Self-trapping of a light particle in a dense fluid: A mesoscopic model

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A light particle (electron, positron, or positronium atom) thermalized in a dense fluid can, in certain instances, become localized in a region of altered fluid density. This process is known as self-trapping. In this paper we formulate a mesoscopic model for the evolution of translational degrees of freedom, which uses quantum mechanics to describe the light particle (LP) and classical mechanics for the fluid molecules. The model self-consistently takes into account the mutual influence between the LP and fluid and the large isothermal compressibility near the liquid-vapor critical point. The dynamical representation of this model leads to a set of hydrodynamic equations which couples the LP wave function to the local fluid density. The equilibrium representation takes the form of a Landau-Ginzberg functional in which the wave function plays the role of order parameter. Optimization of the probability density in state space generates a mean-field theory in which the wave function is coupled to the local fluid density via a local equilibrium condition. The time-independent Schrödinger equation provides the second equation necessary to specify the local density and wave function. When the LP-fluid atom interaction is represented by a Fermi pseudopotential, the two coupled equations can be reduced to dimensionless form by scaling the position with respect to the scattering length and scaling the thermodynamic variables density (ρ) and temperature (T) with respect to their values at the critical point. Together with the principle of corresponding states, they provide a universal description of the trapped state. Scaling transforms the normalization integral into a universal constant which contains all system-specific parameters and determines the response of the gas to the presence of the light particle. The model was applied to the problem of computing the mean decay rate of a localized positronium atom. The van der Waals equation was used to approximate the equation of state. The decay rate and free energy were plotted versus density on isotherms. Trap formation was found to depend on the universal constant, scaled temperature, and density. The model provided good qualitative agreement with the results of experimental measurements of the decay rate of orthopositronium in ethane and argon.

I. INTRODUCTION

When a light particle (electron, positron, or positronium) thermalizes in a fluid, its mean de Broglie wavelength is much larger than the average distance between the atoms of the fluid at the critical density. For sufficiently large densities, the wavelength is greater than its mean free path in the fluid, indicating that the light particle (hereafter LP) simultaneously interacts with many atoms of the fluid.[1] Experimental studies of electron mobility[1] and positron annihilation[2] strongly suggest that, in certain regions of temperature and pressure, the LP can create around itself a region of altered fluid density in which it is localized.[3] The light particle is then said to be in a self-trapped state. Self-trapping occurs most readily near the liquid-vapor critical point where the isothermal compressibility of the gas is large.

Most present theories of localization are macroscopic in nature and start with density-functional theory.[3] A free energy or, in the case of the grand canonical ensemble, a grand thermodynamic potential, which depends both on the average local fluid density and LP wave function, is constructed from thermodynamic principles. Minimizing the free energy leads to a pair of coupled equations for the optimal density and wave function. There are a number of variants of the theory which predict the gross properties of the system with varying suc-

cess. The central purpose of our work is (1) to show that density-functional theories are the natural consequences of a particular dynamical model which preserves the quantum nature of the LP while treating the fluid degrees of freedom classically, and (2) to illustrate that, when properly scaled, the simplest variant of density-functional theory manifests universality, whereby all of the system-specific constants are combined in a single parameter which determines both the existence and properties of localized states over the entire thermodynamic state space. Subsidiary objectives are (1) the provision of two independent criteria for determining the stability of the self-trapped state in terms of scaled quantities, (2) the description of a computational algorithm which solves the coupled equations for the self-trapped state with high speed and precision, (3) the demonstration that localized states always exist at the liquid-vapor critical point, and (4) the investigation of the decay rate of localized orthopositronium over a wide range of density above the liquid-vapor critical temperature of a van der Waals fluid.

The key feature of our dynamical model is the self-consistent treatment of the interaction between the LP and the fluid atoms, which allows for their *mutual* response. It leads to an equilibrium theory, which contains the phenomena of self-trapping, and a kinetic theory which generates a hydrodynamic characterization of the system.

In this paper we apply the model to the problem of self-trapping. We show that a density-functional description of self-trapping naturally arises from the equilibrium formulation of our model in terms of a functional integral. In typical density-functional theories of self-trapping, the LP is represented by a single semimacroscopic average wave function. In common with the mean-field approximation of a Landau-Ginzberg theory, in our model the optimum wave function results from extremizing the argument of a functional integral.[4] Thus, in addition to mean-field theory, the model has the potential for predicting the importance of fluctuations.

Earlier applications of density-functional theory to the problem of self-trapping were provided by Iakubov and Khrapak,[3] Hernandez,[5] Moore, Cleveland, and Gersch,[6] Stott and Zaremba,[7] Ebner and Punyanita,[8] and Nieminen et al.[9] Moore et al. provide a very complete treatment of trapping in an ideal gas. They are the only investigators who have provided *numerically accurate* solutions for the local density and wave function of a trapped particle. Although they refer to the LP as an electron, and specifically study its mobility, because they assume a repulsive-pseudopotential for the LP-molecule interaction their density and wave-function calculations are more suitable for positronium. Naturally the situation is more complex for the interacting gas considered here. However, their thorough work provided the basis for the methods we discuss.

Iakubov and Khrapak were the first to consider the trapping of both positrons and positronium for a van der Waals fluid. Their methods and conclusions are discussed in an important review article.[3] In contrast with the study of Moore et al. and the computational component of this paper, they used Gaussian and related trial functions to represent the LP wave function. The additional effects of intermolecular correlations were considered by Stott and Zaremba in their successful modeling of positron annihilation in helium,[7] and by Ebner and Punyanita in their work on electron mobility in noble gases.[8] Stott and Zaremba employed trial wave functions and an empirical equation of state, while Ebner and Punyanita used the Percus-Yevick equation[10] to consistently model the free-energy density and direct correlation function of the fluid. The LP wave function was then determined by assuming a three-parameter trial function for the radial dependence of the local density and solving the resulting Schrödinger equation numerically. Nieminen, Manninen, Välimaa, and Hautojarvi used similar techniques to analyze positronium and electron bubbles in helium.[9] They specialized to a hard-sphere equation of state, and included an extensive calculation of the density dependence of the effective scattering length for the LP-atom interaction. Most of these treatments of self-trapping can be obtained from the equilibrium version of our model by employing approximations of varying complexity.

In considering the work cited above, it is important to emphasize that, although the mean wave function of the trapped LP varies slowly in position, the density may change by nearly an order of magnitude within a few angstroms. The rapid variation in local density is due to the fact that the fluid is in the critical region where the isothermal compressibility is large. Consequently, a small change in $|\psi|^2$ produces a strong response. Thus, regardless of how elaborate a given representation of the fluid may be, the use of trial functions which force the form of the fluid's response to the excess particle may be a questionable procedure for predictions which require a precise knowledge of the density profile. The annihilation rate of a trapped positron or positronium atom falls into this category.

A second consideration is the inclusion of the nonlocal effects of intermolecular correlation. It is anticipated that they are only significant extremely close to the liquid-vapor critical point, where the pair correlation length can be on the order of the trap diameter. For a model to benefit from this inclusion, the version of the correlation function employed must scale properly at the critical point. In fact, correct scaling is not uniformly obeyed in these treatments.

The chief assumption of density-functional descriptions is that the extremal wave function of the light particle varies slowly over distances on the order of the mean separation between the fluid atoms. Here we first explicitly invoke the assumption of local equilibrium to obtain two coupled equations for the wave function and local fluid density which define the self-trapped state. Second, we assume that the LP-fluid atom interaction is represented by a Fermi pseudopotential. We expect this assumption to be adequate for the case where the LP is positronium and the effects of long-range polarization are weak.[3]

By scaling the thermodynamic variables in relation to the critical point, and suitably scaling the wave function and coordinates, the coupled equations assume a universal dimensionless form. Taken together, the pair of equations define a *nonlinear* eigenvalue problem for the energy and wave function of the trapped LP.[11] Here it is shown that the existence and behavior of solutions is determined by a single dimensionless constant; the normalization integral of the reduced wave function in the reduced coordinates. This constant determines the existence of bound states, and the numerical value of the scaled energy. The constant depends on the fluid properties at its liquid-vapor critical point and the scattering length of the LP-fluid atom interaction potential. It alone controls whether trapping is likely to be observed experimentally in a particular fluid, and over what range of temperature and density of the host fluid the phenomenon is stable.

A numerical algorithm was devised for solving the coupled equations in a completely self-consistent fashion for the spherically symmetric ground and excited states of the trapped LP. With this method, the local density and wave function were calculated. From these we can calculate the normalization integral of the scaled wave function, the change in the system's free energy resulting from trap formation, and other relevant characteristics of the localized state. The selected values of scattering length and critical point parameters can be used to give a graphic representation of the properties of the localized LP as a function of density on isotherms for comparison with real-world experiments.

As an application, we explicitly consider the pick-off

annihilation of orthopositronium in simple fluids.[3] When a positron is injected into a fluid it can quickly annihilate with an electron from one of the fluid atoms or, alternatively, it can combine with a free electron and form a positronium atom. The two forms of positronium, parapositronium (singlet spin state) and orthopositronium (triplet spin state), decay differently. Parapositronium undergoes a rapid 2γ decay with a lifetime of 1.23×10^{-10} sec. In the vacuum, orthopositronium (o-Ps) decays via a 3γ process with a lifetime of 1.47×10^{-7} sec. In condensed matter it usually decays by pick-off annihilation, in which the positron annihilates with an electron in the valence shell of one of the fluid atoms. Future references to positronium will imply orthopositronium.

