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SEMICLASSICAL STATISTICAL MECHANICS OF FLUIDS. II.

AN IMPROVED MEAN FIELD EFFECTIVE PAIR POTENTIAL

By

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Abstract

An improved model is developed for an effective two body potential which incorporates quantum effects into classical equilibrium statistical mechanics. Just as in a previously derived model, a mean field approximation to a first quantum correction is employed in order to obtain nonperturbative expressions which include corrections to all orders. However, unlike the previous model, the resulting thermodynamic functions are exact to first order in $\hbar^2$.

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I. INTRODUCTION

In a recent series of papers,^{1,2,3} an approach was developed which allows one to examine the onset of quantum effects in equilibrium statistical mechanics without resorting to a perturbation expansion in $\hbar$. Because this phase space sampling approach is nonperturbative, it would seem to be much better suited to studying chemically interesting potentials than are the perturbative techniques⁴⁻⁷ which rely on the Wigner-Kirkwood expansion⁸--an expansion which is known to diverge at small distances.⁹ Consequently it would also seem to hold more promise for treating chemical systems with relatively large quantum effects, such as hydrogen bonded substances.¹⁰

However, in order to fulfill these expectations, it is necessary to have a practical formalism which is capable of treating fluids. Towards this end the previous paper in the series³ (hereafter referred to as I) introduced a semiclassical effective potential, $V(\underline{r}_0^1, \dots, \underline{r}_0^N)$, defined by¹¹

$$e^{-\beta \bar{V}} = \left(\frac{\beta}{2\pi m}\right)^{3N/2} \int \dots \int e^{-\beta \bar{H}} d^3 p_0^1 \dots d^3 p_0^N \quad (1.1)$$

where, instead of $\bar{H}$ being the classical Hamiltonian evaluated at the point $(\underline{r}_0^1, \dots, \underline{r}_0^N, \underline{p}_0^1, \dots, \underline{p}_0^N)$ (which would make $\bar{V} = V$), $\bar{H}$ is the action for an imaginary time trajectory starting at that same point.¹ It was then found to be advantageous to approximate the effective potential as a sum of effective pair potentials

$$\bar{V} = \sum_{j,k>j}^N \bar{V}_{jk} \equiv \sum_{j,k>j}^N \bar{V}_{jk}(\underline{r}_0^j, \underline{r}_0^k) \quad (1.2)$$

As it turned out, this semiclassical pairwise interaction approximation was all that was required in order to enable one to write semiclassical equivalents of both the classical integral equations for the radial distribution function and the classical equations for thermodynamic quantities such as internal energy and pressure.³ Because little more was required than substituting the effective pair potential for the true pair potential in classical formulas, we indeed were left with a practical formalism.

Of course there still remained the problem of devising a method for calculating the semiclassical effective pair potential from the classical pair potential and assessing its accuracy. A glance at the quantum correction expansion for Eq. (1.1) in terms of classical pair potentials³

$$e^{-\beta\bar{V}} = e^{-\beta V} \left\{ 1 + \frac{1}{6} \left(\frac{\hbar\beta}{2} \right)^2 \sum_{j,k>j}^N \left[\frac{\beta}{\mu} (\vec{\nabla}_j V_{jk})^2 - \frac{2}{\mu} \nabla_j^2 V_{jk} + \frac{\beta}{2\mu} \vec{\nabla}_j V_{jk} \cdot \sum_{m \neq j,k}^N \vec{\nabla}_m (V_{km} - V_{jm}) \right] + \dots \right\} \quad (1.3)$$

quickly reveals that, even at the level of the first quantum correction, it is impossible to satisfy Eq. (1.2) while preserving the three body term

$$S_{jk} = \frac{\beta}{2\mu} \vec{\nabla}_j V_{jk} \cdot \sum_{m \neq j,k}^N \vec{\nabla}_m (V_{km} - V_{jm}) \quad (1.4)$$

Accordingly, one must therefore approximate S_{jk} as (no more than) a two body term.

Indeed, one can go further than that and simply set $S_{jk} = 0$. This

is the end result of the density independent approximation for $\bar{v}_{jk}$,

$$e^{-\beta \bar{v}_{jk}} = \left(\frac{\beta}{2\pi m}\right)^3 \iint e^{-\beta \bar{H}_{jk}} d^3 p_0^j d^3 p_0^k \quad (1.5)$$

so called because it leaves $\bar{v}_{jk}$ dependent only on r_0^j , r_0^k , and the temperature but not on the density. A somewhat more accurate approximation would be to assume some sort of distribution of r_0^m values, that is, a mean field model. However, both of these approaches, at least as they were implemented in paper I, suffer from two serious faults: (1) They are both low density approximations and (2) Neither of them have even an exact first quantum correction.

