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Semiclassical Statistical Mechanics of Fluids:
Nonperturbative Incorporation of Quantum Effects in Classical Many Body Models

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Abstract

Some of the basic equations of the equilibrium statistical mechanics of fluids involving the radial distribution function are derived in a nonperturbative semiclassical form by employing the phase space sampling approach in conjunction with a semiclassical pairwise interaction approximation. Analysis of the approximation suggests two practical models for effective potentials which automatically introduce the desired quantum effects into the classical equations.

I. Introduction

Although the behavior of matter is fundamentally quantum mechanical, for the most part the chemical literature deals only with the classical aspects of the equilibrium statistical mechanics of gases and liquids. Of course this is not without a certain logic since in many cases of chemical interest the quantum effects are probably so small as to be negligible. Unfortunately even when they are not, it is often completely impractical to use the ponderous machinery of a fully quantum mechanical treatment.

For example, several authors have employed a Monte Carlo evaluation of a Feynman path integral¹ in order to study two and three body quantum statistical mechanics.^{2,3} However, it is by no means clear as to how one would go about extending this to N body problems. Similarly, Chihara⁴ has succeeded in formulating quantum mechanical versions of the Percus-Yevick and hypernetted chain integral equations but at a cost of rendering the calculations extremely difficult.

The attempts to avoid such difficulties by appealing to the comparative smallness of quantum effects have resulted, almost exclusively, in perturbative expressions based on the Wigner-Kirkwood expansion.⁵ In particular, Singh, Ram, and Sinha⁶ as well as Gibson⁷ have obtained radial distribution functions as simultaneous expansions in both density and quantum effects. Yet it has been pointed out⁸ that the Wigner-Kirkwood expansion breaks down in the very chemical cases in which quantum effects are most prominent. Probably even more serious is the fact that this perturbative approach to quantum effects necessitates a perturbative approach to the classical many body effects (i.e., a density expansion). One certainly cannot hope to treat systems

at liquid densities by such a method (not to mention critical phenomena). Nonetheless it is precisely phenomena such as critical points--in which classical forces are delicately balanced by minute calculations--in which it would be expected that "chemical" quantum effects would come to the fore.

Accordingly, this paper proposes a nonperturbative approach to the equilibrium semiclassical statistical mechanics of fluids. This approach is based on the so-called "phase space sampling" formalism⁹ which effectively allots a weight to each point in phase space $(\underline{p}_0, \underline{q}_0)$ based on the action of an imaginary time trajectory starting at the phase space point and continuing on (through the surrounding phase space) for a time $\hbar\beta/2$. As pointed out in the original paper,⁹ having such a phase space weight allows one to write semiclassical statistical mechanics in a completely classical form while at the same time including contributions to infinite order in $\hbar$. Thus the semiclassical partition function would be

$$Q_N^{SC} = h^{-3N} \int \dots \int e^{-\beta \bar{H}} d^3 p_0^1 \dots d^3 p_0^N d^3 r_0^1 \dots d^3 r_0^N \quad (1.1)$$

with the action $\bar{H}(\underline{p}_0^1, \dots, \underline{r}_0^N)$ given by

$$\bar{H} = \frac{2}{\hbar\beta} \int_0^{\hbar\beta/2} H(\tau) d\tau \quad (1.2)$$

and with $H(\tau)$ equal to the classical Hamiltonian $H(p, q)$ as a function of imaginary time (τ) .

$$H(\tau) = H[p^i(\tau), q^i(\tau)] \quad i = 1, \dots, 3N$$

The time dependence $p^i(\tau)$, $q^i(\tau)$ constitutes an imaginary time trajectory satisfying the (almost) classical equations of motion

$$\frac{\partial H}{\partial q_i} = \dot{p}^i, \quad \frac{\partial H}{\partial p_i} = -\dot{q}^i \quad i = 1, \dots, 3N \quad (1.3)$$

with the initial condition that the trajectory start at the original phase point $(p_0^1, \dots, r_0^N)$.

By way of contrast note that the classical partition function is merely equation (1.1) with $\bar{H}$ replaced by H . What this similarity in form immediately suggests is that one will be able to formulate classical many body models which include contributions to all orders in density, such as the Kirkwood, Born-Green-Yvon, Percus-Yevick, and hypernetted chain integral equations,¹⁰ in terms of this semiclassical partition function and its associated particle distribution functions. In so doing one would obtain not only a practical calculational tool, but also a formalism in which the different roles of the classical many body effects and the purely quantum effects could be distinguished. Unlike the purely quantal treatments (which bear no obvious relation to classical models) and the perturbative treatments (which are forced to adopt the very limited classical model of a density expansion) this approach allows quantum corrections to be made within the framework of any given classical model. It is this development upon which the remainder of the article will concentrate.

II. Basic Formalism

As alluded to in the Introduction, this paper will try to take advantage of the similarity in form of the classical and semiclassical approaches--namely that of a phase space integral over a function (or functional) of the classical Hamiltonian. Nonetheless, on closer inspection it is apparent that there is a significant difference between the two formalisms. The classical form can always be written in such a way as to make the phase space weighting separable in momentum and coordinates. In Cartesian coordinates (with N particles)

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + V(r_1, \dots, r_N)$$

$$e^{-\beta H} = \exp\left(-\beta \sum_{i=1}^{3N} \frac{p_i^2}{2m}\right) \exp(-\beta V)$$

this separability combined with the Gaussian behavior of the momentum distribution always permits the momentum integrations to be performed analytically

$$Q_N^{CL} = \left(\frac{2\pi m}{h^2 \beta}\right)^{3N/2} \int \dots \int e^{-\beta V} d^3 r^1 \dots d^3 r^N \quad . \quad (2.1)$$

Consequently almost all of classical statistical mechanics is written solely in terms of coordinate distributions and coordinate integrations.

Semiclassical statistical mechanics, on the other hand, is in general not separable in coordinates and momenta⁹ and certainly does not permit analytic momentum integrations. However, this can be dealt

with formally as follows: Define a semiclassical effective potential $\bar{V}$ as a momentum integral

$$e^{-\beta\bar{V}} = \left(\frac{\beta}{2\pi m}\right)^{3N/2} \int \dots \int e^{-\beta\bar{H}} d^3 p_0^1 \dots d^3 p_0^N \quad (2.2)$$

so that in the classical limit $\bar{V}$ becomes V , the classical potential.