In Fig. 1 measurements of the o-Ps annihilation rate are plotted versus density in ethane at 306.4 K. The results shown are characteristic of a number of gases above the critical temperature. Typically, experimental isotherms of the pick-off decay rate λ_{PO} of o-Ps increase linearly with density until the de Broglie wavelength is comparable with the mean free path.[1,12] As the mean de Broglie wavelength at room temperature is about 60 Å, this consists, for all practical purposes, of the ideal-gas regime. As the density increases further, the annihilation rate starts to dip below the extrapolated low-density line at a prescribed density, say ρ^*. The plot then gently curves downward until it forms a crude plateau.

The linear dependence at low density results from the sequence of random encounters experienced by the o-Ps with the widely separated fluid molecules. The region of maximum curvature is referred to as the transition region. Here it has been suggested that the o-Ps passively samples regions of lower density in the fluid. A semiempirical model based on the assumption that density fluctuations play the key role in reducing the pick-off de-

cay rate was advanced by Sharma and co-workers[12,13] some time ago and used by a number of investigators to fit the data in this density region.[14,15] This model fails in the region of the plateau, where it is expected that self-trapping predominates. Calculations suggest that typical trap diameters are on the order of 30 Å. Indications of trapping have been found in Ar,[14] CO_2,[15] CH_4,[16] C_2H_6,[17] Ne,[18] and He.[19] The range of density and temperature for which self-trapping is apparent depends selectively on the fluid.

To test the usefulness of our model, in this study we used the van der Waals equation to describe the fluid as simply as possible. We found that the central features of the experimental isotherms of the positronium decay rate were qualitatively reproduced by the theory. Although the results reported here deal exclusively with positronium, this method readily lends itself to the trapping of other light particles, such as electrons and positrons.

The paper is structured as follows. In Sec. II the model is formulated. In Sec. III scaling and universality of the mathematical description of trapping are considered. Precise numerical methods for solving the nonlinear eigenvalue problem which defines the trapped state are discussed in Sec. IV. The application to the pick-off decay process is explored in detail for a van der Waals gas in Sec. V. Conclusions and directions for further study are given in Sec. VI.

II. DESCRIPTION OF THE MODEL

A. Deterministic dynamics

The central objective of this research is to construct a *mesoscopic* model of the light-particle–fluid interaction which correctly predicts the phenomena of deep trapping, and offers the possibility for describing the transi-
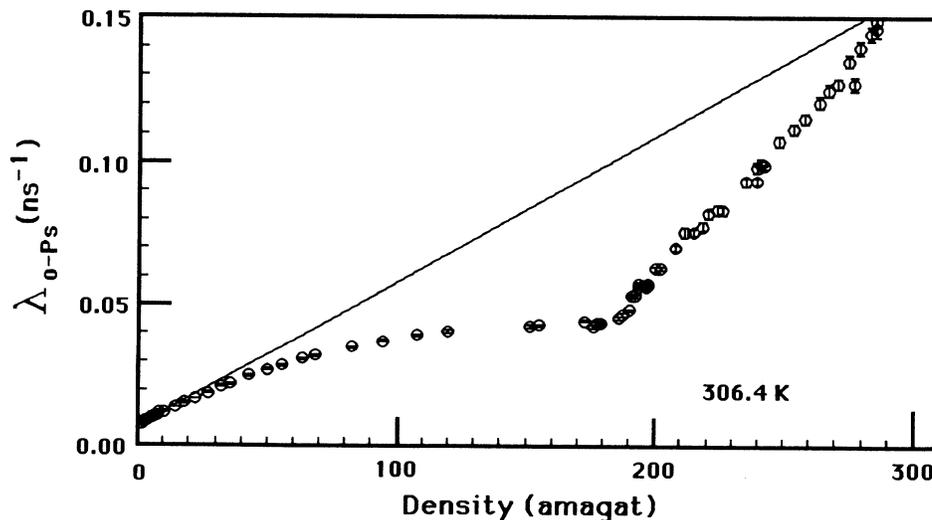
FIG. 1. Decay rate $(\lambda_{o\text{-Ps}})$ of orthopositronium vs density (D) in ethane at 306.4 K. The figure illustrates linear dependence at low density followed by a soft transition to a plateau. (From Ref. 19.)

tional behavior which occurs at fluid densities which are too low to support the formation of stable traps and has eluded a first-principles approach to date.[12,13] By mesoscopic, we mean that the internal quantum states of the fluid molecules are not considered separately and their translational degrees of freedom are treated classically. In order for the model to have the capability of predicting the dynamics of localization, it must be time dependent. With these thoughts in mind, we introduce two potentials, u and w, which represent the intermolecular interaction and the light-particle—molecule interaction, respectively. Each is assumed to depend only on the distance between the appropriate interacting pairs.

Dynamics for the model is defined by the Schrödinger equation and Newton's second law. Represent the instantaneous position and momentum of a molecule by $\mathbf{r}_j(t)$ and $\mathbf{p}_j(t)$, and the LP wave function by $\Psi(\mathbf{r},t)$. Then Ψ and $\mathbf{p}_j$ obey

$$\partial_t \Psi = (1/i\hbar)[(-\hbar^2/2m)\Delta + W]\Psi , \qquad (1)$$

$$\frac{d\mathbf{p}_j}{dt} = -\nabla_j(U + W_q) , \qquad (2)$$

where

$$W(\mathbf{r},\{\mathbf{r}_j\}) = \sum_{1 \leq j \leq N} w(\mathbf{r}-\mathbf{r}_j), \quad U = \sum_{i,j;i<j} u(\mathbf{r}_i-\mathbf{r}_j) . \qquad (3)$$

In (2) W_q is the potential produced by the quantum average of W,

$$W_q(\{\mathbf{r}_j\}) = \int W(\mathbf{r})|\Psi(\mathbf{r},t)|^2 d\mathbf{r} . $$

This deterministic dynamical model describes the system behavior under both equilibrium and nonequilibrium conditions. It treats the molecular motion by a generalized Born-Oppenheimer approximation,[20] is self-consistent, and conserves the right quantities, such as momentum $\mathbf{P}$, angular momentum $\mathbf{L}$, and energy E:

$$\mathbf{P} = \langle \Psi|(\hbar/2i)\nabla|\Psi\rangle + \text{c.c.} + \sum_j \mathbf{p}_j , \qquad (4)$$

$$\mathbf{L} = \langle \Psi|r \times (\hbar/2i)\nabla|\Psi\rangle + \text{c.c.} + \sum_j \mathbf{r}_j \times \mathbf{p}_j , \qquad (5)$$

$$E = \langle \Psi| -(\hbar^2/2m)\Delta + W(r)|\Psi\rangle + \sum_j (\mathbf{p}_j^2/2M) + U . \qquad (6)$$

At each instant of time, the system state is an element of the tensor product space formed from the classical phase space associated with the translational motion of the fluid molecules $\{\mathbf{r}_j, \mathbf{p}_j\}$ and the Hilbert space containing Ψ. We label this composite by Γ. This model differs from the usual adiabatic picture in which it is assumed that, as time progresses, the LP is always in thermodynamic equilibrium with the instantaneous configuration of the host fluid (or solid).[21]

B. Equilibrium

Equilibrium (Gibbs) states of the system are distributed in Γ with probability density $\delta(\langle\psi|\psi\rangle - 1)\exp(-\beta E)/Z_N$, where E is given by (6) and

$$Z_N = (1/N!h^{3N}) \int d\Gamma \, \delta(\langle\psi|\psi\rangle - 1)\exp(-\beta E)$$

$$= \int D_\psi \delta(\langle\psi|\psi\rangle - 1)\exp[-\beta\langle\psi|\hat{\mathbf{P}}^2/(2m)|\psi\rangle]Q_N(\psi) \qquad (7)$$

is the canonical partition function. In constructing the partition function, the sum over all possible normalized wave functions is indicated. The δ function guarantees that only normalized states contribute. As usual, $\hat{\mathbf{P}} = (\hbar/i)\nabla$ where $\hbar$ is Planck's constant divided by 2π. In (7) $Q_N(\psi)$ is the classical partition function of a nonuniform fluid with N molecules,

$$Q_N = (1/h^{3N}N!) \prod_j \int d\mathbf{p}_j \exp\left[-\beta\sum_j P_j^2/2M\right]$$
$$\times \int d\mathbf{r}_j \exp[-\beta w_q(\mathbf{r}_j) - \beta U]$$

$$\equiv (1/\Lambda_{\text{th}})^{3N} Q_{CN} , \qquad (8)$$

where each molecule experiences the "external potential"

$$w_q(\mathbf{r}) = \langle\psi|w(\mathbf{r}-\mathbf{r}')|\psi\rangle = \int w(\mathbf{r}-\mathbf{r}')|\psi(\mathbf{r}')|^2 d\mathbf{r}' . \qquad (9)$$

Λ_{th} is the *molecular* thermal wavelength $(h/\sqrt{2MkT})$, and Q_{CN} is the configurational partition function which remains after integrating over the momenta of the fluid molecules.

