Statistical mechanics of a positron in a classical fluid ⁽¹⁾

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Although the equilibrium theory of classical fluids, simple and complex, has reached the stage of routine accurate evaluation, this is hardly the case for even the next microscopic step, that of a quantum particle in a classical fluid. In many chemical applications, the quantum particle is an electron, but positron annihilation experiments on thermalized positrons and orthopositronium atoms offer a wealth of information to test our theoretical understanding of this general class of systems. Here, we investigate several ways in which the concepts behind classical techniques can be generalized to handle this prototypical quantum problem, in the overt quantum form as well as in the classical polymer representation. Both integral equation and density functional formats are studied and their qualitative characteristics examined.

1. Introduction

The experimentally dominant annihilation of thermalized positrons in fluid matter falls into two classes, that due to bare positrons, e^+ , and to orthopositronium atoms, Ps .¹ If we separate out the self-annihilation of the Ps , and define $n_{pe}(X, x)$ as the joint density of a positron at X , a fluid electron at x , then the instantaneous annihilation rate in both cases takes the form

$$\Lambda = K \int n_{pe}(X, X) d^3 X . \quad (1.1)$$

To make the phenomenology amenable to unencumbered extension of classical many-body theory, we ignore time-correlation effects and idealize the experimental situation by imagining that the positrons or positronium constitute a low density thermal ensemble at reciprocal temperature β of a surrounding atomic fluid. We also assume a rigid electron distribution $w(x)$ about the origin of each atom, so that in terms of the location of the atom, (1.1) translates to

$$\Lambda = K \int \int n_{pa}(X, x) w(X - x) d^3 x d^3 X . \quad (1.2)$$

Eq. (1.2), with a modified w , remains valid when X is taken as the location of the Ps center of mass, rather than of the positron. In either case, incorporating the reaction of the atomic electron density to the presence of the light particle requires further renormalization of w .

The behavior of positrons in ordinary fluids provides a severe test of our understanding of a quantum many-body system at its most primitive level, that in which all continuous degrees of freedom but three — those of the light particle — can be regarded as classical. It is the dependence of Λ on fluid thermodynamic parameters that tests our theoretical understanding.

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To devise a theoretical treatment, we need a definite theoretical model, and we will choose for this purpose a system Hamiltonian

$$\Phi = P^2/2m + \sum_j (v(X - x_j) - \mu) + \frac{1}{2} \sum_{i \neq j} \phi(x_i - x_j). \quad (1.3)$$

Here, X and P specify the light particle, $\{x_j\}$ the atomic locations, with pair interaction $\phi(x - y)$ (the irrelevant classical momenta are dropped), μ the momentum-reduced chemical potential with a grand ensemble understood. The effective light particle-atom interaction, $v(X - x)$, is customarily modeled by a hard repulsive core for Ps , an attractive core for e^+ , and a weak polarization tail in both cases.² Equilibrium properties are then determined by the mixed grand partition function

$$\Xi = \text{Tr}_x \int \exp -\beta \Phi d[x] \quad (1.4)$$

in which the summation over the number of atoms N , the associated weight $1/N!$, and the N -particle integrations are subsumed in the notation $d[x]$. The grand potential

$$\Omega = -(1/\beta) \ln \Xi \quad (1.5)$$

serves as generating function for expectations, and in particular, since

$$\sum v(X - x_j) = \int \int \rho_{pa}(Y, x) v(Y - x) d^3 Y d^3 x, \quad (1.6)$$

in terms of the microscopic pair density

$$\rho_{pa}(Y, x) = \sum \delta(x_i - x) \delta(Y - X), \quad (1.7)$$

we have

$$\int n_{pa}(x + R, x) d^3 x = \delta \Omega / \delta v(R), \quad (1.8)$$

which is all that is required for (1.2).