While this implies that our new potential will be both temperature and density dependent (in general) there is still no reason why one cannot proceed to define semiclassical quantities in terms of this $\bar{V}(\underline{r}_0^1, \dots, \underline{r}_0^N)$ in the same way that classical quantities are defined with $V(\underline{r}_0^1, \dots, \underline{r}_0^N)$. Thus, analogous to the notation of McQuarrie,¹¹ we define the semiclassical "configuration" integral,

$$\begin{aligned} Z_N^{SC} &= \left(\frac{h^2\beta}{2\pi m}\right)^{3N/2} Q_N^{SC} \\ &= \int \dots \int e^{-\beta\bar{V}} d^3 r_0^1 \dots d^3 r_0^N \end{aligned} \quad (2.3)$$

the semiclassical n particle distribution function,

$$\rho_N^{(n)SC}(\underline{r}_0^1, \dots, \underline{r}_0^n) = \frac{N!}{(N-n)!} \frac{1}{Z_N^{SC}} \int \dots \int e^{-\beta\bar{V}} d^3 r_0^{n+1} \dots d^3 r_0^N \quad (2.4)$$

and the semiclassical n particle correlation function

$$g_N^{(n)SC}(\underline{r}_0^1, \dots, \underline{r}_0^n) = \frac{\rho_N^{(n)SC}}{Z_N^{SC}} \int \dots \int e^{-\beta\bar{V}} d^3 r_0^{n+1} \dots d^3 r_0^N \quad (2.5)$$

In the thermodynamic limit (just as in the classical case) we also may write

$$\rho^{(n)SC} = g^{(n)SC} \rho^n \quad (2.6)$$

where $\rho = N/V$, the density and V is the volume.

At this point it is evident that one cannot proceed further without some reasonable expression for $\bar{V}$. Although this development is exact in principle it is simply not practical to perform the Avagadro's number of momenta integrations required by Eq. (2.2). Parenthetically though, it might be pointed out that Eqs. (2.2) and (2.3) are quite tractable for small N . Since it is possible to write virial coefficients in terms of configuration integrals, Z_N , (independently of the choice of classical or quantum statistics),¹¹

$$\begin{aligned} \frac{p\beta}{\rho} &= 1 + B_2\rho + B_3\rho^2 + \dots \\ B_2 &= -\frac{1}{2V} (Z_2 - Z_1^2) \\ B_3 &= -\frac{1}{3V^2} [V(Z_3 - 3Z_2Z_1 + 2Z_1^3) - \\ &\quad 3(Z_2 - Z_1^2)^2] \end{aligned} \quad (2.7)$$

Eqs. (2.7), (2.3), and (2.2) therefore do constitute a practical approach for calculating semiclassical virial coefficients.¹²

Of course this is not sufficient for our purposes so let us, again, follow the lead of classical statistical mechanics. Just as in classical studies it is found to be reasonably accurate to assume that the potential energy can be written as the sum of pairwise contributions

$$V(\tilde{r}^1, \dots, \tilde{r}^N) = \sum_{i,j>i}^N V_{ij} \quad \text{where} \quad V_{ij} = V(\tilde{r}^i, \tilde{r}^j) \quad (2.8)$$

we will assume that the following semiclassical pairwise interaction approximation can also be made:

$$\bar{V}(\underline{r}_0^1, \dots, \underline{r}_0^N) = \sum_{i,j>i}^N \bar{V}_{ij} \quad \text{where} \quad \bar{V}_{ij} = \bar{V}(\underline{r}_0^i, \underline{r}_0^j) \quad (2.9)$$

This approximation is undoubtedly the crucial step of this work and as such it will be discussed in great detail in Section V, but it is nevertheless instructive to make a few preliminary observations.

First of all it should be noted that if Eq. (2.8) is assumed, Eq. (2.9) is only an approximation to the extent that the system is quantum mechanical. In the classical limit Eq. (2.9) becomes precisely Eq. (2.8) so it clearly includes all classical many body effects. Secondly Eq. (2.9) is intrinsically a quantal many body approximation since, even in the full semiclassical formalism, it is trivially exact for two particles

$$\bar{V}(\underline{r}_0^1, \underline{r}_0^2) = \bar{V}_{12}$$

For the purpose of fixing ideas it is helpful to keep in mind this picture of each $\bar{V}_{ij}$ as being given by the exact two particle semiclassical effective potential. Still, since the choice of $\bar{V}_{ij}$ is not unique this is by no means necessary and a better approximation will be discussed later.

Finally, before going on to make use of our ansatz, it is important to realize that by adopting Eq. (2.9) we are encapsulating all the quantum effects in a two body effective potential. Hence for any given classical many body model we can obtain the desired insight into the relationship

between purely classical many body effects and purely quantum effects just by observing the effect of switching our potential from the true V_{ij} to the effective $\bar{V}_{ij}$.

III. Semiclassical Integral Equations for the Radial Distribution Function

In this section the semiclassical pairwise interaction approximation will be used to derive semiclassical analogues for three common classical integral equations governing the pair correlation function $g^{(2)}$ (i.e., three classical many body models). By design these derivations can be accomplished by exactly the same methods as those used to derive the original classical equations and with almost exactly the same results-- the only difference being in the substitution of $\bar{V}_{ij}$ for V_{ij} . Nevertheless, it is useful to briefly describe the derivations in order to understand exactly where the semiclassical approximations come in.