Our objective is to study the equilibrium states associated with stable traps. We expect that their wave functions provide the dominant contribution to Z_N. We construct an extremal wave function $\tilde{\psi}$ by a variational principle in which $\tilde{\psi}$ produces a maximum for the argument of the functional integral subject to the condition of normalization.

Let

$$\Phi_N \equiv \langle\psi|\hat{\mathbf{P}}^2/(2m)|\psi\rangle - (1/\beta)\ln Q_{CN} . \qquad (10)$$

Then

$$Z_N = (1/\Lambda_{\text{th}})^{3N} \int D_\psi \delta(\langle\psi|\psi\rangle - 1)\exp(-\beta\Phi_N) , \qquad (11)$$

and $\tilde{\psi}$ minimizes Φ_N subject to the constraint $\langle\tilde{\psi}|\tilde{\psi}\rangle = 1$. Next, let $\Phi'_N \equiv \Phi_N - \mathcal{E}(\langle\psi|\psi\rangle - 1)$, where we have introduced the requisite Lagrange multiplier $\mathcal{E}$ to guarantee the constraint. Construction of the functional derivative of Φ'_N with respect to Ψ^* is straightforward:

$$\frac{\delta\Phi'_N}{\delta\psi^*} = -(\hbar^2/2m)\Delta\psi(\mathbf{r}) - \mathcal{E}\psi(\mathbf{r})$$
$$+ (1/Q_{CN}) \prod_j \left[\int d\mathbf{r}_j \exp[-\beta w_q(\mathbf{r}_j)]\right]$$
$$\times \exp(-\beta U)\sum_k w(\mathbf{r}-\mathbf{r}_k)\psi(\mathbf{r}) . \qquad (12)$$

Since the last term is a sum of single-particle functions, it may be expressed in terms of the local mean density of the fluid, $\rho(\mathbf{r})$. Nullifying $\delta\Phi'_N/\delta\psi^*$ yields the following time-independent Schrödinger equation for $\tilde{\psi}$:

$$-(\hbar^2/2m)\Delta\tilde{\psi} + \tilde{\psi}\int d\mathbf{r}'w(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}') = \mathcal{E}\tilde{\psi} . \qquad (13)$$

Equation (13) is a general consequence of the dynamical model. However, due to the coupling between $\bar{\psi}$ and ρ, it is incomplete. The existence of a complementary relation between the two functions is a consequence of the fact that Q_N is the partition function of a fluid subjected to the external potential $w_q(\mathbf{r})$. In deriving (13), $\rho(\mathbf{r})$ is implicitly the density produced in the fluid by $\bar{\psi}$. Determining the density profile of a nonuniform fluid is a central, incompletely solved, problem in statistical mechanics;[10] it can be taken as the starting point for understanding any interacting fluid, both uniform and nonuniform. Here we consider the simplest nontrivial closure.

Because the molecular coordinates are already integrated out in Q_{CN}, we expect that $\bar{\psi}$ varies slowly over distances on the order of the mean intermolecular separation, $\rho^{-1/3}$. Thus we are justified in using an approximate form for Q_{CN},

$$Q_{CN} \approx \exp\left[-\beta\left[\int_V d\mathbf{r}[\rho(\mathbf{r})w_q(\mathbf{r})+f(\rho(\mathbf{r}),\beta)]\right]\right] , \quad (14)$$

valid when the external potential w_q also varies slowly in position. In (14) f is the local Hemholtz free energy density in the nonuniform fluid.[10] The condition that the total Helmholtz free energy, $-(1/\beta)\ln Q_N$, is a minimum in the canonical ensemble necessitates that $\rho(\mathbf{r})$ is a functional of the $w_q(\mathbf{r})$, and hence of $\psi(\mathbf{r})$. Minimizing the variation of $\ln Q$ with respect to ρ subject to the constraint $\int \rho(\mathbf{r})d\mathbf{r}=N$ yields the familiar result

$$\int d\mathbf{r}'w(\mathbf{r}-\mathbf{r}')|\bar{\psi}(\mathbf{r}')|^2+\mu[\rho(\mathbf{r})]=\mu_0 . \quad (15)$$

In (15) $\mu=\partial f/\partial\rho$ is the local chemical potential of the fluid. Thus (15) expresses the usual condition of local equilibrium for a fluid in the slowly varying external potential $w_q(\mathbf{r})$. μ_0 is simply the chemical potential far from the location of the trap.[10] We arrive at

$$\Phi_N(\bar{\psi})=\int_V d\mathbf{r}\left[(\hbar^2/2m)|\nabla\bar{\psi}|^2\right.$$
$$+\rho(\mathbf{r})\int d\mathbf{r}'w(\mathbf{r}-\mathbf{r}')|\bar{\psi}(\mathbf{r}')|^2$$
$$\left.+f(\rho(\mathbf{r}),\beta)\right] . \quad (16)$$

Equations (13) and (15) self-consistently determine the extremal wave function and density profile to the extent that the assumption of local equilibrium prevails. They could have been derived as well in the grand canonical ensemble. In Sec. III they will be used to construct the completely scaled description of trapping promised above.

C. Quantum hydrodynamics

Equations (1) and (2) uniquely fix the dynamical evolution of the LP-fluid system. They can be used to formally construct the rates of change of the local *microscopic* densities of conserved dynamical quantities (fluid population, total momentum, and energy). By forming their *conditional average* over the fluid coordinates and momenta for a given wave function, the following coupled, quantum-hydrodynamic equations can be obtained:[22]

$$[-(\hbar^2/2m)\Delta+W]\Psi=i\hbar\partial_t\Psi , \quad (17)$$

$$\partial_t\rho+\nabla\cdot(\rho\mathbf{v})=0 , \quad (18)$$

$$M\rho(\partial_t+\mathbf{v}\cdot\nabla)\mathbf{v}=\rho\mathbf{F}_q-\nabla\cdot\mathbf{P} , \quad (19)$$

$$\rho(\partial_t+\mathbf{v}\cdot\nabla)\varepsilon=-\mathbf{P}:\nabla\mathbf{v}-\nabla\cdot\mathbf{J} . \quad (20)$$

In the above, $\mathbf{v}$ is the macroscopic local fluid velocity, $\mathbf{P}$ is the pressure tensor, ε is the internal energy per fluid atom, $\mathbf{J}$ is the heat flux, and M is the molecular mass. Coupling between the fluid and the LP is produced by $W(\mathbf{r},t)$ and $\mathbf{F}_q(\mathbf{r},t)$, the average interaction potential experienced by the LP at time t, and the average force on a molecule due to the LP at time t;

$$W=\int w(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}',t)d^3r' ,$$
$$\mathbf{F}_q=-\nabla\int w(\mathbf{r}-\mathbf{r}')|\Psi(\mathbf{r}',t)|^2d^3r' . \quad (21)$$

Closure is obtained by asserting the local validity of the equation of state and the constitutive laws of nonequilibrium thermodynamics, in which $\mathbf{P}$ and $\mathbf{J}$ are linearly related to the gradients of $\mathbf{v}$ and T (temperature) via the viscosity and thermal conductivity.[23]

Equations (17)–(20) define the evolution of the system at the macroscopic level. In equilibrium they reduce to (13) and (15), the coupled equations describing trap formation. They may also be applied to the study of trapping dynamics and stability. Wu and Miller[24] used them to analyze the linear dynamical stability of extended, propagating LP states.

III. APPLICATION TO SELF-TRAPPING

A. Scaling and universality

In deriving (13) and (15), an ensemble average over molecular positions was carried out. Thus it is expected that Ψ and ρ vary slowly over distances on the order of the intermolecular separation. If the interaction potential between the LP and the fluid molecules is of sufficiently short range, then $w(\mathbf{r}-\mathbf{r}')$ can be approximated by the Fermi pseudopotential $c\delta(\mathbf{r}-\mathbf{r}')$, where $c\equiv\int w(\mathbf{r})d\mathbf{r}=\hbar^2L_s/2\pi m$ and L_s is the scattering length.[3] With this final simplification, (13) and (15) take the form

$$[(-\hbar^2/2m)\Delta+c\rho(\mathbf{r})]\bar{\psi}(\mathbf{r})=\mathcal{E}\bar{\psi}(\mathbf{r}) , \quad (22)$$

$$c|\bar{\psi}(\mathbf{r})|^2=\mu_0-\mu[\rho(\mathbf{r})] , \quad (23)$$

which may be scaled as follows: (1) Define new coordinates by letting $\mathbf{x}=a\mathbf{r}$, where $a=\sqrt{(2m/\hbar^2)c\rho_0}$ and ρ_0 is the density of the fluid far from the LP; (2) define the scaled wave function ϕ by $|\phi|^2=\beta c|\bar{\psi}|^2$; (3) scale the local density as $\hat{\rho}\equiv\rho/\rho_0$; and (4) scale the energy as $\varepsilon\equiv\mathcal{E}/\rho_0c$.