An alternative expression for (1.4) allows closer contact with classical fluid technology. It is the path integral form, based upon an observation of Dirac,³ extended by Feynman,⁴ and used in the many-body context by many others:⁵

$$\langle X | e^{-\epsilon P^2/2m} | Y \rangle = (m/2\pi i \hbar^2)^{3/2} e^{-(m/2\epsilon \hbar^2)|X-Y|^2} \quad (1.9)$$

for small ϵ , allowing immediate transcription of (1.4), by inserting intermediate states, to

$$\begin{aligned} \Xi = & \int \int \exp -\left\{ (m/2\epsilon \hbar^2) \sum_{\tau=\epsilon}^{\beta} |X(\tau) - X(\tau - \epsilon)|^2 \right\} \\ & \exp -\left\{ \epsilon \sum_{\tau, j} (v(X(\tau) - x_j) - \mu) \right\} \exp -\left\{ \frac{1}{2} \beta \sum_{i \neq j} \phi(x_i - x_j) \right\} \\ & D_{pbc}[X] d[x]. \end{aligned} \quad (1.10)$$

Here, $D_{pbc}[X]$ refers to the constraint that $X(\beta) = X(0)$ and includes the amplitudes required by (1.9). Thus, one has a "ring polymer" $\{X(\tau)\}$, interacting with the classical fluid $\{x_j\}$.

2. Mean Field Approximation

Let us start with a "coarse grained" approach. A standard classical fluid simplification involves the selective neglect of fluctuations, and in the present context, might take the following form. At sufficiently low temperature, the trace in (1.4) is dominated by its ground state contributions. Hence, neglecting excited state transitions, (1.3) and (1.4) translate to

$$\Xi = \int \exp -\beta [E_0(P^2/2m + \sum_j v(X - x_j)) - N\mu + \frac{1}{2} \sum_{i \neq j} \phi(x_i - x_j)] d[x], \quad (2.1)$$

or via the Rayleigh-Ritz principle,

$$\Xi = \max_{\psi} \int \exp -\beta [\langle \psi(X, \{x\}) | P^2/2m + \sum_j v(X - x_j) | \psi(X, \{x\}) - N\mu + \frac{1}{2} \sum_{i \neq j} \phi(x_i - x_j)] d[x] . \quad (2.2)$$

The variational wave function ψ is parametrized by the full set of classical particle coordinates, at each configuration of which, $\int |\psi(X, \{x\})|^2 d^3X = 1$. We now neglect the fluctuations of ψ at fixed X , and so replace it by the effective mean $\psi(X)$. Thus, (2.2) becomes

$$\Xi = \max_{\psi} \Xi_0[\bar{v}_{\psi}] \exp\{-\beta \int (\hbar^2/2m) |\nabla \psi(X)|^2 d^3X\} , \quad \bar{v}_{\psi}(X) = \int v(X - x) |\psi(x)|^2 d^3X \quad (2.3)$$

where $\Xi_0[\bar{v}_{\psi}]$ is the classical fluid grand partition function with external potential $\bar{v}_{\psi}$, and the restriction $\int |\psi(X)|^2 d^3X = 1$ again applies.

At another level of coarse graining, we can regard the classical fluid as locally homogeneous, characterized by the local chemical potential $\mu - \bar{v}_{\psi}$. The grand potential is then additive:

$$\Omega_0[\bar{v}_{\psi}] = - \int P(\mu - \bar{v}_{\psi}(x)) d^3x \quad (2.4)$$

where $P(\mu)$ denotes the bulk fluid equation of state, and (2.3) reduces to⁶

$$\Omega = \min_{\psi} \int (\hbar^2/2m) |\nabla \psi(X)|^2 d^3X - \int P(\mu - \bar{v}_{\psi}(x)) d^3x . \quad (2.5)$$

However, for this to make sense, v cannot have a region of infinite amplitude — as in the hard core Ps contribution — and hence is to be replaced by its equivalent pseudopotential

$$v(X - x) = \lambda \delta(X - x), \quad (2.6)$$

where $\lambda = 2\pi\hbar^2 a/m$, a being the s -wave scattering length. Consequently,

$$\Omega = \min_{\psi} \int [(\hbar^2/2m) |\nabla \psi(X)|^2 - P(\mu - \lambda |\psi(X)|^2)] d^3X , \quad (2.7)$$

in which form thermodynamic parameters of the fluid enter only in the corresponding equation of state. We also observe that now

$$\partial\Omega/\partial\lambda = \int n_{pa}(X, X) d^3X \quad (2.8)$$

which, for short range w , suffices to determine the rate Λ via (1.2). [For an elegant alternative mean field treatment, see ref. 7].

Varying (2.7) with respect to ψ^* , with $\int |\psi(X)|^2 d^3X = 1$, yields the nonlinear Schrodinger equation

$$-(\hbar^2/2m) \nabla^2 \psi(X) + \lambda n(\mu - \lambda |\psi(X)|^2) \psi(X) = \mathcal{E} \psi(X) \quad (2.9)$$

$$\int |\psi(X)|^2 d^3X = 1 ,$$

where $n(\mu)$ is the thermodynamic $n - \mu$ relation. For minimum Ω , $\psi(X)$ can be assumed real and nonnegative, the solution is of course highly degenerate, since any translate is also a solution.