A. Application of Superposition: The SC-BGY Equation

Starting from the semiclassical pair correlation function

$$g_N^{(2)SC}(r_0^1, r_0^2) = \frac{v^2}{Z_N^{SC}} \int \dots \int e^{-\beta \bar{V}} d^3 r_0^3 \dots d^3 r_0^N \quad (3.1)$$

and differentiating both sides with respect to r_0^1 leaves

$$\vec{\nabla}_1 g_N^{(2)SC}(r_0^1, r_0^2) = \frac{v^2}{Z_N^{SC}} \int \dots \int (-\beta \vec{\nabla}_1 \bar{V}) e^{-\beta \bar{V}} d^3 r_0^3 \dots d^3 r_0^N$$

If we now introduce Eq. (2.9) we may write

$$\vec{\nabla}_1 \bar{V} = \vec{\nabla}_1 \left(\sum_{j \neq 1} \bar{V}_{1j} + \sum_{\substack{i, j > 1 \\ i, j \neq 1}} \bar{V}_{ij} \right) = \vec{\nabla}_1 \bar{V}_{12} + \sum_{j \neq 1, 2} \vec{\nabla}_1 \bar{V}_{1j}$$

Substituting back and taking advantage of the fact that particle 3 can be relabeled in $(N-2)$ ways inside the integral

$$\vec{\nabla}_1 g_N^{(2)SC}(\underline{r}_0^1, \underline{r}_0^2) = -\beta(\vec{\nabla}_1 \bar{v}_{12}) g_N^{(2)SC}(\underline{r}_0^1, \underline{r}_0^2) \\ -\beta(N-2) \frac{U^2}{Z_N^{SC}} \int \dots \int (\vec{\nabla}_1 \bar{v}_{13}) e^{-\beta \bar{V}} d^3 r_0^3 \dots d^3 r_0^N .$$

This can be simplified if we bring in the semiclassical three particle correlation function

$$g_N^{(3)SC}(\underline{r}_0^1, \underline{r}_0^2, \underline{r}_0^3) = \frac{U^3}{Z_N^{SC}} \int \dots \int e^{-\beta \bar{V}} d^3 r_0^4 \dots d^3 r_0^N .$$

Hence, in terms of $g^{(3)SC}$ we find, after taking the thermodynamic limit

$$\vec{\nabla}_1 g^{(2)SC}(\underline{r}_0^1, \underline{r}_0^2) = -\beta(\vec{\nabla}_1 v_{12}) g^{(2)SC}(\underline{r}_0^1, \underline{r}_0^2) \\ -\beta \rho \int (\vec{\nabla}_1 \bar{v}_{13}) g^{(3)}(\underline{r}_0^1, \underline{r}_0^2, \underline{r}_0^3) d^3 r_0^3 . \quad (3.2)$$

Eq. (3.2) might be called the semiclassical Born-Green equation. Just like its classical namesake^{10,11,13} it is exact (subject to a pairwise division of the potential) but not immediately useful since it relates an unknown pair correlation function to an unknown triplet correlation function.

However if we now make a semiclassical superposition approximation

$$g^{(3)SC}(\underline{r}_0^1, \underline{r}_0^2, \underline{r}_0^3) = g^{(2)SC}(\underline{r}_0^1, \underline{r}_0^2) g^{(2)SC}(\underline{r}_0^2, \underline{r}_0^3) g^{(2)SC}(\underline{r}_0^3, \underline{r}_0^1) . \quad (3.3)$$

Eq. (3.2) becomes, on rearrangement,

$$\vec{\nabla}_1 \ln g^{(2)SC}(\underline{r}_0^1, \underline{r}_0^2) = -\beta \vec{\nabla}_1 \bar{V}_{12}$$

$$-\beta \rho \int (\vec{\nabla}_1 \bar{V}_{13}) g^{(2)SC}(\underline{r}_0^2, \underline{r}_0^3) g^{(2)SC}(\underline{r}_0^3, \underline{r}_0^1) d^3 r_0^3$$

which is the semiclassical Born-Green-Yvon equation, a practical result.

Before concluding, note that Eq. (3.3) is completely independent of Eq. (2.9) in much the same way that the classical superposition approximation¹³ is independent of Eq. (2.8). Indeed one would expect the semiclassical superposition approximation to be justified under more or less the same conditions as its classical equivalent--except that, interestingly enough, Eq. (3.3) ignores some quantum effects as well as ignoring some classical many body effects.

B. Application of Functional Taylor Series: The SC-PY and SC-HNC Equations.

Analogously to the classical approach¹⁰ consider the effect on our N body system of adding an external potential, $\bar{\psi}$. In particular, fix a particle, 0, and let it interact with each particle, i, via an effective potential $\bar{\psi}_i = \bar{V}_{0i}$ where the $\bar{V}_{0i}$ are such that Eq. (2.9) for the total effective potential becomes

$$\bar{V} + \bar{\psi} = \sum_{i,j>i} \bar{V}_{ij} + \sum_i \bar{V}_{0i}$$

i.e.,

$$\bar{\psi} = \sum_i \bar{\psi}_i \quad (3.4)$$

Because of the nonseparability inherent in Eq. (2.2) it is clear that this is not the same as classically adding a true potential to each

particle. Each $\bar{\psi}_i$ must include the effect of the classical ψ_i on the semiclassical $\bar{v}_{ij}$.

In any case, using Eq. (2.3) we can now define the configuration integral as a functional of $\bar{\psi}$,

$$Z_N^{SC}[\bar{\psi}] = \int \dots \int e^{-\beta(\bar{v} + \bar{\psi})} d^3 r_0^1 \dots d^3 r_0^N$$

$$Z_N^{SC}[\bar{\psi}=0] \equiv Z_N^{SC}$$

as well as the distribution functions as functionals of $\bar{\psi}$ [Eq. (2.4)]

$$\rho_N^{(1)SC}(1, \bar{\psi}) = \frac{N}{Z_N^{SC}} \int \dots \int e^{-\beta(\bar{v} + \bar{\psi})} d^3 r_0^2 \dots d^3 r_0^N$$

$$\rho_N^{(1)SC}(1, \bar{\psi}=0) \equiv \rho_N^{(1)SC}(1) \equiv \rho$$

$$\rho_N^{(2)SC}(1, 2, \bar{\psi}) = \frac{N(N-1)}{Z_N^{SC}} \int \dots \int e^{-\beta(\bar{v} + \bar{\psi})} d^3 r_0^3 \dots d^3 r_0^N$$

$$\rho_N^{(2)SC}(1, 2, \bar{\psi}=0) \equiv \rho_N^{(2)SC}(1, 2)$$

with the notation $f(1, 2, \dots, n)$ referring to $f(r_0^1, r_0^2, \dots, r_0^n)$ and with $f(1, 2, \dots, n, \bar{\psi})$ denoting the same function taken as a functional of $\bar{\psi}$. Similarly we can write the correlation functions, Eq. (2.5) as

$$g_N^{(1)SC}(1, \bar{\psi}) = \frac{\rho_N^{(1)SC}(1, \bar{\psi})}{\rho_N^{(1)SC}(1, \bar{\psi})} = 1$$

corresponding to

$$g_N^{(1)SC}(1) = \frac{\rho_N^{(1)SC}(1)}{\rho} = 1$$

and

$$\varepsilon_N^{(2)SC}(1,2,\bar{\psi}) = \frac{\rho_N^{(2)SC}(1,2,\bar{\psi})}{\rho_N^{(1)SC}(1,\bar{\psi}) \rho_N^{(1)SC}(2,\bar{\psi})}$$

corresponding to

$$\varepsilon_N^{(2)SC} = \frac{\rho_N^{(2)SC}(1,2)}{\rho_N^{(1)SC}(1) \rho_N^{(1)SC}(2)} = \frac{1}{2} \int \rho_N^{(2)SC}(1,2)$$

