

## Equilibrium theory of a semiclassical fluid of nonanalytic potential: Application to the Yukawa-tail fluid

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Using the quantum-mechanical hard-sphere system as a reference system and the attractive interaction as a perturbation, we present computationally convenient theoretical methods for calculating the structural and thermodynamic properties of a fluid in the semiclassical limit. This approach is based on the assumption that, for a dense fluid, the quantum effects are largely determined by the repulsion due to the hard core and the attractive interactions play a minor role. The exponential approximation for the radial distribution function and "(optimized random-phase approximation) +  $B_2$ " for the excess Helmholtz free energy have been applied to calculate the structural and thermodynamic properties of the Yukawa-tail fluid in the semiclassical limit.

### I. INTRODUCTION

The problem of calculating the structural and thermodynamical properties of fluids in the semiclassical limit has been a subject of considerable interest in recent years.<sup>1-17</sup> In the semiclassical limit, quantum effects are small and can be treated as a correction to the classical behavior. The contribution of the quantum correction is usually calculated by using the Wigner-Kirkwood (WK) method<sup>2,3</sup> for the analytic potential and by using the Hemmer-Jancovici (HJ) method<sup>7,8</sup> for the nonanalytic potential. The basis of their methods is an expansion of the physical properties of interest about its classical limit.

Singh and Ram,<sup>9,10</sup> Gibson,<sup>11,12</sup> Nienhuis,<sup>13</sup> and Sinha and Singh<sup>14</sup> have investigated the quantum effects on the structural and thermodynamic properties of fluids. It has been shown that the contributions of higher-order corrections increase with the density. At liquid densities one has to consider several terms of the series even at high temperatures. In all these treatments, however, the correction terms are written in terms of the classical three-body and higher correlation functions. But the evaluation of these correction terms with reasonable accuracy is not possible. Recently, Sinha and Singh,<sup>15</sup> using cluster-expansion and topological-reduction technique, have developed computationally convenient approximations for the structural and thermodynamic properties of fluids in the semiclassical limit. In this approach the classical hard-sphere system is treated as a reference system and the attractive tail and the quantum effects as a perturbation. For a class of potential the series converges slowly and this approach is not suitable except at high temperatures and low densities.

In this paper, we develop a method for evaluating the structural and thermodynamic properties of

fluids in the semiclassical limit, in which the quantum-mechanical hard-sphere system is taken as a reference system and the attractive interaction as a perturbation on this hard-sphere system. The basic physical concept, associated with this approach, is that the quantum effects are largely determined by the repulsion due to the hard core and attractive interactions play a minor role.

A technique of cluster expansion and topological reduction is used here. In Sec. II, we review the cluster theory of the structural and thermodynamic properties of fluids in the presence of two- and three-body Mayer functions in terms of usual diagrams.<sup>15,18-20</sup> In Sec. III, the series is transformed using a topological reduction in terms of  $h_{hs}$  bonds of reference system [ $h_{hs}(i,j) = g_{hs}(i,j) - 1$  is the quantum-mechanical pair-correlation function]. The "renormalized" potential is defined and used in Sec. IV to reduce the series obtained in Sec. III to a compact form. Expressions for the radial-distribution function (RDF) and excess Helmholtz free energy are given in a form suitable for computations. The theory is applied to a fluid of the Yukawa-tail potential in Sec. V. The results are discussed in Sec. VI.

The exchange effect is not considered in this paper.

### II. CLUSTER THEORY OF THE SEMICLASSICAL FLUID

The quantity of central importance in the quantum theory of fluid is the Slater sum. In the semiclassical limit, it can be written<sup>7,8,14</sup>

$$W_N = W_N^c W_N^m, \quad (1)$$

where  $W_N^c$  is the classical value of  $W_N$  and is defined as

$$W_N^c = \exp \left( -\beta \sum_{i < j} u(i,j) \right). \quad (2)$$

Here  $\beta = (kT)^{-1}$ ,  $u(i, j)$  is the pair-potential energy between particles  $i$  and  $j$ . A "modified"  $W$  function  $W_N^m$  is written in terms of "modified" Mayer function  $f_{12 \dots s}^s$  by the relation<sup>14,15</sup>

$$W_N^m = \prod_{i < j} (1 + f_{ij}^{\text{II}}) \prod_{i < j < k} (1 + f_{ijk}^{\text{III}}). \quad (3)$$

Then (2) can be written in the form

$$W_N = \prod_{i < j} (1 + f_{ij}) \prod_{i < j < k} (1 + f_{ijk}^{\text{III}}), \quad (4)$$

where

$$f_{ij} = f_{ij}^c + (1 + f_{ij}^c) f_{ij}^{\text{II}} \quad (5)$$

and

$$f_{ij}^c = e^{-\beta u(i, j)} - 1 \quad (6)$$

is the classical two-body Mayer function.