Let us look for a basic solution, spherically symmetric about the origin, so that $\nabla^2\psi(X) = \psi''(X) + (2/X)\psi'(X)$. Multiplying (2.9) by $2\psi'(X)$ and integrating from 0 to X then yields

$$\begin{aligned} & (\hbar^2/2m)\psi'(X)^2 + P(\mu - \lambda\psi(X)^2) - P(\mu) + \mathcal{E}\psi(X)^2 \\ & = K - \int_0^X (\hbar^2/m)\psi'(X)^2 dX/X, \\ & 4\pi \int_0^\infty \psi(X)^2 X^2 dX = 1. \end{aligned} \quad (2.10)$$

If the integral on the right hand side is dropped, to be inserted iteratively, then $\psi = \psi' = 0$ as $X \rightarrow \infty$ shows that $K = 0$, and we are left with

$$\begin{aligned} & (\hbar^2/2m)\psi'(X)^2 + V(\psi(X)) = 0 \\ & V(\psi) = P(\mu - \lambda\psi^2) - P(\mu) + \mathcal{E}\psi^2. \end{aligned} \quad (2.11)$$

If $\lambda > 0$, as in Ps , $\mathcal{E}$ can always be found to satisfy the normalization condition for ψ ; thus Ps is always localized and $n(\mu - \lambda\psi^2) < n(\mu)$, creating a fluid cavity. If $\lambda < 0$, a rough approximation to e^+ , matters are more complex, as they are when $\mu - \lambda\psi^2$ can cross a phase transition. In any event, the annihilation rate is obtained via (2.8) which, by virtue of (2.9) and (2.11), can be recast as

$$\partial\Omega/\partial\lambda = (1/\lambda) \int (P(\mu) - P(\mu - \lambda\psi(X)^2)) d^3X. \quad (2.12)$$

3. Mean Spherical Approximation

It is the interplay between one-body quantum and many-body classical fluid phenomena that supplies both the substance and the difficulty of our study. The form (1.10) is totally classical, so that perhaps a more uniform treatment may be possible. A major technical difficulty is that the polymer energy is invariant only under the cyclic group of coordinate transformations, whereas a fluid has the full invariance of the symmetric group; this precludes several otherwise promising techniques. The mean spherical approximation,⁸ on the other hand, is very general, simplifying complex distributions by regarding them as Gaussian, guaranteed by an appropriate central limit theorem for small enough fluctuations. In prototypical form, an external potential $u(x)$ is applied to a reference classical fluid of known properties, and the cumulant expansion of Ξ/Ξ_0 truncated at second order:

$$\begin{aligned} \Xi/\Xi_0 &= \langle e^{-\beta \int u(x) \rho(x) d^3x} \rangle_0 \\ &\cong \exp[-\beta \int u(x) n_0(x) d^3x + \frac{1}{2}\beta^2 \iint S_0(x,y) u(x) u(y) d^3x d^3y]. \end{aligned} \quad (3.1)$$

$\rho(x) = \sum \delta(x-x_i)$ is the microscopic density, $n_0(x) = \langle \rho(x) \rangle_0$ the reference density, and $S_0(x,y) = \langle (\rho(x) - n_0(x))(\rho(y) - n_0(y)) \rangle_0$ the reference density-density correlation.

Applying $\delta/\delta u(x)$ to $\Omega = -(1/\beta) \ln \Xi$ of (3.1), we have

$$n(x) = n_0(x) - \beta \int S_0(x,y) u(y) d^3y, \quad (3.2)$$

which is recognized as merely a first order perturbation in u . Nevertheless, let us pursue the implications of (3.2) for the classical form (1.10) of the quantum problem. Now we must operate in the full space $\{x_j, X(\tau)\}$, but it suffices to choose the microscopic density

$$\rho(R) = (\epsilon/\beta) \sum_{i,\tau} \delta(X(\tau) - x_i - R) \quad (3.3)$$

since the interaction in (1.10) is then $\int \rho(R) v(R) d^3 R$ and $\langle \rho(R) \rangle = \int n_{pa}(x + R, x) d^3 x$ is, as in (1.8), the quantity of major interest. In the absence of interaction, the light particle and fluid are decoupled, so that in this two-system reference, $n_{00}(R) = n$, the bulk fluid density, whereas