That these criticisms are valid for the density independent model is an unavoidable consequence of the nature of the model. It is the price one pays for allowing facile calculation. The mean field model, on the other hand, is certainly not so constrained. As will be demonstrated in the remainder of this article, it is fairly easy to improve on the crude implementation discussed in I. Moreover, the resulting improved effective pair potential will turn out to lead not only to quantum corrections to all orders, but also to an exact first quantum correction for all measurable (thermodynamic) quantities as well.

II. AN IMPROVED MEAN FIELD APPROXIMATION

The guiding assumption of a mean field model for the effective pair potential is that the three body term S_{jk} [Eq. (1.4)] is well approximated by a continuous distribution of "m" particles

$$S_{jk} = \frac{\beta}{2\mu} (N-2) \vec{v}_j \cdot \vec{v}_{jk} \cdot \int \vec{v}_m (v_{km} - v_{jm}) \rho_{jk}(m) d(m) \quad (2.1)$$

where the (N-2) factor comes from the (N-2) possible particles $m \neq j, k$ and the notation (m) refers to $\vec{r}^m$. Once this assumption is made though, the fact that we require $\rho_{jk}(m)$ to be the normalized equilibrium distribution of $\vec{r}^m$ for fixed $\vec{r}^j$ and $\vec{r}^k$ rigorously implies that $\rho_{jk}(m)$ is the "unsymmetrical" classical distribution function defined by¹²

$$\rho_{12}^{(3)} = \frac{\int \dots \int e^{-\beta V} d(4) \dots d(N)}{\int \dots \int e^{-\beta V} d(3) \dots d(N)}$$

or, in terms of the two and three particle correlation functions

$$\rho_{j,k}(m) = \frac{g(j,k,m)}{vg(j,k)}$$

Substituting this expression into Eq. (2.1) and taking the thermodynamic limit gives an expression proportional to the density ρ

$$S_{jk} = \frac{\beta\rho}{2\mu} \frac{1}{g(j,k)} \vec{v}_j \cdot \vec{v}_{jk} \cdot \int \vec{v}_m (v_{km} - v_{jm}) g(j,k,m) d(m) \quad (2.2)$$

We can now simplify Eq. (2.2) considerably by taking advantage of the time independent BBGKY hierarchy¹³

$$\beta \rho \int \vec{\nabla}_1 v_{13} g(1,2,3) d(3) = -\beta (\vec{\nabla}_1 v_{12}) g(1,2) - \vec{\nabla}_1 g(1,2) \quad (2.3)$$

Thus, in combination with the relation

$$\vec{\nabla}_1 v_{12} = -\vec{\nabla}_2 v_{12}$$

and with suitable interchanges of particle labels we finally end up with the desired mean field approximation for S_{jk}

$$S_{jk} = -\frac{\beta}{\mu} (\vec{\nabla}_j v_{jk})^2 - \frac{1}{\mu} \vec{\nabla}_j v_{jk} \cdot \vec{\nabla}_j \ln g(j,k) \quad (2.4)$$

From Eq. (1.3) we also see that the corresponding mean field approximation for the quantum correction expansion is

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

$$e^{-\beta \bar{V}} = e^{-\beta V} \left\{ 1 - \frac{1}{6\mu} \left(\frac{\hbar \beta}{2} \right)^2 \sum_{j,k>j}^N [2 \nabla_j^2 v_{jk} + \vec{\nabla}_j v_{jk} \cdot \vec{\nabla}_j \ln g(j,k)] + \dots \right\} \quad (2.5)$$

Equations (2.4) and (2.5) then, are the necessary mean field expressions. Since to first order in quantum effects they involve only particles taken two at a time, they at least permit $\bar{V}$ to be expressed as a sum of pair interactions. This means that we can now proceed to find a $\bar{V}_{jk}$ consistent with Eq. (1.2). Note however that Eq. (2.5) alone is not adequate for our purposes, in as much as it is manifestly a perturbation expansion. Rather what is now required is that we find a procedure for calculating $\bar{V}_{jk}$ to infinite order subject only to the restriction that the first quantum correction to $\bar{V}_{jk}$ be in accord with Eq. (2.5).

