atom, experiences nearly the same environment, then the variance of λ is small and its probability density function (PDF) is tightly distributed about the mean. Consequently, it will be possible to construct an excellent fit of the orthopositronium annihilation rate data (in the 10–100 nsec range) to a single-exponential decay. In contrast, a fluctuating environment will have important consequences for the experimental measurements. There are two extreme possibilities to consider: either the environment of a given LP may fluctuate strongly in time, or one may find that different metastable environments are accessible. In either case, the variance is a good indicator of the expected variation in the LP environment. In principle, it may be determined by careful experiments. We derive an expression for its computation here within the context of the RPI.

We need only consider $\langle\hat{\lambda}^2\rangle$ since $\langle\hat{\lambda}\rangle$ was obtained earlier. By following the discussion of (21)–(23), and separating terms depending explicitly on the position of one fluid molecule from those depending on a pair, we can express $\langle\hat{\lambda}^2\rangle$ in terms of the appropriate two- and three-point distribution functions of the RPI:

$$\langle\hat{\lambda}^2\rangle=\left\langle\left[\sum_{1\le j\le N} f(\mathbf{x}-\mathbf{R}_j)\right]^2\right\rangle=(1/p)\int d\mathbf{x}\int d\mathbf{R}\, f(\mathbf{x}-\mathbf{R})^2 n_{LF}^{(2)}(\mathbf{x}-\mathbf{R})$$
$$+(1/p)\int d\mathbf{x}\int d\mathbf{R}\int d\mathbf{R}' f(\mathbf{x}-\mathbf{R})f(\mathbf{x}-\mathbf{R}')n_{LFF}^{(3)}(\mathbf{x}-R,\mathbf{x}-R')\,, \tag{24}$$

where $n_{LF}^{(2)}(\mathbf{r})$ is defined above and

$$n_{LFF}^{(3)}(\mathbf{r},\mathbf{r}')=\left\langle\sum_{1\le\alpha\le p}\ \sum_{1\le j,k\le N}{}' \delta(\mathbf{r}-(\mathbf{x}_\alpha-\mathbf{R}_j))\delta(\mathbf{r}'-(\mathbf{x}_\alpha-\mathbf{R}_k))\right\rangle=\rho_P\rho^2 g_{LF}(r)g_{LF}(r')[1+h_{LFF}^{(3)}(\mathbf{r},\mathbf{r}')] \tag{25}$$

is the three-point distribution function for a polymer site and a pair of fluid molecules.[19] In (25) the prime on the summation indicates that terms with $j=k$ are omitted, and the definition of $h_{LFF}^{(3)}(\mathbf{r},\mathbf{r}')$ ensures that it vanishes when either r or r' is significantly greater than the two-point (LF) correlation length. This finally yields

$$\langle(\hat{\lambda}-\langle\lambda\rangle)^2\rangle=\rho\int d\mathbf{r}\, f(r)^2 g_{LF}(r)+\rho^2\int d\mathbf{r}\int d\mathbf{r}' f(r)f(r')g_{LF}(r)g_{LF}(r')h_{LFF}^{(3)}(\mathbf{r},\mathbf{r}') \tag{26}$$

for the variance in the decay rate.

The probability distribution for the momentum of the LP is the expectation of $\delta(\hat{\mathbf{p}}-\mathbf{p})$:

$$P(\mathbf{p})=\langle\delta(\hat{\mathbf{p}}-\mathbf{p})\rangle=(1/2\pi)^3\int d\mathbf{k}\, e^{-i\mathbf{k}\cdot\mathbf{p}}\langle e^{i\mathbf{k}\cdot\hat{\mathbf{p}}}\rangle\,,$$
$$\langle e^{i\mathbf{k}\cdot\hat{\mathbf{p}}}\rangle=\langle\exp[\mathbf{k}\cdot\hbar\nabla]\rangle=(1/Z)\int d\tilde{\mathbf{R}}\, e^{-\beta U}\int d\mathbf{x}\int d\mathbf{x}'\langle\mathbf{x}|e^{\mathbf{k}\cdot\hbar\nabla}|\mathbf{x}'\rangle\langle\mathbf{x}'|e^{-\beta H'}|\mathbf{x}\rangle\,. \tag{27}$$

We recall that the operator $\exp(i\mathbf{y}\cdot\hat{\mathbf{p}})$ induces the translation $\mathbf{y}\hbar$ so that

$$\langle\mathbf{x}|e^{\mathbf{k}\cdot\hbar\nabla}|\mathbf{x}'\rangle=\delta(\mathbf{x}-\mathbf{x}'+\mathbf{k}\hbar)\,, \tag{28}$$

and

$$(2\pi)^{-3}\int d\mathbf{k}\, e^{-i\mathbf{k}\cdot\mathbf{p}}\delta[\mathbf{x}-\mathbf{x}'+\mathbf{k}\hbar]=\langle\mathbf{x}|\delta(\hat{\mathbf{p}}-\mathbf{p})|\mathbf{x}'\rangle=(2\pi\hbar)^{-3}\exp(i\mathbf{p}\cdot\mathbf{r}/\hbar)\,, \tag{29}$$