$$\begin{aligned} S_{00}(R, R') &= (\epsilon^2/\beta^2) \sum_{\tau\tau'} \langle \sum_{i,j} \delta(X(\tau) - x_j - R) \delta(X(\tau') - x_i - R') \rangle_{\{X,x\}} - n^2 \\ &= (\epsilon^2/\beta^2) \sum_{\tau\tau'} \langle S_0(X(\tau) - R_1, X(\tau') - R') + n^2 \rangle_{\{X\}} - n^2 \\ &= (\epsilon^2/\beta^2 V) \sum_k \tilde{S}_0(k) \sum_{\tau\tau'} \langle e^{ik \cdot (X(\tau) - X(\tau'))} \rangle_{\{x\}} e^{ik \cdot (R' - R)}, \end{aligned} \quad (3.4)$$

V the system volume, k in units of $2\pi/V^{1/2}$, and $\tilde{S}_0$ the Fourier transform of $S_0(X - Y)$. For the harmonic chain $\{X(\tau)\}$ of (1.10), one readily finds

$$\begin{aligned} \tilde{\gamma}(k) &= (\epsilon^2/\beta^2) \sum_{\tau,\tau'} \langle e^{ik \cdot (X(\tau) - X(\tau'))} \rangle_{\{X\}} \\ &= \int_0^1 \exp[-\beta(\hbar^2 k^2/2m)\tau(1-\tau)] d\tau \sim 1/(1 + \beta\hbar^2 k^2/4m), \end{aligned} \quad (3.5)$$

the approximation being valid for small and large k . It follows from (3.3), (3.4), (3.5) that, in convolution notation,

$$\begin{aligned} \langle \rho(R) \rangle &= n - S_0(R) * \beta v(R) * \gamma(R) \\ \text{where } \gamma(R) &\sim 2/\lambda_{TH}^2 e^{-\sqrt{8\pi}R/\lambda_{TH}}/R, \end{aligned} \quad (3.6)$$

and $\lambda_{TH} = (2\pi\beta\hbar^2/m)^{1/2}$ is the thermal de Broglie wave length of the light particle.

There are three length scales involved in (3.6): the range a of $v(R)$, the correlation length ℓ of S_0 , and λ_{TH} . In the idealization $a \ll \ell \ll \lambda_{TH}$, (3.6) reduces to

$$\langle \rho(R) \rangle = n - \int \beta v(R') d^3 R' S_0(R) * \gamma(R), \quad (3.7)$$

and hence to

$$\begin{aligned} \langle \rho(R) \rangle &= n - \int \beta v(R') d^3 R' \int S_0(R') R' dR' \gamma(R) \\ &\text{for large } R \end{aligned} \quad (3.8)$$

whereas

$$\langle \rho(0) \rangle = n - (8\pi/\lambda_{TH}^2) \int \beta v(R') d^3 R' \int S_0(R') R' dR'. \quad (3.9)$$

Eq. (3.6) is directly useful if the interaction potential v is sufficiently weak, which is certainly not the case for the hard core potential that is the most frequent representation of a Ps -atom interaction. This is where the mean spherical model, in its generalized form,⁹ is particularly useful. Consider the approximate relation (3.1). It is equivalent to the statement that the expectation of any functional of ρ is given by

$$\begin{aligned} \langle G[\rho] \rangle &= \int G[\rho] \exp[-\frac{1}{2} \iint C_0(x, y) (\rho(x) - n_0(x)) (\rho(y) - n_0(y)) dx dy] D\rho \\ &(\text{Det } C_0/2\pi)^{1/2}, \end{aligned} \quad (3.10)$$

where $C_0 = S_0^{-1}$, the complete direct correlation function. If $u = \infty$ in some region Λ_1 , this clearly cannot be applied to $G[\rho] = \exp -\beta \int \rho(x) u(x) d^3 x$ within giving ∞ as the answer, because the