We can accomplish this with our model in much the same way that paper I did with its much cruder mean field model. Let us derive an effective classical potential U_{jk} such that the desired $\bar{V}_{jk}$ will be the result of using the density independent approximation [Eq. (1.5)] on the classical Hamiltonian H_{jk}

$$H_{jk} = \frac{(p^j)^2}{2m} + \frac{(p^k)^2}{2m} + U_{jk}$$

$$e^{-\beta \bar{U}_{jk}} = \left(\frac{\beta}{2\pi m}\right)^3 \int \int e^{-\beta H_{jk}} d^3 p_0^j d^3 p_0^k$$

$$e^{-\beta \bar{U}} = \exp\left\{-\beta \sum_{j,k>j}^N \bar{U}_{jk}\right\}$$

Because the density independent version does contain quantum corrections to infinite order, this will certainly meet our requirements of being nonperturbative, but more importantly, it will also incorporate a physically reasonable density dependence, since we are explicitly requiring that the first quantum correction to the semiclassical effective potential calculated from U_{jk} in the density independent formalism, Eq. (2.6)¹⁴

$$\begin{aligned} e^{-\beta \bar{V}} &= e^{\beta(U-V)} e^{-\beta \bar{U}} \text{ (density independent model)} \\ &= e^{-\beta V} \left\{ 1 + \frac{1}{6} \left(\frac{\hbar\beta}{2}\right)^2 \sum_{j,k>j}^N \left[\frac{\beta}{\mu} (\vec{\nabla}_j U_{jk})^2 - \frac{2}{\mu} \nabla_j^2 U_{jk} \right] + \dots \right\} \\ U &= \sum_{j,k} U_{jk}, \quad V = \sum_{j,k} V_{jk} \end{aligned} \quad (2.6)$$

exactly match the first quantum correction to the SC effective potential calculated from V_{jk} in the mean field approximation, Eq. (2.5).

This requirement implies that

$$\frac{\beta}{\mu} (\vec{\nabla}_j U_{jk})^2 - \frac{2}{\mu} \nabla_j^2 U_{jk} = \frac{\beta}{\mu} (\vec{\nabla}_j V_{jk})^2 - \frac{2}{\mu} \nabla_j^2 V_{jk} + S_{jk} \quad (2.7)$$

which is identical to the corresponding equation in paper I (except for the different S_{jk} function). Accordingly we may solve it in the same fashion. Defining

$$r \equiv r_{jk} \equiv |\vec{r}_j - \vec{r}_k|, \quad U_{jk} \equiv U_{jk}(r)$$

$$\chi_{jk}(r) \equiv \frac{d}{dr} [U_{jk}(r) - V_{jk}(r)] \equiv U'_{jk}(r) - V'_{jk}(r)$$

and remembering that for any function $f(r_{jk})$

$$\nabla_j^2 f(r_{jk}) = f'' + \frac{2}{r} f',$$

reduces Eq. (2.7) to the Ricatti equation¹⁵

$$\frac{2}{\mu} \chi'_{jk}(r) - \frac{\beta}{\mu} \chi_{jk}^2(r) + \frac{2}{\mu r} [2 - \beta r V'_{jk}(r)] \chi_{jk}(r) + S_{jk}(r) = 0 \quad (2.8)$$

where from Eq. (2.4) we see that

$$S_{jk}(r) = - \frac{V'_{jk}(r)}{\mu} [\beta V'_{jk}(r) + \frac{g'_{jk}(r)}{g_{jk}(r)}] \quad (2.9)$$

Once Eq. (2.8) is solved for $\chi_{jk}(r)$ (either numerically or by density expansion as in paper I) it is a simple matter to calculate the classical effective potential U_{jk}

$$U_{jk}(r) = V_{jk}(r) - \int_r^\infty \chi(s) ds \quad (2.10)$$

and from that the desired effective potential

$$\begin{aligned}
 & e^{-\beta \bar{V}_{jk}} \text{ (improved mean field model)} \\
 & = e^{\beta(U_{jk} - V_{jk})} e^{-\beta \bar{U}_{jk}} \text{ (density independent model)} \quad . \quad (2.11)
 \end{aligned}$$

Thus, as in paper I, we find that it is possible to specify an infinite order semiclassical effective pair potential in the context of a mean field approximation to a quantum correction expansion.