Finally, by artificially introducing an integral over the 0 particle it also can be shown¹⁰ that

$$\rho_N^{(1)SC}(1,\bar{\psi}) = \frac{\rho_N^{(2)SC}(1,0)}{\rho_N^{(1)SC}(0)}$$

$$\rho_N^{(2)SC}(1,2,\bar{\psi}) = \frac{\rho_N^{(3)SC}(1,2,0)}{\rho_N^{(1)SC}(0)}$$

These formal developments lead to the two basic functional relations which are needed to derive the desired integral equations. If we look at the variation of $\ln Z_N^{SC}$ with $\bar{\psi}$

$$\delta \ln Z_N^{SC}[\bar{\psi}] = (Z_N^{SC})^{-1} \int \dots \int (-\beta \delta \bar{\psi}) e^{-\beta(\bar{V}+\bar{\psi})} d^3 r_0^1 \dots d^3 r_0^N$$

and use (3.4), the resulting equations simplifies (upon relabeling particle 1 the N possible ways), to

$$\delta \ln Z_N^{SC}[\bar{\psi}] = -\beta \int \delta \bar{\psi}_1 \rho_N^{(1)SC}(1,\bar{\psi}) d^3 r_0^1$$

Hence we have the expression

$$-1/\beta \frac{\delta \ln Z_N^{SC}[\bar{\psi}]}{\delta \bar{\psi}_1} = \rho_N^{(1)SC}(1, \bar{\psi}) \quad (3.5)$$

In the same fashion Eq. (3.5) can be used to evaluate the variation of $\rho_N^{(1)SC}$

$$\begin{aligned} \delta \rho_N^{(1)SC}(1, \bar{\psi}) &= \frac{N}{Z_N^{SC}[\bar{\psi}]} \int \cdots \int (-\beta \delta \bar{\psi}) e^{-\beta(\bar{V} + \bar{\psi})} d^3 r_0^2 \dots d^3 r_0^N \\ &\quad - \rho_N^{(1)SC}(1, \bar{\psi}) \delta \ln Z_N^{SC}[\bar{\psi}] \\ &= -\beta \delta \bar{\psi}_1 \rho_N^{(1)SC}(1, \bar{\psi}) - \beta \int \delta \bar{\psi}_2 \rho_N^{(2)SC}(1, 2, \bar{\psi}) d^3 r_0^2 \\ &\quad + \beta \rho_N^{(1)SC}(1, \bar{\psi}) \int \delta \bar{\psi}_2 \rho_N^{(1)SC}(2, \bar{\psi}) d^3 r_0^2 \end{aligned}$$

leaving us with

$$\begin{aligned} -1/\beta \frac{\delta \rho_N^{(1)SC}(1, \bar{\psi})}{\delta \bar{\psi}_2} &= -\rho_N^{(1)SC}(1, \bar{\psi}) \rho_N^{(1)SC}(2, \bar{\psi}) \\ &\quad + \rho_N^{(1)SC}(1, \bar{\psi}) \delta(r_0^1 - r_0^2) + \rho_N^{(2)SC}(1, 2, \bar{\psi}) \quad (3.6) \end{aligned}$$

It is now straightforward to construct the semiclassical integral equations. Defining the semiclassical direct correlation function in the standard manner,

$$c^{SC}(1, 2, \bar{\psi}) = \frac{\delta(r_0^1 - r_0^2)}{\rho_N^{(1)SC}(1, \bar{\psi})} + \beta \frac{\delta \bar{\psi}(2)}{\delta \rho_N^{(1)SC}(1, \bar{\psi})} \quad (3.7)$$

using the definition of the inverse functional derivative,

$$\int \frac{\delta \rho_n^{(1)SC}(1, \bar{\psi})}{\delta \bar{\psi}(3)} \frac{\delta \bar{\psi}(3)}{\delta \rho_N^{(1)SC}(2, \bar{\psi})} d^3 r_0^3 = \delta(\mathbf{r}_0^1 - \mathbf{r}_0^2) \quad (3.8)$$

substituting Eqs. (3.6) and (3.7) into Eq. (3.8), and then taking the thermodynamic and $\bar{\psi} = 0$ limits, we eventually end up with a semi-classical Ornstein Zernike equation which is precisely the classical equation^{10,11,13}

$$h^{SC}(1,2) = c^{SC}(1,2) + \rho \int c^{SC}(2,3) h^{SC}(1,3) d(3) \quad (3.9)$$

(where $h \equiv (g^{(2)} - 1)$ is the total correlation function and (3) refers to $\mathbf{r}_0^3$). In fact, this identity between the semiclassical and classical versions suggests that Eq. (3.9) could even have been taken as an ad hoc postulate. Because Eq. (3.9) contains no reference to a potential, such an approach would have the obvious advantage of being independent of any pairwise interaction assumptions.

However by starting instead with Eq. (3.7), the path to the Percus Yevick and hypernetted chain equations becomes clear. In both of these classical models the fundamental assumption is that some quantity is expanded to first order in a functional Taylor series¹⁴ about $\rho_N^{(1)SC}(1, \bar{\psi})$.

$$f(1, \bar{\psi}) = f(1) + \int d(2) [\rho_N^{(1)SC}(2, \bar{\psi}) - \rho_N^{(1)SC}(2)] \cdot \left[\frac{\delta f(1, \bar{\psi})}{\delta \rho_N^{(1)SC}(2, \bar{\psi})} \right]_{\bar{\psi}=0} + \dots \quad (3.10)$$

For the PY equation this $f(1, \bar{\psi})$ is given by $\rho_N^{(1)SC}(1, \bar{\psi}) e^{\beta \bar{\psi}}$ whereas

$f(1, \bar{\psi})$ is the logarithm of the same functions for the HNC model. For both of these, $\bar{\psi}$ is taken as $\bar{V}_{01}$.