Gaussian model does not restrict $\rho(x)$ to be nonnegative. But the vanishing of $\rho(x)$ for $x \in \Lambda_1$ can be inserted directly into (3.10). If subscripts 1 and 2 indicate projections onto subspaces Λ_1 and $\Lambda_2 = \bar{\Lambda}_1$ respectively, and we use abbreviated vector-matrix notation, (3.10) then tells us that

$$\begin{aligned} \Xi/\Xi_0 &= \int \exp -\frac{1}{2} [(\rho_2 - n_{0,2}) \cdot C_{0,22}(\rho_2 - n_{0,2}) - 2(\rho_2 - n_{0,2}) \cdot C_{0,21}n_{0,1} \\ &\quad + n_{0,1} \cdot C_{0,11}n_{0,1}] D\rho_2 (\text{Det } C_0/2\pi)^{1/2} \\ &= \int \exp -\frac{1}{2} (\rho_2 - n_{0,2} - C_{0,22}^{-1}C_{0,21}n_{0,1}) \cdot C_{0,22}(\rho_2 - n_{0,2} - C_{0,22}^{-1}C_{0,21}n_{0,1}) D\rho_2 \\ &\quad \exp \frac{1}{2} (n_{0,1} \cdot C_{0,12}C_{0,22}^{-1}C_{0,21}n_{0,1}) (\text{Det } C_0/2\pi)^{1/2} , \end{aligned} \quad (3.11)$$

and consequently that

$$n(x) = n_2(x) = n_{0,2}(x) + C_{0,22}^{-1}C_{0,21}n_{0,1}(x) , \quad (3.12)$$

which now replaces (3.2). From $C_0 S_0 = I$, we have $C_{0,21}S_{0,11} + C_{0,22}S_{0,21} = 0$, so that (3.12) has the alternative form

$$n(x) = n_{0,2}(x) - S_{0,21}S_{0,11}^{-1}n_{0,1}(x) . \quad (3.13)$$

Application of (3.13) to the hard core light particle-atom interaction $v(R) = \infty$ for $R \leq a$ is immediate. We have seen, (3.4,3.5), that

$$\begin{aligned} S_{00}(R, R') &= (S_0 * \gamma)(R - R') \\ \gamma(R) &\sim (2/\lambda_{TH}^*) e^{-\sqrt{8\pi}R/\lambda_{TH}} / R \end{aligned} \quad (3.14)$$

and that $n_{00}(R) = n$. It follows that

$$\begin{aligned} S_{00,11}(R, R') &= (S_0 * \gamma)(R - R')\theta(a - R)\theta(a - R') \\ n_{00,1}(R) &= n\theta(a - R) , \end{aligned} \quad (3.15)$$

where θ is the Heaviside step function. The combination $S_{0,11}^{-1}n_{0,1} \equiv \beta\nu\theta$ thus replaces $\beta\nu$ in (3.6), and Eq. (3.13) then reads

$$\begin{aligned} \langle \rho(R) \rangle &= n - S_0(R) * \gamma(R) * (\beta\nu(R)\theta(a - R)) \quad \text{for } R \geq a \\ \text{where } S_0(R) * \gamma(R) * (\beta\nu(R)\theta(a - R)) &= n \quad \text{for } R \leq a . \end{aligned} \quad (3.16)$$

Hence, only a subsidiary problem on the space $R \leq a$ has to be solved, for which and subsequent to which, the discussion of (3.6) remains relevant.

4. Density Functional Model

Whereas the (generalized) mean spherical approximation deals effectively with hard cores, or with weak interactions, it does not interpolate between them in a unique way. This defect can be removed by a density functional approach¹⁰ (although it will reappear in the elementary treatment presented here), in which one utilizes the same input data. The density functional format is normally one in which one makes use of uniform system microscopic information to fit functional parameters to a model of the nonuniform system free energy, entropy, ..., depending upon which quantities are to serve as independent variables. In the present case, interest is precisely in the distribution $n(R) \equiv \langle \rho(R) \rangle = \int n_{pa}(x + R, x) d^3x$ of relative quantum particle-fluid particle separation, which both enters directly into the annihilation rate and is the most

compact description of the relevant physics. If the associated interaction is again given by $v(R)$, and we define the local chemical potential

$$\mu(R) = \mu - v(R), \quad (4.1)$$

then

$$n(R) = -\delta\Omega / \delta\mu(R). \quad (4.2)$$

Under the Legendre transformation

$$A[n] = \Omega + \int n(R) \mu(R) d^3 R, \quad (4.3)$$

we then have

$$\mu(R) = \delta A[n] / \delta n(R). \quad (4.4)$$

The simplest way of developing our expression for $A[n]$ is to look instead at $\mu(R)$: start with a solved reference system, then “turn on” the change in $n(R)$ to find the required change in $\mu(R)$:

$$\begin{aligned} \mu(R) - \mu_0(R) &= \int \delta\mu(R)/\delta n(R')|_0 (n(R') - n_0(R')) d^3 R' \\ &+ \frac{1}{2} \int \int \delta^2 \mu(R)/\delta n(R') \delta n(R'')|_0 (n(R') - n_0(R')) \\ &\quad (n(R'') - n_0(R'')) d^3 R' d^3 R'' \dots \end{aligned} \quad (4.5)$$