These operations reduce the coupled equations to the dimensionless form

$$(-\Delta_x+\hat{\rho})\phi=\varepsilon\phi , \quad (24)$$

$$|\phi|^2=\beta(\mu_0-\mu) . \quad (25)$$

The significance of this version is that the equations will

take the same form for many fluids. This occurs because the principle of corresponding states[25] assures us that $\beta\mu$ has a universal dependence on the reduced density ρ' ($\equiv \rho_0/\rho_c$) and temperature T' ($\equiv T/T_c$). As usual, the subscript c refers to the liquid-vapor critical point. Thus the right-hand side of (25) is a universal function of $\hat{\rho}$, ρ', and T'. There are no system-specific parameters in either (24) or (25). In the above it has been assumed that $c > 0$, corresponding to a repulsive interaction on the average (e.g., positronium). For an attractive interaction, i.e., for a positron, $c < 0$, resulting in obvious sign changes in (24) and (25).[3]

Taken together, the pair (24) and (25) constitutes a nonlinear eigenvalue problem for $\phi(x)$ and ε. The formal mathematical properties of partial differential equations produced by functionals such as Φ_N [Eq. (15)] have been studied by Berestycki and Lions.[11] They prove that the eigenvalue spectrum for spherically symmetric solutions is continuous. Since $\hat{\rho}$ asymptotically approaches 1 as $|x|$ goes to infinity (far from the trap), $0 \leq \varepsilon \leq 1$ for bound states. Thus each spherically symmetric solution is parametrized solely by ε.

The central question is how do we determine ε for the ground state of a trapped LP at a specific density and temperature. To see how this is accomplished, define the reduced normalization integral by $I_n \equiv (1/4\pi)\int |\phi|^2 dx$. Clearly, $I_n = I_n(\varepsilon)$. The normalization condition for $\tilde{\psi}$, $\int |\tilde{\psi}|^2 d\mathbf{r} = 1$, along with the definitions of ϕ and x, fix the value of the reduced normalization integral,

$$I_n(\varepsilon) = \beta c (2mc\rho_0/\hbar^2)^{3/2}/4\pi , \qquad (26)$$

and hence determine possible values for ε. I_n can be expressed in terms of the reduced variables ρ', T', and three characteristic lengths

$$I_n = (\rho'^{3/2}/T')[\lambda_c^2 L_s^{5/2}(4\pi)^{1/2}/l_c^{9/2}]$$
$$\equiv (\rho'^{3/2}/T')\Lambda . \qquad (27)$$

In (27) λ_c is the thermal wavelength of the LP at the critical temperature and l_c ($\equiv \rho_c^{-1/3}$) is the average distance between the atoms of the fluid at the critical density. Clearly, all of the system-specific parameters of the model are contained in the constant Λ, a scaled dimensionless quantity that completely determines the properties of the trapped state above T_c.

B. Stability

The most important property of the trapped state is its stability. A primitive quantitative measure of stability is provided, in an obvious notation, by $\Phi_N(\tilde{\psi})$. It has the disadvantage of containing the contribution of the bulk fluid to the Helmholtz free energy, and hence masks the effect of the LP in the thermodynamic limit. To remove this annoyance, it is convenient to subtract $\Phi_N(\psi_{ex})$ from $\Phi_N(\tilde{\psi})$ and then take the thermodynamic limit. Here ψ_{ex} is the extremal solution corresponding to an "extended" state consisting of a plane wave propagating in the average fluid density $\bar{\rho} = N/V$ (where V is the fluid volume). Let

$$\Phi \equiv \lim_{N \to \infty, V \to \infty, N/V = \bar{\rho}} [\Phi_N(\tilde{\psi}) - \Phi_N(\psi_{ex})]$$

$$= \lim_{N \to \infty, V \to \infty, N/V = \bar{\rho}} \int_V d\mathbf{r}[(\hbar^2/2m)|\nabla\tilde{\psi}|^2$$

$$+ \rho(\mathbf{r})\int d\mathbf{r}' w(\mathbf{r} - \mathbf{r}')|\tilde{\psi}(\mathbf{r}')|^2$$

$$+ f(\rho(\mathbf{r}),\beta) - f(\bar{\rho},\beta)] - \bar{\rho}c$$

$$\qquad (28)$$

in the local equilibrium approximation. We have assumed that the extended reference state is low lying, so that its kinetic energy vanishes in the thermodynamic limit. In the above, note that $\bar{\rho} \neq \rho_0$ for finite V. Thus $f(\rho(\mathbf{r}),\beta) - f(\bar{\rho},\beta) \neq 0$ almost everywhere, creating a convergence problem for the integral if the limits of spatial integration are extended naively. This difficulty is avoided by expanding $f(\bar{\rho},\beta)$ in a Taylor series about $f(\rho_0,\beta)$ and making use of $\partial f/\partial\rho = \mu$. It is easily seen that only the first-order corrections survive in the limit $V \to \infty$, yielding

$$\Phi = \int d\mathbf{r} \left[(\hbar^2/2m)|\nabla\tilde{\psi}|^2 + \rho(\mathbf{r})\int d\mathbf{r}' w(\mathbf{r} - \mathbf{r}')|\tilde{\psi}(\mathbf{r}')|^2 \right.$$

$$+ f(\rho(\mathbf{r}),\beta) - f(\rho_0,\beta)$$

$$\left. - \mu_0[\rho(\mathbf{r}) - \rho_0] \right] - \rho_0 c , \qquad (29)$$

where now the integration is over all space. This expression can be recast in a computationally useful form by (1) employing the scaling introduced earlier, (2) asserting the first law of thermodynamics ($f = \mu\rho - P$, where P is the ordinary hydrostatic pressure), and (3) recalling that $\tilde{\psi}$ is the solution of (13):

$$\Phi/c\rho_c = \rho' \left[\varepsilon - 1 + (1/I_n)\int_0^\infty dx \, x^2[\beta P_0/\rho_0 - (\beta P/\rho)\hat{\rho} \right.$$

$$\left. - \beta(\mu_0 - \mu)\hat{\rho}] \right] . \qquad (30)$$

In the thermodynamic limit it is no longer necessary to distinguish between $\bar{\rho}$ and ρ_0, and we opt for the latter. Equations (29) and (30) can be regarded as the difference between the two Helmholtz free energies (in the canonical ensemble) or two grand potentials[8] (in the grand canonical ensemble), since, in the limit, they are identical.[23] Again, according to the principle of corresponding states, $\beta P/\rho$ depends only on the reduced density and temperature. Thus, in common with (13) and (15), the right-hand side of (30) contains no system-specific constants, and can be regarded as a function of ε, ρ', and T'. For a particular trap, its value is determined by (27), the normalization condition. $\Phi/c\rho_c$ is one useful measure of the stability of the self-trapped state. A negative value indicates relative stability. A positive value still indicates the existence of trapped solutions; however they are relatively unstable when compared with propagating modes. We consider a second stability criterion below.

The number of molecules displaced from the vicinity of the trap is

$$N_D = \int (\rho_0 - \rho) dr = (\beta_c C \rho_c)(\rho'/T'I_n) \int_0^\infty dx\, x^2 (1 - \hat{\rho}) \; ,$$

$$(31)$$

and the effective radius of a trap is defined as

$$R = \tfrac{4}{3} \int_0^\infty dr\, r |\psi|^2$$

$$= \tfrac{4}{3}(4\pi/\beta c)(\beta c/4\pi I_n)^{4/3} \int_0^\infty dx\, x^3 |\phi|^2 \; . \quad (32)$$

We compare the number of displaced molecules with the spontaneous root-mean-square fluctuation of the population, $\langle (\Delta N)^2 \rangle^{1/2}$, in a volume of size R. We expect that when $\langle (\Delta N)^2 \rangle^{1/2} \approx N_D$ stability against spontaneous density fluctuations is marginal. From the compressibility equation of equilibrium statistical mechanics[23] $\langle (\Delta N)^2 \rangle = \rho^2 v K_T/\beta$, where here the volume v is $(4\pi/3)R^3$ and K_T is the isothermal compressibility. The quantity of interest is then

$$S = \frac{\langle (\Delta N)^2 \rangle^{1/2}}{N_D}$$

$$= \frac{16\pi}{9} \left[\frac{K_T}{\beta c} \right]^{1/2} \frac{\left[\int dx\, x^3 \phi^2 \right]^{3/2}}{\left[\int dx\, x^2 (1 - \hat{\rho}) \right]} \; . \quad (33)$$

C. Decay rate

The decay rate of a positron, whether it is isolated or bound in a positronium atom, is proportional to the local electron density.[3] For orthopositronium, the decay rate consists of the sum of the vacuum contribution, due to the electron partner, and the pick-off (PO) contribution, due to the presence of electrons bound in the fluid molecules. If the positronium thermalizes prior to annihilation then, within the context of the equilibrium statistical ensemble described in Sec. II, its decay rate can be represented by

$$\lambda_{PO} = B \left\langle \sum_j \int d\mathbf{r}' \rho_{el}(\mathbf{r}') |\psi(\mathbf{r}_j + \mathbf{r}')|^2 \right\rangle \; . \quad (34)$$