After some functional calculus manipulations and with the aid of Eqs. (3.10), (3.9), (3.7), and (3.6) as well as the functional chain rule

$$\frac{\delta f(1, \bar{\psi})}{\delta \rho_N^{(1)SC}(2, \bar{\psi})} = \int \frac{\delta f(1, \bar{\psi})}{\delta (-\beta \bar{\psi}(3))} \frac{\delta (-\beta \bar{\psi}(3))}{\delta \rho_N^{(1)SC}(2, \bar{\psi})} d(3)$$

we can write the semiclassical Percus-Yevick equation

$$g^{(2)SC}_{(1,0)} e^{\beta \bar{V}(1,0)} = g^{(2)SC}_{(1,0)} - c^{SC}_{(1,0)} \quad (3.11)$$

and the semiclassical hypernetted chain equation

$$\ln[g^{(2)SC}_{(1,0)} e^{\beta \bar{V}(1,0)}] = h^{SC}_{(1,0)} - c^{SC}_{(1,0)} \quad (3.12)$$

Again, it is obvious that the results might have been predicted in advance from the appropriate classical equations.^{10,11,13} Yet this would have left no firm theoretical foundation for these formulas. Since, as pointed out earlier, the effective potential $\bar{\psi}$ is itself a complex functional of the two potentials there is no telling whether such an ad hoc prescription--which neglects this fact--would be valid.¹⁵ Indeed, in the next section the β and ρ dependence of the effective potential will be shown to cause some qualitative changes.

IV. Semiclassical Thermodynamics

Unlike the calculations of the preceeding section, thermodynamic calculations often require derivatives with respect to temperature and volume, so in our formalism the classical and semiclassical results may be expected to differ. Consider the ensemble average energy. One immediate consideration is that, semiclassically, the energy will not be correctly given as a phase space average over the classical Hamiltonian.⁹ Instead it is necessary to use the quantum mechanically exact expression in terms of the partition function

$$\langle E \rangle = -\partial \ln Q / \partial \beta$$

From Eq. (2.3)

$$\begin{aligned} \langle E \rangle_{SC} &= \frac{3}{2} NkT - (Z_N^{SC})^{-1} \frac{\partial}{\partial \beta} Z_N^{SC} \\ &= \frac{3}{2} NkT + (Z_N^{SC})^{-1} \int \cdots \int (\bar{V} + \beta \frac{\partial \bar{V}}{\partial \beta}) e^{-\beta \bar{V}} d^3 r_0^1 \cdots d^3 r_0^N. \end{aligned}$$

Now making the semiclassical pairwise interaction approximation, Eq. (2.9) and using (3.1) we find that

$$\langle E \rangle_{SC} = \frac{3}{2} NkT + \frac{1}{2} N(N-1) \frac{1}{2} \iint [\bar{V}_{12} + \beta \frac{\partial \bar{V}_{12}}{\partial \beta}] g_N^{(2)SC}(1,2) d^3 r_0^1 d^3 r_0^2$$

which goes over in the thermodynamic limit (and with spherically symmetric potentials) to

$$\begin{aligned} \langle E \rangle_{SC} &= \frac{3}{2} NkT \\ &+ \frac{1}{2} N\rho \int [\bar{V}(r_0) + \beta \frac{\partial \bar{V}(r_0)}{\partial \beta}] g^{(2)SC}(r_0) d^3 r_0. \end{aligned} \quad (4.1)$$

Here $\bar{V}(r_0)$ is understood to mean the effective pair potential $\bar{V}_{ij}$ as a function of $r_0 = |\underline{r}_0^i - \underline{r}_0^j|$. With the exception of the replacement of this $\bar{V}_{ij}$ by V_{ij} , Eq. (4.1) differs from the usual classical equation^{10,11,13} only in the presence of a temperature derivative of $\bar{V}_{ij}$.

Proceeding similarly we can also look at the semiclassical equation of state. The classical compressibility equation of state^{10,11}

$$kT\left(\frac{\partial \rho}{\partial P}\right)_T = 1 + \rho \int [g^{(2)}(r) - 1] d^3r \quad (4.2)$$

has no explicit dependence on the potential so one might expect it to be equally correct for both classical and semiclassical correlation functions, $g^{(2)}(r)$. Indeed this is found to be the case. By applying a statistics independent, grand canonical technique it can be shown that¹¹

$$\left\langle \frac{N!}{(N-n)!} \right\rangle = \rho^n \int \dots \int g^{(n)}(1, \dots, n) d^3r^1 \dots d^3r^n$$

where N is now considered variable. However for $n = 2$ this equation provides a simple connection with the isothermal compressibility

$$\kappa_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P}\right)_T = \frac{\langle (N - \langle N \rangle)^2 \rangle}{\langle N \rangle} \frac{\beta}{\rho}$$

Thus, even as it is normally written, Eq. (4.2) can be seen to be of quite general validity. Moreover it is also evident that Eq. (4.2) is independent of any pairwise assumptions.

On the other hand, the pressure equation of state^{10,11,13} involves a volume derivative and consequently will change in the process of becoming semiclassical. Starting from the thermodynamic relation

$$P = \frac{1}{\beta} \left(\frac{\partial \ln Q_N}{\partial v} \right)_T = \frac{1}{\beta} \left(\frac{\partial \ln Z_N}{\partial v} \right)_T$$

we can employ a standard scaling approach¹³ to evaluate the derivative.