Now imagining R as fixed, suppose the reference system is uniform at the local density $n_0(R') = n(R)$, and with chemical potential given by the bulk equation of state as $\mu_b(n(R))$. Hence (4.5) becomes

$$\begin{aligned} \mu(R) &= \mu_b(n(R)) + \int \delta\mu(R)/\delta n(R')|_{n(R)} (n(R') - n(R)) d^3 R' \\ &+ \frac{1}{2} \int \int \delta^2 \mu(R)/\delta n(R') \delta n(R'')|_{n(R)} (n(R') - n(R)) (n(R'') - n(R)) d^3 R' d^3 R'' \dots \end{aligned} \quad (4.6)$$

Eq. (4.6) has two drawbacks. First, it is not — at any level of truncation — integrable, i.e. it does not satisfy the condition $\delta\mu(R)/\delta n(R') = \delta\mu(r')/\delta n(R)$, equivalent to being derivable from a thermodynamic potential, as in (4.4). Second, only the first order linear response $\delta\mu(R)/\delta n(R')|_n$ is available experimentally, or theoretically, in any reliable fashion. Because of this, $\Lambda[n]$ can be modeled by any expression that gives (4.6) through first order.

We choose here an unambiguous approach, restricted however to slowly varying $n(R)$. In this case, a gradient expansion $n(R') - n(R) = (R' - R) \cdot \nabla n(R) + \frac{1}{2}(R' - R)(R' - R) : \nabla \nabla n(R) + \dots$ is valid. Incorporating the classical fluctuation-dissipation result that

$$\delta\beta\mu(R)/\delta n(R') = C(R, R') \quad (4.7)$$

is precisely the inverse density-density correlation of (3.4) (direct verification is not hard), Eq. (4.6) becomes, through second order in gradients,

$$\begin{aligned} \beta\mu(R) &= \beta\mu_b(n(R)) + \int C_0(RR', n(R))(R' - R) d^3 R' \cdot \nabla n(R) \\ &+ \frac{1}{2} \int \int [C_0(R, R'; n(R))(R' - R)(R' - R) : \nabla \nabla n(R) \\ &+ \delta C_0(R, R')/\delta n(R'')|_{n(R)}(R' - R) \cdot \nabla n(R)(R'' - R) \cdot \nabla n(R)] d^3 R' d^3 R'' \dots \end{aligned} \quad (4.8)$$

Now $C_0(R, R'; n(R))$ will be an even function of $R' - R$, so that the integral multiplying $\nabla n(R)$ vanishes. Also we can use the identity

$$(R' - R)(R'' - R) + (R'' - R)(R' - R) = (R' - R)(R' - R) + (R'' - R)(R'' - R) - (R'' - R')(R'' - R') , \quad (4.9)$$

together with the symmetry at uniform $n = n(R)$ of $\delta C_0(R, R')/\delta n(R'')$ with respect to $R' - R$, $R - R''$, $R'' - R'$, and isotropy, to reduce the second integral, yielding

$$\begin{aligned} \beta\mu(R) = & \beta\mu_b(n(R)) + \frac{1}{6} \int C_0(R, R'; n(R)) |R' - R|^2 d^3 R' \nabla^2 n(R) \\ & + \frac{1}{12} \int \int \delta C_0(R, R')/\delta n(R'')|_{n(R)} |R' - R|^2 d^3 R' d^3 R'' |\nabla n(R)|^2 . \end{aligned} \quad (4.10)$$

Since $\int \delta/\delta n(R'') d^3 R'' = \partial/\partial n$ for a uniform fluid, (4.10) attains the very simple form

$$\begin{aligned} \beta\mu(R) = & \beta\mu_b(n(R)) - \frac{1}{2} K(n(R)) \nabla^2 n(R) - \frac{1}{4} K'(n(R)) |\nabla n(R)|^2 \\ \text{where } K(n) = & -\frac{1}{3} \int C_0(R, R'; n) |R' - R|^2 d^3 R' . \end{aligned} \quad (4.11)$$