where, of course, $\mathbf{r}=\mathbf{x}-\mathbf{x}'$. This yields

$$P(\mathbf{p})=(1/Z)\int d\tilde{\mathbf{R}}\, e^{-\beta U}\int d\mathbf{x}\int d\mathbf{x}'(2\pi\hbar)^{-3}\exp(i\mathbf{p}\cdot\mathbf{r}/\hbar)\langle\mathbf{x}'|e^{-\beta H'}|\mathbf{x}\rangle$$
$$=\int d\mathbf{x}\int d\mathbf{x}'(2\pi\hbar)^{-3}\exp(i\mathbf{p}\cdot\mathbf{r}/\hbar)(1/Z)\int d\tilde{\mathbf{R}}\, e^{-\beta U}\langle\mathbf{x}'|e^{-\beta H'}|\mathbf{x}\rangle$$
$$=\int d\mathbf{x}\int d\mathbf{x}'(2\pi\hbar)^{-3}\exp(i\mathbf{p}\cdot\mathbf{r}/\hbar)\langle\rho_d(\mathbf{x},\mathbf{x}')\rangle$$
$$=\Omega\int d\mathbf{r}(2\pi\hbar)^{-3}\exp(i\mathbf{p}\cdot\mathbf{r}/\hbar)\langle\rho_d(\mathbf{r})\rangle\,, \tag{30}$$

where Ω is the system volume, which proves that the momentum distribution is simply the Fourier transform of the *thermal-averaged* LP density matrix, $\langle\rho_d(\mathbf{x},\mathbf{x}')\rangle$. The development of a path-integral representation for $\langle\rho_d(\mathbf{x},\mathbf{x}')\rangle$ is analogous to that for $\langle\rho_d(\mathbf{x},\mathbf{x})\rangle$ in (16)–(19), the sole, and important, difference being that in (30) the end points of the polymer, or the smooth path in the limit $p\rightarrow\infty$, are separated by $\mathbf{r}$, so that the polymer is no longer ring shaped, but rather open ended.

IV. DISCUSSION AND CONCLUSIONS

This paper addresses two central issues in our understanding of self-trapping, or localization, of light particles in fluids. The first concerns the relationship between the mean-field theories of localized states investigated from the mid-1950s until the present, and the adiabatic model, which is facilitated by the introduction of the polymer isomorphism. The second concerns the calculation of experimentally accessible LP properties such as the annihilation rate of positronium or orthopositronium, its variance, and the momentum distribution.

Mean-field theory predicts the existence of two types of LP states, trapped (localized) and extended (propagating). Extended states always exist in the fluid, whereas localized states coexist with trapped states only for specific regions of density and temperature. For a given density and temperature of the fluid, the dominant type is determined in principle by estimating the free energy of each state, which fixes their relative stability. In practice, this has not been possible because these are macroscopic calculations and there is no clearcut method for computing the microscopic degeneracy associated with each type. It was pointed out in the Introduction that mean-field theory predicts discontinuities in the LP properties. These arise where the localized solutions appear or disappear.

Measurements of the properties of thermalized positronium atoms (para and ortho) indicate that discontinuities do not occur. They are an artifact of the mean-field approximation, and are not predicted by the more rigorous adiabatic approximation.[13] Here we have demonstrated that a particular Gibbsian measure introduced by one of us is a subset of the adiabatic model and can be obtained from it by a Gutzwiller type of approximation similar to that employed in the Hubbard model. Miller has shown elsewhere that mean-field theory generates the optimal states for this measure.[5,15] This establishes the connection between the models, and clearly demonstrates that the older mean-field theory can be derived from the adiabatic model by a sequence of approximations.

The second issue we have addressed is the ability of the ring-polymer isomorphism to represent important properties of the localized LP. For scalar functions of the LP position which only depend on the position of a few fluid atoms, e.g., the decay rate operator and its variance, the model is successful. It demonstrates that the average decay rate depends directly on the degree to which each polymer site alters the fluid density in its neighborhood. However, if one requires more information, such as the decay rate or momentum probability distributions, the model has to be altered. In particular, the momentum distribution is the Fourier transform of the distribution function governing the displacement between the ends of a broken polymer. In deriving these results we learn that mean decay rates and momentum distributions provide complimentary information concerning the nature of the localized state: The former provides information concerning the alteration of the fluid density in the region of the LP, and the latter tells us the extent that the LP-FP interaction reduces the spatial extent of the LP density matrix.

The expressions derived here for the average decay rate, its variance, and the momentum distribution of the LP are all amenable to computation using the Monte Carlo methods of Berne and co-workers and others.[13] We are also confident that the decay rate and momentum distribution can be computed for real gases by extending the analytical RISM (reference interaction site model) polaron procedure developed by Chandler, Singh, and Richardson for hard spheres to include a more realistic FP-FP interaction, such as a Leonard-Jones potential.[13] It will be interesting to see how well these computations agree with experimental measurements of positron and orthopositronium decay rates which have been carried out for a number of gases.[19,20]

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