Recently, this problem has been discussed by Sinha and Singh.<sup>15</sup> Thus the cluster series for the correlation function and the Helmholtz free energy can be written

$$\rho^2 h(1, 2) = \xi_h, \quad (7)$$

where  $\xi_h$  is defined as the sum of all distinct connected diagrams (CD) with two white  $\rho$  circles labeled 1, 2, respectively, some or no black  $\rho$  circles, at most one  $f$  bond connecting any two circles, at most one  $f^{\text{III}}$  bond connecting any three circles, at least one  $f$  and/or  $f^{\text{III}}$  bond and no articulation circles; and

$$-\beta \Delta A = H[\rho, f], \quad (8)$$

where  $H[\rho, f]$  is the sum of all distinct connected irreducible diagrams (CID) with no white circles, two or more black  $\rho$  circles, at least one  $f$  and/or  $f^{\text{III}}$  bond and no articulation circles. An articulation circle is a circle in a connected diagram, whose removal divides the diagram into two or more separate parts in such a way that at least one part contains no white circles.

Here  $\Delta A$  is the excess Helmholtz free energy of the fluid relative to that of an ideal gas at the same temperature, density, and volume.

Equations (7) and (8) are reduced further in the following sections.

### III. EXPANSION IN TERMS OF EFFECTIVE MAYER FUNCTION

Our aim in this section is to develop a scheme in which the quantum-mechanical hard-sphere system is treated as the reference system. The pair potential is divided into two parts

$$u(r) = u_{hs}(r) + u_p(r), \quad (9)$$

where  $u_{hs}(r)$  is the hard-sphere potential and  $u_p(r)$

is the perturbation. Equation (5) can be written

$$f_{ij} = f_r(i, j) + [1 + f_r(i, j)] f_p^c(i, j), \quad (10)$$

where

$$f_r(i, j) = f_{hs}^c(i, j) + [1 + f_{hs}^c(i, j)] f_{ij}^{\text{II}}, \quad (11)$$

$$f_{hs}^c(i, j) = e^{-\beta u_{hs}(i, j)} - 1,$$

and

$$f_p^c(i, j) = e^{-\beta u_p(i, j)} - 1.$$

Substituting (10) into (7) and (8), we can define  $\xi_h$  and  $H[\rho, f]$  in terms of  $f_r$  and  $f_p^c$ . We then introduce the effective reference Mayer function  $f_r^{\text{eff}}$  defined as

$$\begin{aligned} f_r^{\text{eff}}(1, 2) &= f_r(1, 2) + [1 + f_r(1, 2)] \mathcal{L}_{12} \\ &= f_{hs}^c(1, 2) + [1 + f_{hs}^c(1, 2)] f_{12}^{\text{II}} \\ &\quad + [1 + f_{hs}^c(1, 2)] [1 + f_{12}^{\text{II}}] \mathcal{L}_{12}, \end{aligned} \quad (12)$$

where  $\mathcal{L}_{12}$  is defined as a set of CID with two white 1 circle labeled 1 and 2, respectively, one or more black  $\rho$  circles, one  $f^{\text{III}}$  bond connecting any three circles, some or no  $f_r$  bonds connecting any two black circles or one black and one white circles, no articulation circles and 1, 2 irreducible. 1, 2 irreducible means there is no direct link between circles 1 and 2 and if there is more than one black circle, then we can pass between any two of them without going through either circle.