Eq. (4.11) in fact is now integrable, and integrates back to

$$\beta A[n] = \int \left(n(R) \beta f(n(R)) + \frac{1}{4} K(n(R)) |\nabla n(R)|^2 \right) d^3 R \quad (4.12)$$

where f is the free energy per particle of the fluid. In our application, we write

$$K(n) = \frac{1}{3} \nabla_k^2 \tilde{C}_{00}(k; n)|_{k=0} \quad (4.13)$$

where the uniform reference is the double reference of Sec. 3,

$$\tilde{C}_{00}(k; n) = \tilde{C}_0(k; n) / \tilde{\gamma}(k) \quad (4.14)$$

according to (3.4), (3.5), so that, observing that $\tilde{C}_0(0; n) = (1/n) \partial \beta P_0 / \partial n$,

$$K(n) = K_0(n) + \frac{1}{36\pi} \frac{\lambda_{TH}^2}{n} \partial \beta P_0 / \partial n , \quad (4.15)$$

where $P_0(n)$ is the fluid equation of state. Without going into detail, it is clear from (4.15) that a small mass particle will give rise to a large effective mass K and hence typically a smaller extension in space. Indeed, (4.12) has the same general form as mean field, (2.7), without requiring the battery of simplifying assumptions.

5. Concluding Remarks

We have seen that the theoretical tools developed during the past few decades for analyzing the equilibrium properties of classical fluids have quite direct extensions to the problem of a quantum particle interacting with the same system. In fact, a surprisingly small amount of additional machinery needs to be incorporated when attention is restricted to the relative quantum particle-fluid atom density. This is an obvious advantage as well as a suggestion for caution: the tried and true approximations developed laboriously for classical fluids are not automatically suitable in the extended framework. It is clear that a comparison with detailed "ab initio" numerical computations, such as those of Fan and Miller (ref. 5) is called for before one proceeds

to more sophisticated integral equation and density functional techniques. But it is also clear that experimental information available in the quantum particle-classical fluid context, such as that of fluctuations in annihilation rates, can feed back to classical fluid studies as well. Moreover, one can anticipate the development of relatively simple but accurate empirical descriptions going hand in hand with the burgeoning collection of experimental data, and as a welcome byproduct, a viewpoint that may be invaluable when interaction of quantum particles must be taken into account, or is perhaps the whole story!

References

1. Iakubov, I. T. and Khrapak, A. G., *Prog. Phys.* 45 (1982) 697.
2. Au, C. K. and Drachman, R. J., *Phys. Rev. Lett.* 56 (1986) 324.
3. Dirac, P. A. M., "Quantum Mechanics", 3rd ed., Oxford Press (1947) 127.
4. Feynman, R. P. and Hibbs, A. R., "Quantum Mechanics and Path Integrals", McGraw-Hill (1965).
5. Kunkin, W. and Percus, J. K., *J. Math. Phys.* 11 (1970) 1029.
Chandler, O., Singh, Y., and Richardson, D. M., *J. Chem. Phys.* 81 (1984) 1975.
Fan, Y. and Miller, B. N., *J. Chem. Phys.* 93 (1990) 4322.
6. Percus, J. K., in "Positron Annihilation Studies of Fluids", ed. S. Sharma, World Scientific (1988)
Miller, B. N. and Reese, T., *Phys. Rev. A* 39 (1989) 4735.
7. Yau, X-Z. and Tsai, S-T., *Phys. Rev. A* 46 (1992) 4704.
8. Berlin, T. and Kac, M., *Phys. Rev.* 86 (1952) 821
Lebowitz, J. L. and Percus, J. K., *Phys. Rev.* 144 (1966) 251.
9. Percus, J. K. and Yevick, C. J., *Phys. Rev.* 136 B (1964) 290
Li, H. and Kardar, M., *Phys. Rev. Lett.* 67 (1991) 3275
Chandler, D., preprint.
10. Evans, D., in "Inhomogeneous Fluids", ed. D. Henderson, Dekker (1991) Chap. 5.
11. Lebowitz, J. L. and Percus, J. K., *J. Math. Phys.* 4 (1963) 248.
12. Davis, H. T., *J. Chem. Phys.* 67 (1977) 3636
Percus, J. K., *Proc. N. Y. Acad. Sci.* 491 (1987) 36.