III. ANALYSIS OF THE IMPROVED MEAN FIELD MODEL

In developing the formalism of the last section we found it necessary to rely on two somewhat different assumptions. Unfortunately, the more fundamental of these is at the same time the more subtle and the more difficult to check: namely, the conjecture that we can force the density independent model to yield reasonably accurate higher order corrections by simply constraining the first correction to meet our requirements. While this does seem like a realistic supposition, it is by no means an obvious one, so perhaps some verification through numerical examples would be in order.

However, in order to concentrate on the newer development of this article--the improved mean field model itself--we will defer this verification to a later publication. Instead we will now deal with the consequences of the mean field approximation, both for thermodynamic quantities and for the three body term that is actually being approximated. Let us begin with the latter.

Probably the simplest route to take is that of a density expansion. From classical statistical mechanics we know that the radial distribution function can be expanded¹⁶

$$g(1,2) = e^{-\beta V_{12}} \{ 1 + \rho \int (e^{-\beta V_{13}} - 1)(e^{-\beta V_{23}} - 1) d(3) + \dots \}$$

Substituting this into our mean field approximation for the three body term [Eq. (2.4)] gives

$$s_{jk} = \frac{\beta \rho}{\mu} \int \vec{V}_1 V_{12} \cdot \vec{V}_1 V_{13} e^{-\beta V_{13}} (e^{-\beta V_{23}} - 1) d(3) + O(\rho^2) \quad (3.1)$$

an expression whose leading term is proportional to the density. Moreover, the coefficient of the density is an integral over the position of the third particle which clearly has a significant contribution only when particles 1, 2, and 3 are clustered together. If either r_{12} or r_{13} are large then $\vec{\nabla}_1 V_{12} \cdot \vec{\nabla}_1 V_{13}$ vanishes and if r_{23} becomes large then $(e^{-\beta V_{23-1}})$ will vanish. Apparently then, the new mean field model is similar to the original version in predicting that S_{jk} will become significant only when the density becomes high enough to allow three particle clusters.

Turning now to the thermodynamic aspects, it can be shown that the exact quantum correction expansions for the configuration integral and the Helmholtz free energy are given by⁷

$$Z_{QM} = Z_{CL} \left\{ 1 - \frac{1}{12\mu} \left(\frac{\hbar\beta}{2} \right)^2 \rho^2 \iint g(j,k) \nabla_j^2 V_{jk} d(j)d(k) + \dots \right\} \quad (3.2)$$

$$A_{QM} = A_{CL} + \frac{\hbar^2\beta}{48\mu} \rho^2 \iint g(j,k) \nabla_j^2 V_{jk} d(j)d(k) + \dots \quad (3.3)$$

The mean field model on the other hand requires that the semiclassical configuration integral satisfy

$$Z_{SC}^{MF} = \int \dots \int e^{-\beta \bar{V}} d(1) \dots d(N)$$

or from Eq. (2.5)

$$\begin{aligned} Z_{SC}^{MF} = & \int \dots \int e^{-\beta V} d(1) \dots d(N) - \frac{1}{6\mu} \left(\frac{\hbar\beta}{2} \right)^2 \sum_{j,k>j}^N \int \dots \int e^{-\beta V} [2 \nabla_j^2 V_{jk} \\ & + \vec{\nabla}_j V_{jk} \cdot \vec{\nabla}_j \ln g(j,k)] d(1) \dots d(N) + \dots \end{aligned}$$

By subsequently introducing the two particle correlation function and

relabeling particles the $N(N-1)/2$ possible ways, we find in the thermodynamic limit that

$$\begin{aligned} Z_{SC}^{MF} &= Z_{CL} - \frac{1}{12\mu} \left(\frac{\hbar\beta}{2}\right)^2 Z_{CL} \rho^2 \iint g(j,k) [2\nabla_j^2 v_{jk} + \vec{\nabla}_j v_{jk} \cdot \vec{\nabla}_j \ln g(j,k)] d(j)d(k) + \dots \\ &= Z_{CL} \left\{ 1 - \frac{1}{12\mu} \left(\frac{\hbar\beta}{2}\right)^2 \rho^2 \iint g(j,k) \nabla_j^2 v_{jk} d(j)d(k) \right. \\ &\quad \left. - \frac{1}{12\mu} \left(\frac{\hbar\beta}{2}\right)^2 \rho^2 \iint g(j,k) [\nabla_j^2 v_{jk} + \vec{\nabla}_j v_{jk} \cdot \vec{\nabla}_j \ln g(j,k)] d(j)d(k) \right. \\ &\quad \left. + \dots \right\} \end{aligned}$$

which certainly seems to be different from Eq. (3.2).