In order to evaluate  $\mathcal{L}_{12}$ , we substitute the value of  $f_r$  from (11) and eliminate  $f_{hs}^c$  in favor of  $h_{hs}^c$  bonds of classical hard-sphere system, by using lemma 6 of Ref. 18, where  $h_{hs}^c(i, j) = g_{hs}^c(i, j) - 1$  is the pair-correlation function of the classical hard-sphere system. This form of  $\mathcal{L}_{12}$  is similar to one recently taken by Sinha and Singh.<sup>15</sup> Evaluating the first few diagrams, we get

$$\begin{aligned} \mathcal{L}_{12} &= \rho \int d\vec{r}_3 g_{hs}^c(1, 3) g_{hs}^c(2, 3) \\ &\quad \times f_{123}^{\text{III}} (1 + f_{13}^{\text{II}}) (1 + f_{23}^{\text{II}}) + \dots \end{aligned} \quad (13)$$

But in the semiclassical limit it is expected that all such diagrams in  $\mathcal{L}_{12}$ , which involve overlap of  $f^{\text{II}}$  and  $f^{\text{III}}$  are of no importance.

Now with the help of (12) and the definition of  $\mathcal{L}_{12}$ , the equations (7) and (8) reduce to

$$\rho^2 h(1, 2) = \rho^2 \hat{h}(1, 2) + L_{12}, \quad (14)$$

and

$$-\beta \Delta A = -\beta \Delta \hat{A} + L. \quad (15)$$

Here we have

$$\rho^2 \hat{h}(1, 2) = \hat{\xi}_h, \quad (16)$$

where  $\hat{\xi}_h$  is defined as the sum of CD with two

white  $\rho$  circles labeled 1 and 2, respectively, some or no black  $\rho$  circles, at most one  $f_r^{\text{eff}}$  and  $f_p^c$  bond connecting any two circles and no articulation circles; and

$$-\beta\Delta\hat{A}=\hat{H}[\rho, f^{\text{eff}}], \quad (17)$$

where  $\hat{H}[\rho, f^{\text{eff}}]$  is the sum of CID with no white circles, two or more black  $\rho$  circles, at most one  $f_r^{\text{eff}}$  and  $f_p^c$  bond connecting any two circles and no articulation circles.  $L_{12}$  is a set of diagrams belonging to  $\xi_h$ , which involve overlap of  $f_p^c$  and  $f^{\text{III}}$  between black and white circles or involve two or more  $f^{\text{III}}$  bonds, all  $f^{\text{III}}$  bonds have at least one black circle common or connected together at least by two  $f_r$  bond, while  $L$  belongs to  $H[\rho, f]$ , which involve overlap of  $f_p^c$  and  $f^{\text{III}}$  or involve two or more  $f^{\text{III}}$  bonds and all pair of circles connected with  $f^{\text{III}}$  and/or  $f_r$  bonds.

Neglecting diagrams appearing in  $L_{12}$  and  $L$ , we approximate  $h(1, 2)$  and  $H[\rho, f]$ , respectively, by  $\hat{h}(1, 2)$  and  $\hat{H}[\rho, f^{\text{eff}}]$ .

#### IV. EXPRESSIONS FOR CORRELATION FUNCTION AND HELMHOLTZ FREE ENERGY

Our next problem is to sum the series appearing in  $\hat{h}(1, 2)$  and  $\hat{H}[\rho, f^{\text{eff}}]$ . This can be done if we write the perturbation Mayer function as

$$\begin{aligned} f_p^c(i, j) &= \exp[-\beta u_p(i, j)] - 1 \\ &= \sum_{n=1}^{\infty} \frac{1}{n!} [\phi(i, j)]^n, \end{aligned} \quad (18)$$

where  $\phi(i, j) = [-\beta u_p(i, j)]$ .

Substituting (18) into (16) and (17) and eliminating  $f_r^{\text{eff}}$  bonds in favor of  $h_{hs}$  bonds of the reference system [ $h_{hs}(i, j) = g_{hs}(i, j) - 1$  is the pair-correlation function of the quantum-mechanical hard-sphere system], by using lemma 6 of Ref. 18, we obtain

$$\rho^2 \hat{h}(1, 2) = \rho^2 h_{hs}(1, 2) + S_h, \quad (19)$$

where  $S_h$  is the sum of CD with two white  $\rho$  circles labeled 1 and 2, respectively, some or no black  $\rho$  circles, at most one  $h_{hs}$  and any number of  $\phi$  bond connecting any two circles, at least one  $\phi$  bond, no articulation circles and no reference articulation pair circles; and