Here, the $\rho_{el}(\mathbf{r}')$ is the effective density of molecular electrons available for annihilation and B is a constant which, in principle,[26] could be computed from field theory. The density-functional formalism provides an avenue for expressing λ_{PO} in terms of $\tilde{\psi}$. Employ the canonical probability "density" to write

$$\lambda_{PO} = B(1/Z_N) \int D_\psi \delta(\langle \psi | \psi \rangle - 1) \exp[-\beta \langle \psi | \hat{\mathbf{P}}^2/(2m) | \psi \rangle] Q_N(\psi) \int d\mathbf{r}' \int d\mathbf{r}\, \rho_{el}(\mathbf{r}') |\psi(\mathbf{r}+\mathbf{r}')|^2 \rho(\mathbf{r}|\psi)$$

$$= B(1/Z_N) \int D_\psi \delta(\langle \psi | \psi \rangle - 1) \exp(-\beta \Phi_N) \int d\mathbf{r}' \int d\mathbf{r}\, \rho_{el}(\mathbf{r}') |\psi(\mathbf{r}+\mathbf{r}')|^2 \rho(\mathbf{r}|\psi) \; , \quad (35)$$

where we have used the fact that λ_{PO} involves a sum over single-particle terms to express the average in terms of the conditional local fluid density $\rho(\mathbf{r}|\psi)$. To the extent that we are willing to ignore the effects of fluctuations in the local density and wave function, or, if possible, simply incorporate them into the constant B, we may use the mean-field theory derived in Sec. III to write

$$\lambda_{PO} \approx B \int \rho(\mathbf{r}) \tilde{\psi}(\mathbf{r}) d\mathbf{r} = B \rho_c (\rho'/I_n) \int_0^\infty dx\, x^2 \hat{\rho} \phi^2 \; . \quad (36)$$

We expect the mean-field approximation to be adequate when Φ has a stable minimum at $\tilde{\psi}$. Similar to $\Phi/c\rho_c$, $\lambda_{PO}/B\rho_c$ is a scaled decay rate which depends solely on ε and ρ'. The normalization condition determines $\varepsilon = \varepsilon(\rho', T')$, and hence $\lambda_{PO}/B\rho_c$, when a trap exists in a given system.

D. Thermodynamics

All of the thermodynamics necessary to perform the mean-field analysis of self-trapping described above can be obtained directly from the equation of state. From Eqs. (25) and (30) we note that the only function required in addition to the hydrostatic pressure is the difference in chemical potential, $\mu_0 - \mu$. This is easily obtained by recalling that $\mu = \partial f/\partial \rho$ and appealing once more to the first law in the form $\mu \rho = f + P$. Eliminating μ from this pair yields

$$P = \rho \frac{\partial f}{\partial \rho} - f = \rho^2 \partial \frac{(f/\rho)}{\partial \rho} \; , \quad (37)$$

which can be integrated to obtain

$$f/\rho - f_0/\rho_0 = -\int_\rho^{\rho_0} d\rho''(P/\rho''^2) \; . \quad (38)$$

Substituting back into the first law yields the required functions,

$$\mu_0 - \mu = P_0/\rho_0 - P/\rho + \int_\rho^{\rho_0} d\rho''(P/\rho''^2) \; , \quad (39)$$

$$f(\rho(\mathbf{r}), \beta) - f(\rho_0, \beta) - \mu_0 [\rho(\mathbf{r}) - \rho_0]$$

$$= P_0(1 - \hat{\rho}) - \rho \int_\rho^{\rho_0} d\rho''(P/\rho''^2) \; , \quad (40)$$

for use in (25), (29), and (30).

Below we will illustrate the predictions of trapping obtained from the van der Waals equation of state, $(P + a\rho^2)(1 - b\rho) = \rho kT$. Carrying out the necessary integration over density yields

$$\beta(\mu_0 - \mu) = 2a(\rho - \rho_0)/kT$$

$$- kT \ln|\rho(1 - b\rho_0)/[\rho_0(1 - b\rho)]|$$

$$+ b(\rho_0 - \rho)/[(1 - b\rho)(1 - b\rho_0)] \; . \quad (41)$$

The critical point, defined as the density and temperature where the compressibility goes to zero $(\partial P/\partial \rho = 0$, $\partial^2 P/\partial \rho^2 = 0)$, defines the relation between the parameters a and b, and the density and temperature at the critical

point, ρ_c and T_c. This operation gives $a = 9kT_c/(8\rho_c)$ and $b = 1/(3\rho_c)$ where T_c and ρ_c are the temperature and density at the critical point, respectively. If we insert these relations into (28) it takes the form

$$\beta(\mu_0 - \mu) = 9\rho'(\hat{\rho} - 1)/(4T') + \ln|(3 - \rho')\hat{\rho}/(3 - \hat{\rho}\rho')|$$
$$+ 3/(3 - \rho') - 3/(1 - \rho'\hat{\rho}) , \qquad (42)$$

which demonstrates the law of corresponding states for this simple case. Similarly, to compute Φ, we require

$$(\beta/c\rho_c)[f - f_0 - \mu_0(\hat{\rho} - \rho)]$$
$$= -9\rho'(\hat{\rho} - 1)/(8T') - (\hat{\rho} - 1)/(1 - \rho'/3)$$
$$+ \hat{\rho}\ln|\hat{\rho}(1 - \rho'/3)/(1 - \hat{\rho}\rho'/3)| , \qquad (43)$$

which is also free of any dependence on the system parameters.

IV. NUMERICAL METHOD OF COMPUTATION

A modified shooting method[27] was employed to numerically construct spherically symmetric solutions of (24) and (25) on the half space $0 \le x \le \infty$. To remove the singularity at the origin, (24) was transformed to $-d^2u/dx^2 + \hat{\rho}u = \varepsilon u$, where, as usual, $u \equiv x\phi$. The second-order equation was then written as the system of first-order equations $du/dx = v$, $dv/dx = (\hat{\rho} - \varepsilon)u$.

Since we were interested in obtaining solutions for a range of ε at a large number of points in the thermodynamic phase space (ρ', T') of the fluid, we required a very efficient algorithm to iterate the first-order system. Starting at $x = 0$, the fourth-order Runge-Kutta scheme was used to obtain the first four iterations. This provided sufficient information to shift to the equally precise, but much faster, fourth-order Adams-Bashfourth algorithm.[27] The initial value of u is fixed at zero. Using bisection, the initial value of v was systematically adjusted until convergence to a solution with the desired number of nodes was obtained, i.e., no nodes for the ground state, one node for the first spherically symmetric excited state, etc. Simpson's rule was then used to compute properties of interest, such as the reduced normalization integral, free energy, effective trap size, number of displaced molecules, and decay rate.

The procedure was tested for self-consistency by using the usual technique of reducing the step size and looking for significant changes. A further test consisted of computing $\int[(du/dx)^2 + \hat{\rho}u^2]dx / \int u^2dx$, and comparing the result with ε. No unusual problems were encountered.

The single most problematic aspect of the numerical procedure was the inversion of (25) to obtain $\hat{\rho}$ from the current value of ϕ^2 ($= u^2/x^2$). The difficulty occurs because, near the critical point, where trapping is most likely, $\partial\mu/\partial\rho$ becomes small and the standard inversion methods (Newton, Newton-Raphson, etc.) fail. We found that the most effective method consisted of simply constructing a large table of values of $\beta(\mu_0 - \mu)$ for a fine partition of $\hat{\rho}$. The singularity in $\beta(\mu_0 - \mu)$ at $\hat{\rho} = 0$ had to be treated carefully.

The required code was written in FORTRAN 86 and the computations were carried out in double precision on an Intel 360 minicomputer. The table for inverting (25) was constructed by partitioning the unit interval for $\hat{\rho}$ into 10 000 segments. The step size for iteration in x was chosen as 0.005, and the initial value of v was located to within one part in 10^4. This yielded an error of less than 0.5% for all quantities of physical interest. At each phase point (ρ', T') the unit interval for ε was partitioned into 100 segments and the solution for ϕ was obtained at each boundary point. Linear interpolation was carried out on $\ln(I_n)$ to fix the final value of ε from the normalization requirement.

V. RESULTS

A. Normalization and existence of solutions

To explore the predictions of this model, we used the van der Waals equation to explicitly close (24) and (25), and solved the coupled equations using the numerical methods described in Sec. IV. The normalization integral, as well as the energy, free energy, displaced molecules, effective size, and decay rate were computed for 100 values of ε between 0 and 1.0 in increments of 0.01 at each temperature and density. The values of T' considered were 1.0, 1.2, 2.0, and 6.0. At each temperature, the allowed range of ρ' (the van der Waals equation is nonsingular for $0 < \rho' < 3$) was divided equally into 30 intervals. Thus 12 000 iterations for the normalization were calculated.

As explained above, the existence and stability of trapped states depends entirely on values of the reduced normalization integral. Except at the critical point, plots of I_n versus ε exhibit a single minimum. At a given temperature and density, the sole permissible value of I_n is determined by Λ (19) yielding none, one, or possibly two values for ε where trapping may occur. Where two values occur, the higher-energy state has a positive value of Φ.[6] Thus Λ, T', and ρ' determine the particular solution of the nonlinear eigenvalue problem for ϕ and $\hat{\rho}$. The remaining properties of the trapped state, such as the free energy, displaced mass, mean size, and decay rate, can then be determined for each ρ' and T' in the fluid phase where trapping exists.