Define a dimensionless new variable $R_0^i = r_0^i v^{-1/3}$. Since

$$d^3 r_0^1 \dots d^3 r_0^N = v^N d^3 R_0^1 \dots d^3 R_0^N$$

we can therefore write

$$\begin{aligned} Z_N^{SC} &= \int_0^v \dots \int_0^v e^{-\beta \bar{V}} d^3 r_0^1 \dots d^3 r_0^N \\ &= v^N \int_0^1 \dots \int_0^1 e^{-\beta \bar{V}} d^3 R_0^1 \dots d^3 R_0^N \end{aligned}$$

Once the volume dependence is gone from the limits of integration we can actually perform the volume differentiation. After transforming back to the old variables we obtain the formally exact equation

$$P = \frac{NkT}{v} - \frac{1}{Z_N^{SC}} \int \dots \int \frac{\partial \bar{V}}{\partial v} e^{-\beta \bar{V}} d^3 r_0^1 \dots d^3 r_0^N \quad (4.3)$$

If we again apply Eq. (2.9) while keeping in mind the possible density dependence of $\bar{V}$

$$\frac{\partial \bar{V}}{\partial v} = \sum_{i,j>i} \frac{\partial \bar{V}_{ij}}{\partial v} = \sum_{i,j>i} \left(\frac{\partial \bar{V}_{ij}}{\partial r_0^{ij}} \frac{dr_0^{ij}}{dv} + \frac{\partial \bar{V}_{ij}}{\partial \rho} \frac{d\rho}{dv} \right)$$

and if we then use the following equalities

$$\frac{dr_{0ij}}{d\bar{v}} = \frac{d}{d\bar{v}} (R_{0ij}^{1/3}) = \frac{R_{0ij}^{1/3}}{3\bar{v}^{2/3}} = \frac{r_{0ij}}{3\bar{v}}$$

$$\frac{d\rho}{d\bar{v}} = \frac{d}{d\bar{v}} (N/\bar{v}) = -\rho/\bar{v} \quad ,$$

Eq. (4.3) becomes [with Eq. (3.1)]

$$P = \frac{NkT}{\bar{v}} - \frac{N(N-1)}{6\bar{v}^3} \int [r_{0ij}^{12} \frac{\partial \bar{v}_{12}}{\partial r_{0ij}} - 3\rho \frac{\partial \bar{v}_{12}}{\partial \rho}] g_N^{(2)SC}(\bar{v}_{12}) d^3 r_{0i} d^3 r_{0j} \quad .$$

The final form for our semiclassical pressure equation of state comes from assuming a spherical potential and taking the thermodynamic limit. Thus, in the notation of the energy equation, Eq. (4.1), we find

$$P = \frac{NkT}{\bar{v}} [1 - \frac{\beta\rho}{6} \int (r_0 \frac{\partial \bar{V}(r_0)}{\partial r_0} - 3\rho \frac{\partial \bar{V}(r_0)}{\partial \rho}) g^{(2)SC}(r_0) d^3 r_0] \quad . \quad (4.4)$$

Just as with the energy, note that the pressure differs from its classical analogue not only by the expected substitution of $\bar{V}_{ij}$ for V_{ij} but also by the presence of a density derivative.

V. The Semiclassical Pairwise Interaction Approximation

Because our pairwise interaction assumption is so intimately involved in the formalism of the last two sections, it is clearly necessary to investigate some of the different concrete representations this approximation can have. The simplest such representation, which might be termed the density independent form, was mentioned in Section II

$$e^{-\beta \bar{V}}_{ij} \equiv \left(\frac{\beta}{2\pi m}\right)^3 \iint e^{-\beta \bar{H}}_{ij} d^3 p_0^i d^3 p_0^j \quad (4.1)$$

In using this expression for the effective potential we are merely replacing the classical $e^{-\beta V}_{ij}$ by a semiclassical approximate two particle Slater sum. Moreover, as discussed previously,⁹ for spherically symmetric potentials this can be rewritten in such a way as to make computation facile:

$$e^{-\beta \bar{V}(r_0)} = \left(\frac{\beta}{2\pi \mu}\right)^{3/2} \left(\frac{2\pi \hbar^2}{r_0^2}\right) \sum_{\ell}' (2\ell+1) \int_{-\infty}^{\infty} e^{-\beta \bar{H}_{\ell}} dp_0^r \quad (4.2)$$

with

$$\bar{H}_{\ell} = \frac{2}{\hbar \beta} \int_0^{\hbar \beta / 2} \left[\frac{p^r^2}{2\mu} + V(r) + \frac{\hbar^2 (\ell + \frac{1}{2})^2}{2\mu r^2} \right] d\tau$$

$$p^r = \mu \dot{r}$$

$$\dot{p}^r = \frac{\partial V(r)}{\partial r} - \frac{\hbar^2 (\ell + \frac{1}{2})^2}{\mu r^3}$$

and with the primed summation indicating a sum over even angular momenta for bosons and odd angular momenta for fermions.

Figure 1 shows the results of just such a computation¹² as a function of temperature. As the temperature decreases, the quantum effects become more pronounced, making the effective potential both shallower and longer ranged. However at higher temperatures the effective potential becomes indistinguishable from the true classical potential. Thus, to the extent that our approximation is valid, one would expect quantum mechanics to increase the role of the attractive part of the potential. But just how valid is the approximation?

From the previous work⁹ it is clear that the semiclassical expression for the two particle Slater sum is quite accurate--even for He⁴ at temperatures below 30°K--so that, for the density independent model, the major task becomes that of demonstrating the usefulness of writing the N body Slater sum (Eq. (2.2)) as a product of two body Slater sums (Eq. (2.9)).¹⁶ To do this let us consider the respective quantum correction expansions of the exact and approximate methods.

Expanding Eq. (2.2) we find that in general¹⁷

$$e^{-\beta \bar{V}} = e^{-\beta V} \left\{ 1 + \frac{1}{6} \left(\frac{\hbar \beta}{2} \right)^2 \sum_{i=1}^N \left[\frac{\beta}{m} (\vec{\nabla}_i V)^2 - \frac{2}{m} \nabla_i^2 V \right] + \dots \right\} \quad (4.3)$$

If a pairwise interacting classical potential, Eq. (2.8), is now assumed we obtain, after lengthy algebra, the following exact expression.

$$e^{-\beta \bar{V}} = e^{-\beta V} \left\{ 1 + \frac{1}{6} \left(\frac{\hbar \beta}{2} \right)^2 \sum_{j,k>j}^N \left[\frac{\beta}{\mu} (\vec{\nabla}_j V_{jk})^2 - \frac{2}{\mu} \nabla_j^2 V_{jk} \right. \right. \\ \left. \left. + \frac{\beta}{2\mu} \vec{\nabla}_j V_{jk} \cdot \sum_{m \neq j,k} \vec{\nabla}_m (V_{km} - V_{jm}) \right] + \dots \right\} \quad (4.4)$$