$$\hat{H}[\rho, f^{\text{eff}}] = H_{hs}[\rho, f_r^{\text{eff}}] + S_H, \quad (20)$$

where  $S_H$  is sum of CID with no white circles, two or more black  $\rho$  circles, at most one  $h_{hs}$  bond and any number of  $\phi$  bond connecting any two circles, at least one  $\phi$  bond, no articulation circles, and no reference-articulation pair circles. A "reference-articulation pair circles" is a pair of circles in a connected diagram, whose removal divides the diagram into two or more separate

parts, such that at least one part contains no white circles.

In classical statistical mechanics, the summation of the series is done by introducing the concept of renormalized potential.<sup>21-25</sup> Recently Sinha and Singh<sup>15</sup> have introduced a "renormalized" Mayer function in the semiclassical statistical mechanics. One can use any one of the above two methods to sum the series. Here we follow the method of Andersen and Chandler<sup>25</sup> and define the renormalized potential  $\mathcal{C}(\vec{r}_1, \vec{r}_2)$  by the relation

$$\begin{aligned} \rho^2 \mathcal{C}(\vec{r}_1, \vec{r}_2) &= (2\pi)^{-3} \int d\vec{k} e^{i\vec{k}\cdot\vec{r}} \\ &\times \left( \frac{P(\vec{k})}{1-P(\vec{k})} \right) F_{hs}(\vec{k}), \end{aligned} \quad (21)$$

where

$$P(\vec{k}) = F_{hs}(\vec{k})\phi(\vec{k}).$$

$\phi(\vec{k})$  and  $F_{hs}(\vec{k})$  are the Fourier transforms of  $\phi(r)$  and  $F_{hs}(r)$ , respectively.  $F_{hs}(r)$  is the hyper-vertex function and is given by

$$F_{hs}(\vec{r}_1, \vec{r}_2) = \rho\delta(\vec{r}_1 - \vec{r}_2) + \rho^2 h_{hs}(\vec{r}_1, \vec{r}_2). \quad (22)$$

The details of the method of writing the series for the correlation function and Helmholtz free energy in terms of  $\mathcal{C}(r)$  are given by Stell and Lebowitz,<sup>23</sup> Andersen and Chandler,<sup>25</sup> and others.<sup>22,24,26</sup> We discuss here only the final results, which are obtained under different approximations. In the optimized random-phase approximation (ORPA), we get an expression for the radial distribution function  $g(r)$ :

$$\hat{g}_{\text{ORPA}}(\vec{r}_1, \vec{r}_2) = g_{hs}(\vec{r}_1, \vec{r}_2) + \mathcal{C}(\vec{r}_1, \vec{r}_2). \quad (23)$$

The LEXP approximation for  $g(r)$  gives

$$\hat{g}_{\text{LEXP}}(\vec{r}_1, \vec{r}_2) = g_{hs}(\vec{r}_1, \vec{r}_2)[1 + \mathcal{C}(\vec{r}_1, \vec{r}_2)]. \quad (24)$$

A better result can be obtained from the exponential (EXP) approximation

$$\hat{g}_{\text{EXP}}(\vec{r}_1, \vec{r}_2) = g_{hs}(\vec{r}_1, \vec{r}_2) \exp[\mathcal{C}(\vec{r}_1, \vec{r}_2)], \quad (25)$$

where  $g_{hs}(\vec{r}_1, \vec{r}_2)$  is the quantum-mechanical hard-sphere RDF. To calculate the excess Helmholtz free energy, we let

$$\hat{a}(\rho, \beta) = -(\beta\Delta\hat{A}/V) = V^{-1}\hat{H}[\rho, f^{\text{eff}}], \quad (26)$$

and we get

$$\hat{a}_{\text{ORPA}} = a_{hs} + a_{\text{HTA}} + a_{\text{RING}}. \quad (27)$$