In Fig. 2 we have plotted $\ln(I_n)$ versus ε both for the ground and spherically symmetric first excited state at the critical point $(\rho' = T' = 1.0)$. In contrast with all other ρ', T' values, they are monotonically decreasing and fail to exhibit a minimum on the open ε interval. This phenomenon has not been previously reported. It demonstrates that the critical point is unique in that trapped solutions always exist there for $\Lambda > 0$. To verify this feature in more detail, first solutions were obtained for 100 values of ε in the region $0.99 < \varepsilon < 1.0$. Even here, the negative slope persisted. Second, the behavior of $I_n(\varepsilon)$ was studied on the critical isotherm for nearby values of ρ'. In each case, the slope turned positive as $\varepsilon = 1$ was approached. The horizontal line corresponds to $\Lambda = 35$ and shows a single solution for each state. Naturally, the energy eigenvalue of the excited state is consid-
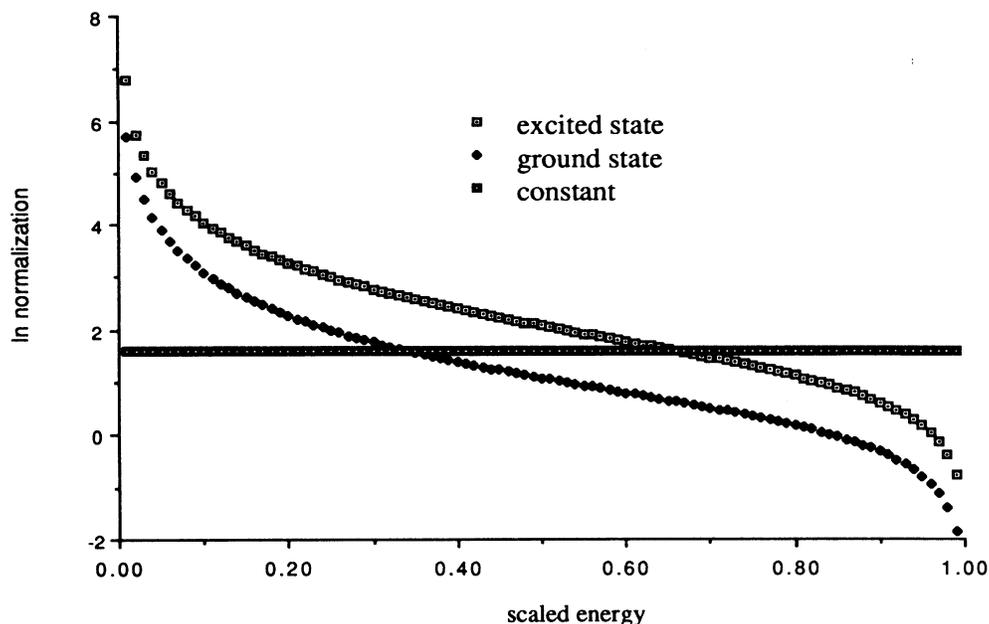
FIG. 2. Natural logarithm of the normalization integral vs scaled energy at the critical point for the ground and first excited states. The straight line represents the log of the universal constant Λ. Its intersection with the normalization curve determines the particular solution. At the critical point, plots of the normalization are strictly decreasing.

erably larger than the ground state.

Plots of $\ln(I_n)$ versus ε are given for three values of reduced density ρ' on the critical isotherm in Fig. 3. They illustrate the characteristic minimum near the right-hand boundary of the interval. Two features to note are (1) the minimum is more pronounced and (2) trapped solutions

less likely as we move away from the critical point. In the ideal gas regime, the minimum occurs near $\varepsilon = 0.8$.[6]

B. Stability and the free energy

Stability is investigated by computing the scaled free energy (or grand potential) $\Phi/c\rho_c$. The dependence of
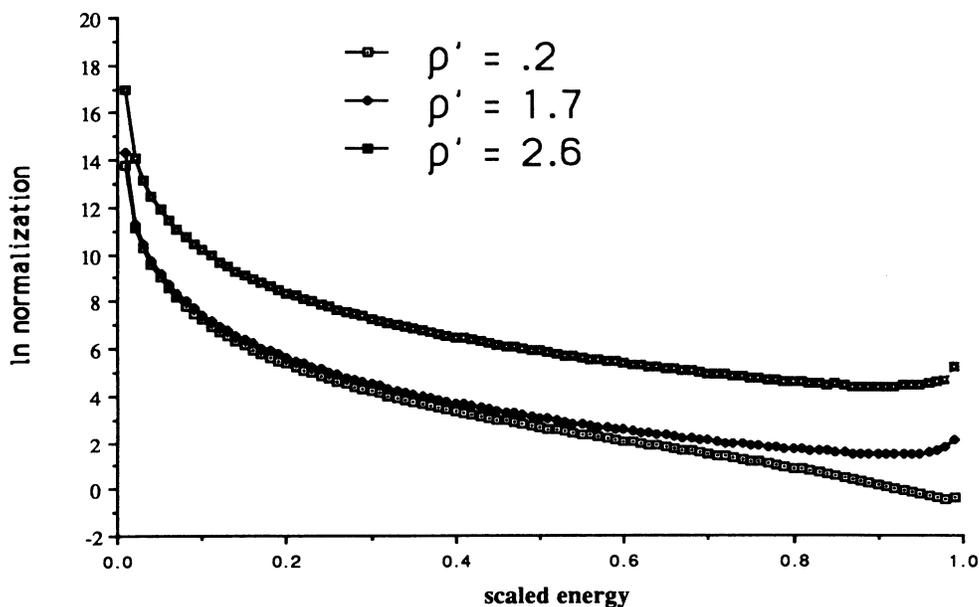
FIG. 3. Natural logarithm of the ground-state normalization integral vs scaled energy at the critical temperature for three reduced densities (0.2, 1.7, and 2.6). In contrast with Fig. 1, all three plots have a minimum. The location of the minimum shifts to the left with increasing density.
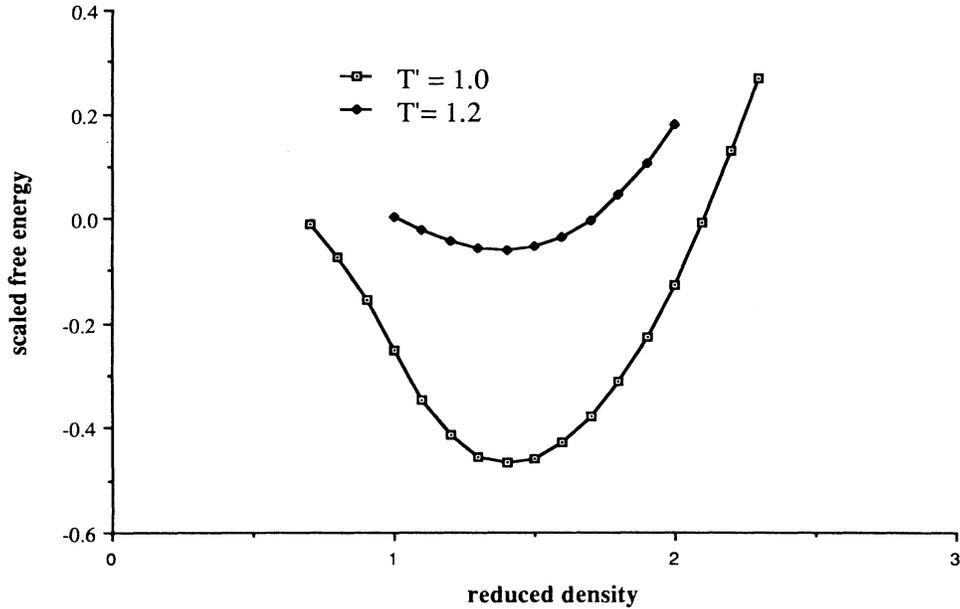
FIG. 4. Plots of the free energy vs reduced density for two different temperatures. The stability of the trap decreases with increasing temperature.

the free energy on the universal constant Λ is illustrated in Fig. 4, where plots of $\Phi/c\rho_c$ versus ρ' are shown for $\Lambda = 35$. Back of the envelope estimates indicate that these Λ values span a realistic range for a number of fluids. These curves show a pronounced minimum, indicating maximum stability, near the center of the interval in which traps are possible. It is clear that larger values of Λ produce more stable traps over a wider range of density. The plots shown in Fig. 5(a) were computed on the critical isotherm ($T' = 1.0$), where trapping is most likely to occur, and those on 5(b) at $T' = 1.2$. Although most of the solutions are stable ($\Phi/c\rho_c < 0$), the existence of metastable solutions is evident near the boundaries of the allowed density range. Gersch has pointed out that the increase in entropy due to the translational motion of the bubble as a whole should stabilize the localized state with respect to propagating modes.[28] For the present purposes Φ provides a useful measure of relative stability among different trapped states. In Fig. 5, we see that the density range and stability of trapped states decrease as we move away from the critical isotherm. For the two values of Λ considered in this study, there was one solution at $T' = 2.0$ ($\Lambda = 35$) and no solutions at $T' = 6.0$.

The mean number of molecules excluded by the trap, N_D, was computed for the van der Waals fluid by evaluating $\langle \phi | 1 - \bar{\rho} | \phi \rangle$. The ratio S of the spontaneous root-mean-square fluctuation of the molecular population in a sphere of radius R to N_D was determined by evaluating $\langle \phi | x | \phi \rangle$, the additional integral appearing in (33). S is plotted on isotherms for various values of reduced temperature T' in Fig. 6. The plots indicate that over a large density range on the critical isotherm, spontaneous fluctuations are much smaller than the displaced populations.