However, on closer examination the difference term

$$\begin{aligned} I_{jk} &= \iint g(j,k) [\nabla_j^2 v_{jk} + \vec{\nabla}_j v_{jk} \cdot \vec{\nabla}_j \ln g(j,k)] d(j)d(k) \\ &= \iint [\nabla_j^2 v_{jk} g(j,k) + \vec{\nabla}_j v_{jk} \cdot \vec{\nabla}_j g(j,k)] d(j)d(k) \end{aligned}$$

is seen to vanish on integration by parts

$$\begin{aligned} I_{jk} &= \iint \vec{\nabla}_j \cdot [g(j,k) \vec{\nabla}_j v_{jk}] d(j)d(k) \\ I_{jk} &= 0 \end{aligned}$$

since for any realistic potential the force at infinity must be zero.

We therefore find that

$$Z_{SC}^{MF} = Z_{CL} \left\{ 1 - \frac{1}{12\mu} \left(\frac{\hbar\beta}{2}\right)^2 \rho^2 \iint g(j,k) \nabla_j^2 v_{jk} d(j)d(k) + \dots \right\} \quad (3.4)$$

which is precisely Eq. (3.2). This, in turn, implies that the free energy is given by

$$A = -\frac{1}{\beta} \ln Q = -\frac{1}{\beta} \ln \left(\frac{2\pi m}{h^2 \beta} \right)^{\frac{3N}{2}} Z$$

$$A_{SC}^{MF} = A_{CL} + \frac{\hbar^2 \beta}{48\mu} \rho^2 \iint g(j,k) \nabla_j^2 V_{jk} d(j)d(k) + \dots \quad (3.5)$$

which is nothing but Eq. (3.3). In fact, by extension any thermodynamic property calculated in our semiclassical mean field approximation will necessarily have an exact first quantum correction.

At first glance it may seem somewhat surprising to discover that an approximation to a first order correction leads to an exact first order correction. Yet we can understand this by simply noting that the mean field formalism replaces an average of an exponential by an exponential of an average---a procedure which is correct to first order. This strongly suggests that higher order quantum corrections will not be exact.

More physically, this behavior can be viewed in terms of the fact that the mean field approximation is merely an artifice which enables us to write quantum equations in a classical form. Therefore what our results imply is that a classical form may be acceptable because, in some sense, quantum effects do not cause qualitative changes in classical many body behavior to first order. This is in accord with the observation of De Witt and Fishbane¹⁷ that the classical Mayer irreducible cluster theorem does not break down until second order in quantum effects or equivalently, that quantum effects do not affect the topology of classical graphs to first order.

IV. CONCLUDING REMARKS

The fact that the improved mean field approximation leads to thermodynamic functions with an exact first quantum correction means that we now have a satisfactory nonperturbative procedure for studying the role of quantum effects in the equilibrium statistical mechanics of fluids. Given a classical pair potential and a classical many body model (such as an integral equation for $g(j,k)$) this procedure would work as follows: 1) Calculate the classical radial distribution function and from that the mean field version of S_{jk} from Eq. (2.9); 2) Substitute S_{jk} into the Ricatti equation [Eq. (2.8)] and then use (2.10) to calculate the effective classical potential U_{jk} from χ_{jk} ; 3) Calculate the semiclassical effective potential from Eq. (2.11), and finally, 4) use the semiclassical integral equations of paper I (for example) to compute the semiclassical radial distribution function.

It should be noted that if we are to take advantage of the nonperturbative character of our formalism, both the imaginary time trajectory used in computing $\bar{v}_{jk}$ (step 3)¹⁸ and the Ricatti equation (step 2) must be solved numerically for every desired temperature and density. However both of these are effectively one dimensional differential equations which may be solved routinely.

One could also envision several improvements which may streamline this procedure. For example, it may be possible to combine the trajectory and Ricatti equations into a single equation. In a more speculative vein, it might even be profitable to change the formalism in such a way as to improve the higher order behavior by replacing the two particle trajectory, a rather elementary computation, with a three or four particle trajectory.

Indeed, the two particle trajectory is a direct result of the use of the density independent model [Eq. (2.11)]--a step which needs further study in any case.

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