A better approximation, known as "ORPA +  $B_2$ " approximation, for  $a$  is

$$\hat{a}_{\text{ORPA}} + B_2 = a_{hs} + a_{\text{HTA}} + a_{\text{RING}} + B_2, \quad (28)$$

where

$$a_{\text{HTA}} = \frac{1}{2} \rho^2 \int d\vec{r} g_{hs}(r) \phi(r), \quad (29)$$

$$a_{\text{RING}} = - \frac{1}{2(2\pi)^3} \int d\vec{k} \{ P(\vec{k}) + \ln[1 - P(\vec{k})] \}, \quad (30)$$

$$B_2 = \frac{1}{2} \rho^2 \int d\vec{r} h_{hs}(r) \frac{1}{2} [\epsilon(r)]^2 + \frac{1}{2} \rho^2 \int d\vec{r} g(r) \sum_{n=3}^{\infty} \frac{1}{n!} [\epsilon(r)]^n, \quad (31)$$

and  $a_{hs}$  is the excess Helmholtz free energy of the quantum-mechanical hard-sphere fluid.

One may expect that the exp approximation for the RDF and the ORPA +  $B_2$  approximation for the excess Helmholtz free energy provide an accurate theory for semiclassical fluids with the non-analytic potential.

#### V. YUKAWA-TAIL FLUID

In this section, we consider the Yukawa-tail fluid and represent the pair interaction by

$$u(r) = \begin{cases} \infty, & r < d, \\ -\epsilon \frac{e^{-z[(r/d)-1]}}{(r/d)}, & r > d, \end{cases} \quad (32)$$

where  $\epsilon$  and  $z$  are constants and  $d$  is the hard-sphere diameter of the molecule. Though unrealistic in certain of its aspects, the Yukawa-tail potential is a very useful model, which takes into account both the attractive and repulsive features of interactions.

We divide the pair potential into two parts: the hard-sphere potential  $u_{hs}(r)$  treated as the reference potential and perturbation  $u_p(r)$ . Thus

$$u(r) = u_{hs}(r) + u_p(r), \quad (33)$$

where

$$u_{hs}(r) = \begin{cases} \infty, & r < d, \\ 0, & r > d, \end{cases} \quad (34)$$

and

$$u_p(r) = - \frac{e^{-z[(r/d)-1]}}{(r/d)}. \quad (35)$$

For the sake of convenience, we take  $z = 1$ .

We take the quantum-mechanical hard-sphere system as the reference system. The RDF for the quantum mechanical hard-sphere system is determined by the exponential approximation, given by Sinha and Singh.<sup>15</sup>