C. Decay rate

The reduced local density which develops with the onset of trapping decreases the number of electrons available to the positron for annihilation. The enhanced lifetime which results is the key experimental signature of self-trapping. The reduced decay rate, $\lambda_{PO}/B\rho_c$, is plotted versus density on isotherms in Fig. 7 for $\Lambda = 35$ at $T' = 1.0$, 1.2, and 2.0; and in Fig. 8 for $\Lambda = 5$ at $T' = 1.0$ and 1.2 (there are no trapped solutions at $T' = 2.0$ when $\Lambda = 5$). As expected, Fig. 7 reflects the fact that deeper traps form over a wider range of average density as the critical temperature is approached. Figure 8 illustrates the same phenomenon, but to a lesser degree, due to the smaller value of the universal constant Λ. In each figure, the straight line indicates the extrapolated low density behavior in the absence of trap formation.

VI. CONCLUSIONS

We have outlined a mesoscopic model for describing the properties of trapped light-particle states in fluids. The model is formulated from a consistent dynamical evolution which includes the response of the fluid to the presence of the light particle. It naturally leads to a state space in which equilibrium statistical mechanics can be formulated via a functional integral, and ordinary (mean-field) density-functional theory arises from a variational principle. Applying mean-field theory to the dynamical equations results in a complete set of hydrodynamic equations which couple the LP wave function to

the local fluid velocity and density.[22]

Under the approximations of local equilibrium, and a contact LP-fluid interaction potential, the trapped state is defined, in mean-field theory, by a pair of coupled equations for the LP wave function and local fluid density. We have shown that scaling the coordinates, wave function, and thermodynamic variables reduces the equations to a universal form in which all of the system-specific quantities appear in a single dimensionless parameter. The parameter, Λ, depends on the thermodynamic prop-

erties of the fluid at its critical point, which are known, and the scattering length of the LP-molecule interaction, which is generally not known. Since Λ varies as the $\frac{5}{2}$ power of the scattering length, it is sensitive to small variations in L_s. For the compounds in which trapping has been indicated experimentally (see Sec. I), we estimate that Λ varies from about 5 to 1900, with values above 50 only occurring for the quantum fluids H_2 and H_e. Above the critical temperature, the constant determines the
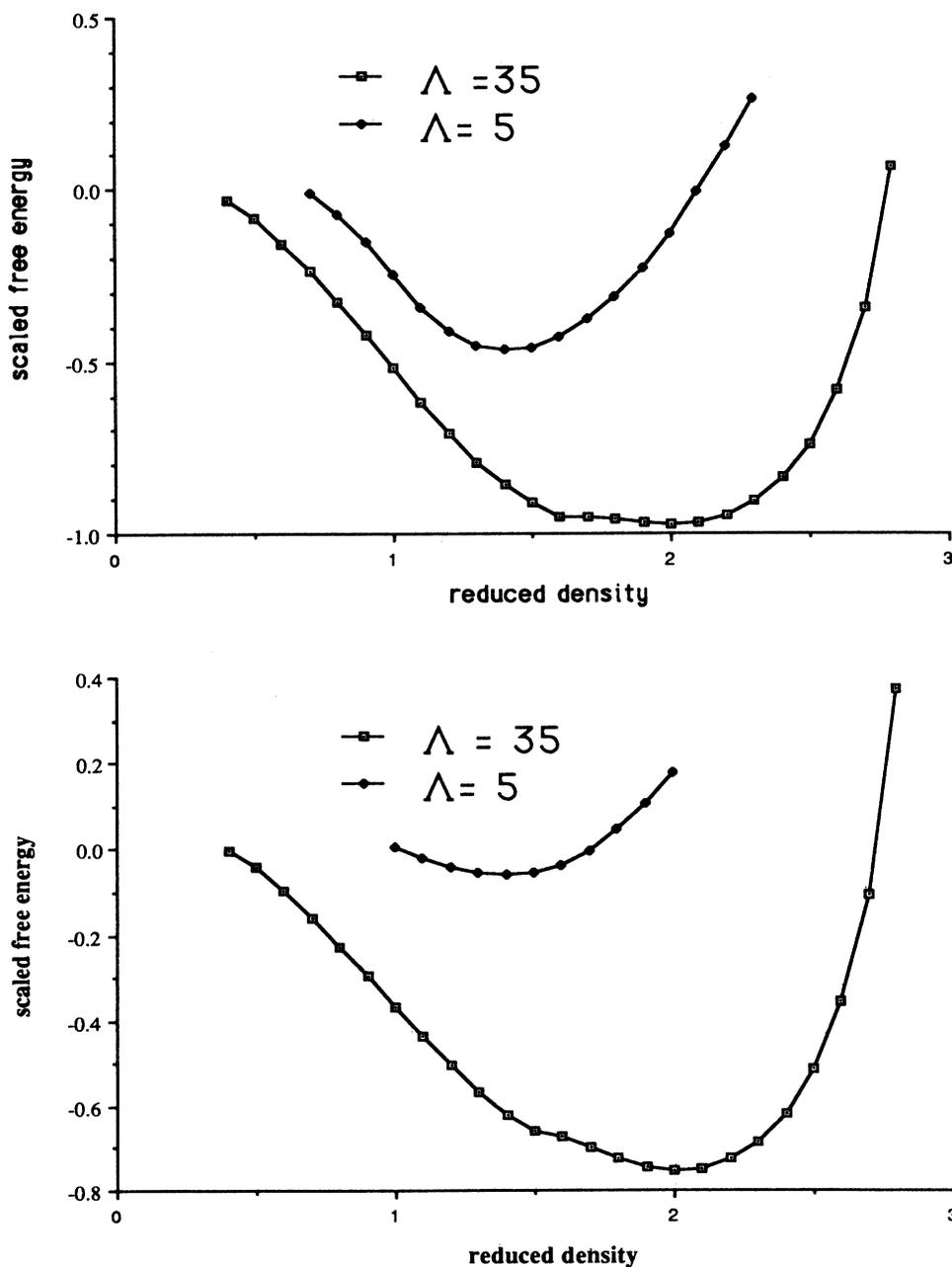
FIG. 5. Free energy vs reduced density for $\Lambda = 5$ and 35. (a) $T' = 1.0$, (b) $T' = 1.2$. The larger Λ value manifests deeper trapping over a larger density interval indicating increasing trap stability with Λ. Typically, maximum stability occurs near the center of the density range, while the end points are metastable.
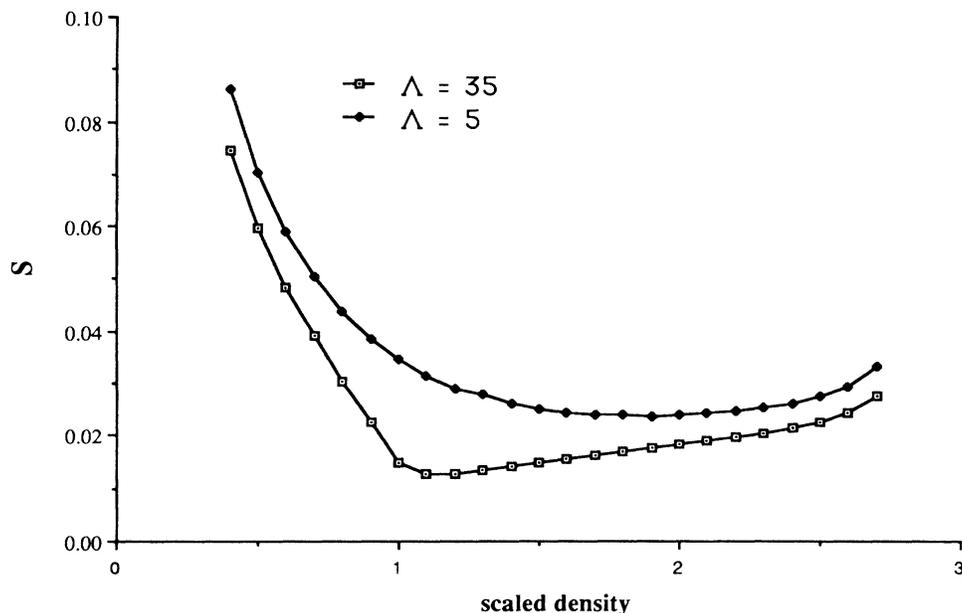
FIG. 6. Plot of S vs reduced density at $T' = 1.0$. S is defined as the ratio of the root-mean-square fluctuation in population in a sphere of radius R (the effective trap radius) of the normal fluid to the number of molecules displaced by the trap.

response of the system to the light particle as well as the range of density and temperature where stable localized states are found.

A numerical algorithm was developed to rapidly solve the coupled equations with good precision. The method was used to investigate the existence and stability of the self-trapped state in a van der Waals fluid. Plots of the normalization integral versus energy demonstrate that localized states always exist at the liquid-vapor critical point. An open question is whether this feature occurs in models which explicitly include the nonlocal effects of correlations.