On the other hand Eqs. (2.9) and (4.1), taken together, assume

$$e^{-\beta \bar{V}} = \prod_{i,j>i} e^{-\beta \bar{V}_{ij}}$$

with each $\bar{V}_{ij}$ satisfying Eq. (4.3) with $N = 2$

$$e^{-\beta \bar{V}_{ij}} = e^{-\beta V_{ij}} \left\{ 1 + \frac{1}{6} \left(\frac{\hbar \beta}{2} \right)^2 \left[\frac{\beta}{\mu} (\vec{\nabla}_j V_{jk})^2 - \frac{2}{\mu} \nabla_j^2 V_{jk} \right] + \dots \right\} .$$

Hence the density independent model leads to the approximation

$$e^{-\beta \bar{V}} = e^{-\beta V} \left\{ 1 + \frac{1}{6} \left(\frac{\hbar \beta}{2} \right)^2 \sum_{j,k>j}^N \left[\frac{\beta}{\mu} (\vec{\nabla}_j V_{jk})^2 - \frac{2}{\mu} \nabla_j^2 V_{jk} \right] + \dots \right\} . \quad (4.5)$$

By comparing Eqs. (4.5) and (4.4) one can see that our simple model for $\bar{V}_{ij}$ (to first order in $\hbar^2$) neglects the quantal three body term

$$S_{jk} = \frac{\beta}{2\mu} \vec{\nabla}_j V_{jk} \cdot \sum_{m \neq j,k} \vec{\nabla}_m (V_{km} - V_{jm}) . \quad (4.6)$$

However closer inspection suggests that one would expect this to be reasonably accurate unless r_{jk} , r_{km} and r_{jm} are all simultaneously small--in which case the derivatives of V_{jk} , V_{km} and V_{jm} would all be significant.¹⁸ This requirement is equivalent to insisting on the absence of three particle clusters or, in plainer language, equivalent to requiring a low density. Still, it should be emphasized that this is a requirement only in order to insure accurate representation of the many body quantum effects. All the classical effects and two body quantum effects are manifestly included in any case.

We can quantify the nature of this approximation some more by adopting

a simple mean-field model for S_{jk} . Assume that the position of atom m is described by a normalized distribution $\rho(\underline{r}_m)$. In that case Eq. (4.6) may be written

$$\begin{aligned} S_{jk} &= \frac{\beta}{2\mu} V'(r_{jk}) \int [V'(r_{mk}) \hat{r}_{mk} \cdot \hat{r}_{jk} - V'(r_{mj}) \hat{r}_{mj} \cdot \hat{r}_{jk}] \rho(\underline{r}_m) d^3 r_m \\ &= \frac{\beta}{2\mu} V'(r_{jk}) \int_0^\pi \int_0^{2\pi} \int_0^\infty [V'(r_{mk}) \cos\beta + V'(r_{mj}) \cos\alpha] \rho(\underline{r}_m) (\sin\phi) r_{mj}^2 dr_{mj} d\alpha d\phi \end{aligned}$$

where we have used the following relations:

$$\vec{\nabla}_a V_{ab} = \frac{dV(r_{ab})}{dr_{ab}} \hat{r}_{ab} = V'(r_{ab}) \hat{r}_{ab}$$

$$r_{ab} = |\underline{r}_a - \underline{r}_b|, \quad \hat{r}_{ab} = (\underline{r}_a - \underline{r}_b)/r_{ab}.$$

Now let us further assume that $\rho(\underline{r}_m)$ is equal to the overall density (ρ , a constant) outside a distance σ and that it vanishes for $|\underline{r}_m| < \sigma$. Without making any conditions on the density, we may also follow the reasoning of the last paragraph and expand our expression in powers of $d = (r_{mk} - r_{mj})$ since the only sizeable contributions to S will always come when both r_{jm} and r_{km} are small (which implies d is small, see Figure 2). To first order in d then

$$\begin{aligned} S_{jk} &= \frac{\beta}{2\mu} \rho V'(r_{jk}) \int_\sigma^\infty \int_0^{2\pi} 2r_{mj}^2 d\alpha dr_{mj} \\ &\quad \{V'(r_{mj}) [\cos\alpha + \frac{r_{jk}}{2r_{mj}}] + [V''(r_{mj}) \frac{r_{jk}}{2r_{mj}} + V'(r_{mj}) \frac{1}{r_{jk}} - V'(r_{mj}) \frac{r_{jk}}{2r_{mj}^2}] d + \dots\}. \end{aligned}$$

But d itself (to first order) is given by

$$d = \frac{1}{2r_{mj}} (r_{jk}^2 - 2r_{jk}r_{mj}\cos\alpha)$$

so that

$$S_{jk} = + \frac{2\pi\beta\rho}{\mu} r_{jk} V'(r_{jk}) \left\{ \int_0^{\infty} r_{mj} V'(r_{mj}) dr_{mj} + \frac{r_{jk}^2}{4} \int_0^{\infty} [V''(r_{mj}) - \frac{1}{r_{mj}} V'(r_{mj})] dr_{mj} \right\}$$

Integrating by parts subject to the condition $V(\sigma) = 0$ leaves us with the desired expression for S_{jk}

$$S_{jk} = - \frac{2\pi\beta\rho}{\mu} r_{jk} V'(r_{jk}) \left\{ \int_0^{\infty} V(r) dr + \frac{r_{jk}^2}{4} [V'(\sigma) + \int_0^{\infty} \frac{1}{r^2} V(r) dr] \right\} \quad (4.7)$$

By applying this simple model it is easy to see that the error made in the density independent form of the pairwise interaction approximation consists of leaving out a term which is proportional to the density and which dies off at large distances (large r_{jk}). Moreover Eq. (4.7) also supplies us with the first quantum correction to the approximation since from (4.4) and (4.5)

$$e^{-\beta\bar{V}_{\text{exact}}} = e^{-\beta\bar{V}_{\rho \text{ indep.}}} \left\{ 1 + \frac{1}{6} \left(\frac{\hbar\beta}{2} \right)^2 \sum_{j,k>j}^N S_{jk} + \dots \right\} \quad (4.8)$$

But most importantly, (4.7) suggests a way to improve the density independent form because it expresses S_{jk} as a function only of the coordinates r_j and r_k .