As an application of the method, the pick-off decay rate of trapped orthopositronium was investigated. The predictions are qualitatively similar to experimental measurements on ethane (see Fig. 1) and argon, which indicate that trapping occurs over a similar range of reduced temperature ($1 < T' < 1.5$) and density. However, the objective was not to represent a particular set of data, but rather to test the usefulness of the model and the sensi-
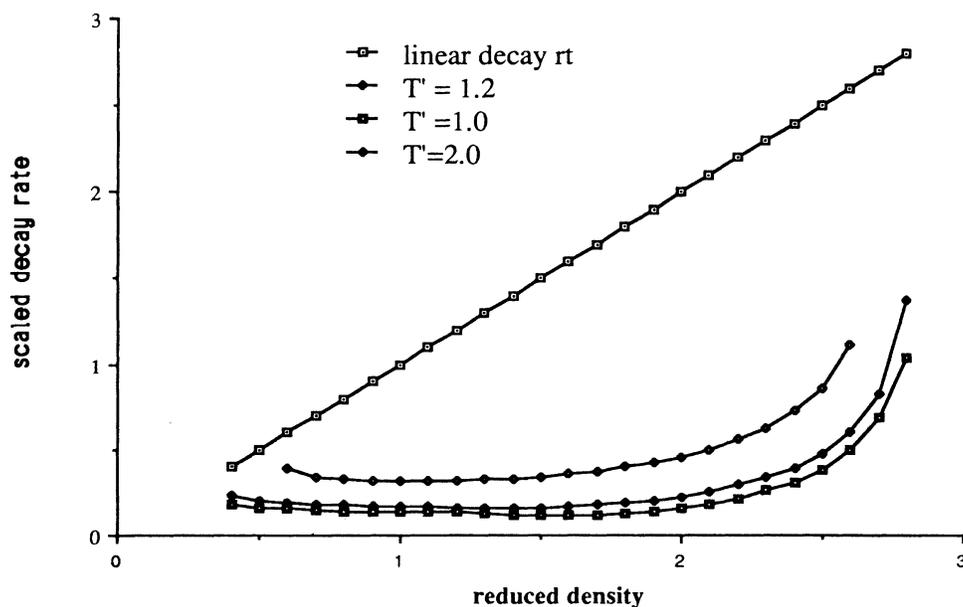
FIG. 7. Decay rate vs reduced density for $\Lambda = 35$ at $T' = 1.0$, 1.2, and 2.0.
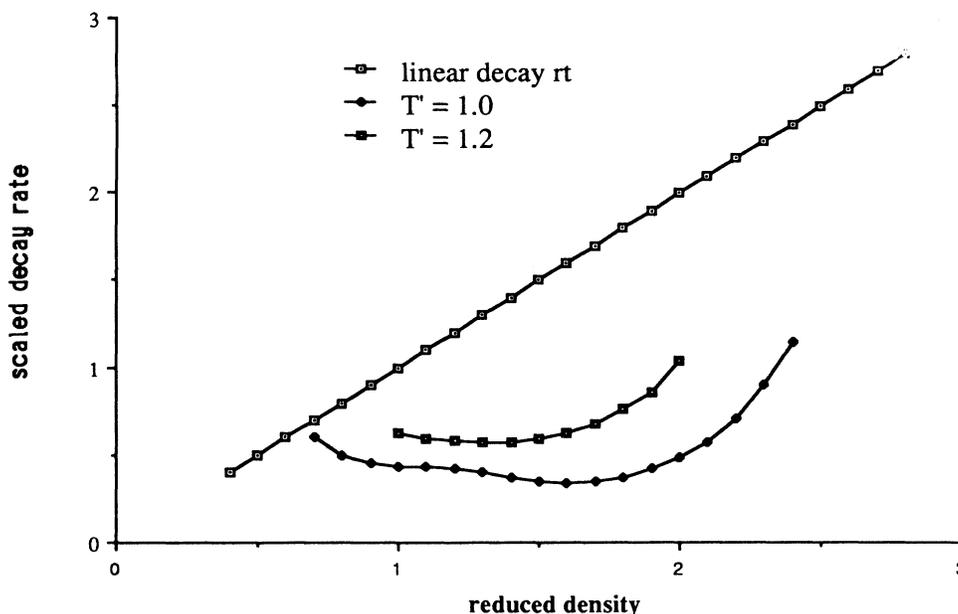
FIG. 8. Decay rate vs reduced density for $\Lambda = 5$ at $T' = 1.0$ and 1.2.

tivity of its predictions to changes in the value of Λ. The theoretical decay rates are smaller than those observed experimentally, indicating a predicted average density in the trapped state that is too low. They also show a smoother increase with density than the experimental data near the critical isotherm. The apparent elbow (or kink) found for ethane (see Fig. 1) is missing. On the other hand, they compare favorably with the most recent theoretical calculations of Tuomisaari et al.,[14] for argon, based on the earlier work of Nieminen et al.,[9] which fail to account either for the finite density range of the plateau, or rapid increase in the decay rate at higher densities.[29]

A peculiarity of this, and other, density-functional models is the existence of a lower bound for the normalization integral $I_n(\varepsilon)$ (except, as we have shown, at the critical point). The result is that nonvanishing solutions of the Euler equation[29] (here the nonlinear Schrödinger equation) for an infinite system only exist for specific regions of density and temperature, say $A(\rho, T)$. Thus mean-field theory taken by itself suggests that, in the complement of A, the optimum states are propagating waves of infinitesimal amplitude.[6] There are two consequences of this behavior for the positronium annihilation rate as predicted by density-functional methods. First,

there is a discontinuity in the annihilation rate at the boundary of A. Second, in the complement of A the annihilation rate varies linearly with density. Neither of these features is even approximately observed in experiments. The statistical theory outlined in Sec. II does not suffer from these problems. The optimized state is simply an approximation to the true phenomena under conditions where fluctuations play a minor role. In future work we plan to study the role of fluctuations in the transition region, i.e., that part of the complement of A where the decay rate lacks linearity, as well as (1) the relation of the path-integral formulation to regular quantum statistics, (2) its usefulness for describing the role of fluctuations, and (3) improvements to the mean-field theory garnered from a more realistic equation of state.

ACKNOWLEDGMENTS

[1]N. Gee and G. R. Freeman, Can. J. Chem. **64**, 1810 (1986).

[2]E. M. Juengerman, R. H. Arganbright, M. H. Ward, and S. C. Sharma, J. Phys. B **20**, 867 (1987).

[3]For a review of both the experimental and theoretical physics of positron annihilation in fluids, see I. T. Iakubov and A. G. Khrapak, Prog. Phys. **45**, 697 (1982).

[4]Shang-Keng Ma, Modern Theory of Critical Phenomena (Benjamin, Reading, MA, 1976).

[5]John P. Hernandez, Phys. Rev. B **11**, 1289 (1975).

[6]R. L. Moore, C. L. Cleveland, and H. A. Gersch, Phys. Rev. B **18**, 1183 (1978).

[7]M. J. Stott and E. Zaremba, Phys. Rev. Lett. **38**, 1493 (1977).

[8]C. Ebner and C. Punyanita, Phys. Rev. A **19**, 856 (1979).

[9]R. M. Nieminen, M. Manninen, I. Välimaa, and P. Hautojarvi, Phys. Rev. A **21**, 1677 (1980).

[10]See, e.g., J. K. Percus, Non-Uniform Fluids **31**, F. W. Mon-

troll and J. L. Leibowitz, *The Liquid State of Matter: Fluids Simple and Complex* (North-Holland, Amsterdam, 1982).

[11]P. L. Lions, Nonlinear Anal., Theory Methods Appl. **4**, 1063 (1979), and references cited therein.

[12]B. N. Miller, H. L. Lehtihet, J. Kowalski, and S. C. Sharma, in *Positron Annihilation*, edited by P. C. Jain, R. M. Singru, and K. P. Gopanathan (World Scientific, Singapore, 1985), Vol. 406; J. Phys. A (to be published).

[13]S. C. Sharma, A. Eftekhari, and J. D. McNutt, Phys. Rev. Lett. **48**, 953 (1982).

[14]M. Tuomisaari, K. Rytsola, and P. Hautojarvi, Phys. Lett. **112A**, 279 (1988).

[15]S. C. Sharma (unpublished).

[16]J. D. McNutt and S. C. Sharma, J. Chem. Phys. **68**, 130 (1978).

[17]S. C. Sharma, R. H. Arganbright, and M. H. Ward, J. Phys. B **20**, 867 (1987); S. C. Sharma and E. H. Juenguman, Phys. Lett. A **144**, 47 (1986).

[18]K. F. Canter and L. O. Roellig, Phys. Rev. A **12**, 386 (1975).

[19]T. B. Daniel and R. Stump, Phys. Rev. **115**, 1599 (1959).

[20]M. Born and J. R. Oppenheimer, Ann. Phys. (N.Y.) **84**, 457 (1927).

[21]David Chandler, Yashwant Singh, and Diane M. Richardson, J. Chem. Phys. **81**, 1975 (1984).

[22]B. N. Miller, Phys. Rev. A **30**, 3343 (1984).

[23]L. E. Reichl, *A Modern Course in Statistical Physics* (University of Texas Press, Austin, 1980).

[24]Zhihong Wu and B. N. Miller, in *Proceedings of the International Symposium on Positron Annihilation Studies of Fluids*, edited by S. C. Sharma (World Scientific, Singapore, 1989), Vol. 253.

[25]R. K. Pathria, *Statistical Mechanics* (Pergamon, New York, 1972).

[26]M. A. Stroscio, Phys. Rev. Lett. **48**, 571 (1982).

[27]John R. Rice, *Numerical Methods, Software and Analysis* (McGraw-Hill, New York, 1983).

[28]H. A. Gersch, Phys. Rev. B **19**, 1351 (1979).

[29]Morton I. Kamien and Nancy L. Schwartz, *Dynamic Optimization: The Calculus of Variations and Optimal Control in Economics and Management* (North-Holland, New York, 1981).