If we were to take the validity of (4.7) for granted, the "exact" expression would become

$$e^{-\beta\bar{V}} = e^{-\beta V} \left\{ 1 + \frac{1}{6} \left(\frac{\hbar\beta}{2} \right)^2 \sum_{j,k>j}^N \left[\frac{\beta}{\mu} (\vec{\nabla}_j V_{jk})^2 - \frac{2}{\mu} \nabla_j^2 V_{jk} + \kappa r_{jk} V'(r_{jk}) (1 + \delta r_{jk}^2) \right] + \dots \right\} \quad (4.9)$$

where the (presumably small) constant κ and the constant δ would be given by

$$\begin{aligned}\kappa &= -\frac{2\pi\beta\rho}{\mu} \int_{\sigma}^{\infty} V(r) dr \\ \delta &= \frac{V'(\sigma) + \int_{\sigma}^{\infty} \frac{1}{r^2} V(r) dr}{4 \int_{\sigma}^{\infty} V(r) dr}.\end{aligned}\quad (4.10)$$

However there is no reason why one cannot find a modified classical potential $U(r_{jk}) = V(r_{jk}) + A(r_{jk})$ (for some A) such that (4.9) being true for V implies (4.11) is true for U

$$e^{-\beta\bar{V}} = e^{-\beta V} \left\{ 1 + \frac{1}{6} \left(\frac{\hbar\beta}{2} \right)^2 \sum_{j,k>j}^N \left[\frac{\beta}{\mu} (\vec{\nabla}_j U_{jk})^2 - \frac{2}{\mu} \nabla_j^2 U_{jk} \right] + \dots \right\} \quad (4.11)$$

Except for the exponential prefactor, Eq. (4.11) is precisely Eq. (4.5) with U substituted for V . What this means, though, is that by applying our full semiclassical machinery, Eq. (4.2), with U instead of V we can find a new semiclassical effective pair potential which contains quantum many body effects to all orders in $\hbar$ (instead of just to $\hbar^2$ as in Eq. (4.8)). Let us proceed with this plan by solving for U .

Taken together, Eqs. (4.9) and (4.11) imply that

$$\frac{\beta}{\mu} (\vec{\nabla}_j U_{jk})^2 - \frac{2}{\mu} \nabla_j^2 U_{jk} = \frac{\beta}{\mu} (\vec{\nabla}_j V_{jk})^2 - \frac{2}{\mu} \nabla_j^2 V_{jk} + S_{jk}.$$

This quickly leads to a first order nonlinear differential equation for $\chi(r) \equiv A'(r) \equiv U'(r) - V'(r)$

$$\frac{2}{\mu} \chi'(r) - \frac{\beta}{\mu} \chi^2(r) + \frac{2}{\mu r} [2 - \beta r V'(r)] \chi(r) + S_{jk}(r) = 0 \quad (4.12)$$

where the primes denote differentiation with respect to $r = r_{jk}$. In general (4.12), a Riccati equation,¹⁹ cannot be solved analytically although it can be solved numerically by any number of techniques. Nevertheless we can solve it approximately if we take advantage of the smallness of the inhomogeneous (S) term.

Using $\chi = 0$ as a particular solution of the homogeneous equation ($S_{jk} = 0$), one can solve a first order linear differential equation to obtain the $S_{jk} = 0$ general solution¹⁹

$$\chi(r) = \omega \exp\left\{\int_r^{\infty} [\beta V'(t) - \frac{2}{t}] dt\right\} \cdot \left\{1 - \frac{\beta \omega}{2} \int_r^{\infty} \exp\left\{\int_s^{\infty} [\beta V'(t) - \frac{2}{t}] dt\right\} ds\right\}^{-1} \quad (4.13)$$

where ω is a constant of integration. By then requiring that (4.13) be a solution of (4.12) with $\omega = \omega(r)$ one finds (to first order in S_{jk})

$$\omega(r) = - \int_r^{\infty} \frac{\mu}{2} S_{jk}(s) \exp\left\{-\int_s^{\infty} [\beta V'(t) - \frac{2}{t}] dt\right\} ds \quad (4.14)$$

Hence Eqs. (4.13) and (4.14) constitute the desired solution for $\chi(r)$.²⁰

From here on the procedure is straightforward. Knowing $\chi(r)$ immediately provides the modified classical potential $U(r)$ upon integration by parts

$$U(r) = V(r) + A(r) = V(r) - \int_r^{\infty} \chi(s) ds \quad (4.15)$$

Then, merely substituting this potential into Eq. (4.2) and remembering to correct for the prefactor in Eq. (4.11) gives the required semiclassical effective pair potential

$$e^{-\beta \bar{V}_{12}(\text{improved})} = e^{\beta A(r_0)} e^{-\beta \bar{V}(r_0)} \text{ (with classical potential } U) \quad .(4.16)$$

In view of the model used to generate Eq. (4.7) one might call this new effective potential the mean field formulation.

VI. Conclusions

By adopting a semiclassical pairwise interaction approximation we have been able to obtain semiclassical equations for fluids which, because of their classical form, promise to be not only computationally useful but also readily generalizable. For example, it is clear that improved semiclassical integral equations would result if one carried out functional Taylor series expansions to second order instead of only to first order (just as the PY II equation results from the PY equation classically). In addition the effective potential formalism automatically lends itself to a graph theoretic approach--differing from the classical approaches only in the replacement of V by $\bar{V}$ in the bond function--so that any topological arguments which apply to classical graphs also apply to semiclassical graphs. Indeed the integral equations of Section III could have easily been derived this way.

Of at least equal importance to this generalizability is the fact that this approach leads to some insight into what exactly quantum mechanics does to the classical many body problem. One might even hope that such developments as an improvement over the crude models of Section V and some detailed study of the semiclassical superposition approximation, Eq. (3.3), would serve as some halting steps in this direction.

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Figure Captions

1. A sample classical potential (solid line) and the corresponding density independent semiclassical effective potentials (broken lines) Eq. (4.2). The case illustrated is He^4 in a Lennard-Jones potential ($\epsilon = 10.22^\circ\text{K}$, $\sigma = 2.556 \text{ \AA}$).
2. The geometry of a cluster of atoms j, k, and m.

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Figure 1

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Figure 2

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