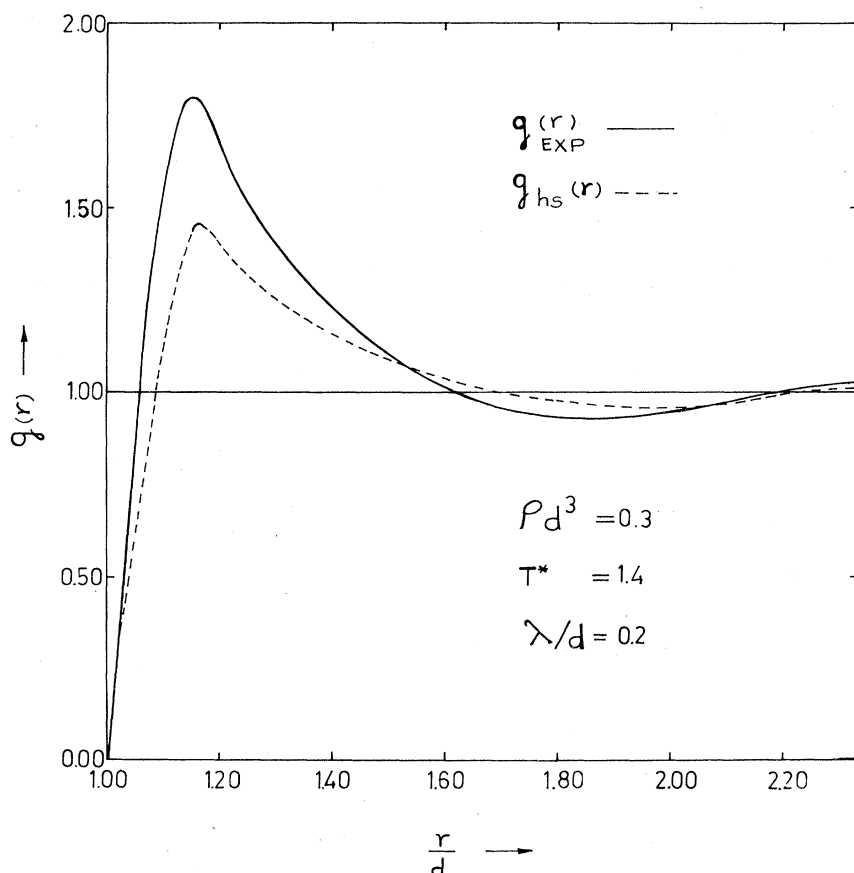


FIG. 1. RDF for a Yukawa-tail fluid in the semiclassical limit at  $\rho d^3 = 0.3$ ,  $\lambda/d = 0.2$ , and  $T^* = 1.4$ .

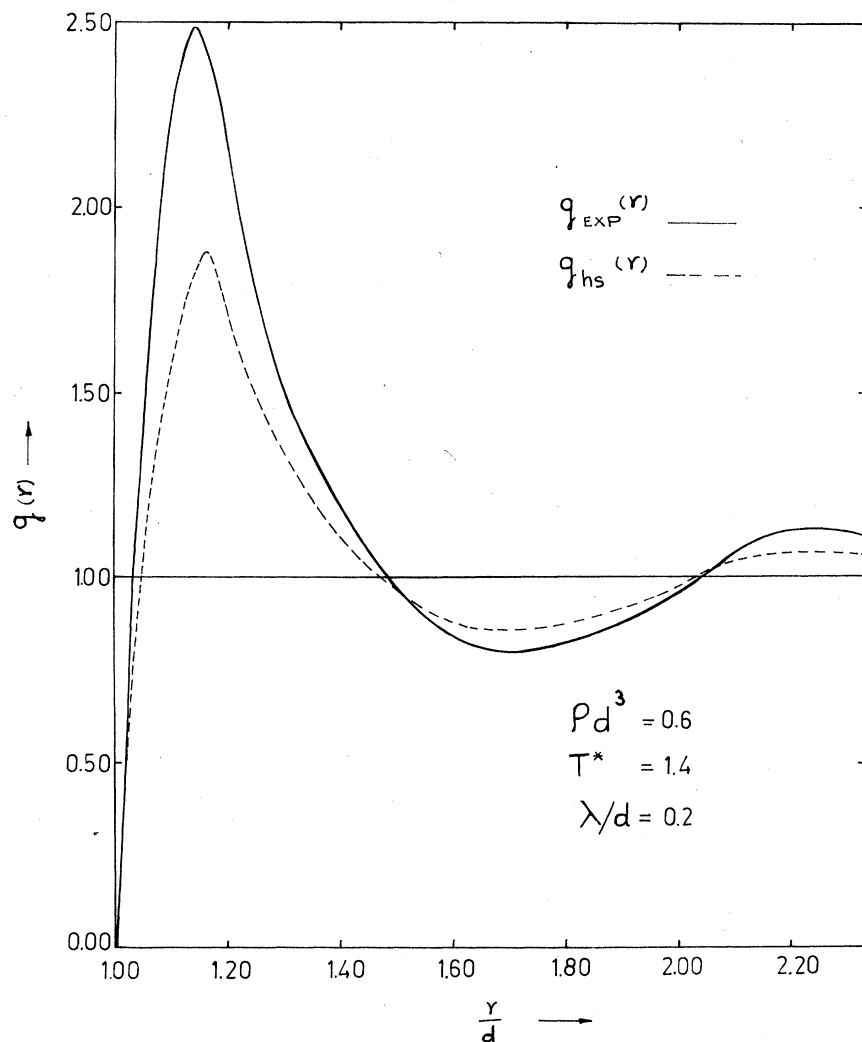


FIG. 2. RDF for a Yukawa-tail fluid in the semiclassical limit at  $\rho d^3 = 0.6$ ,  $\lambda/d = 0.2$ , and  $T^* = 1.4$ .

The values of the RDF obtained from the exp approximation are given in Figs. 1 and 2 for  $\rho d^3 = 0.3$  and  $0.6$ , respectively, at  $\lambda/d = 0.2$ ,  $T^* (= kT/\epsilon) = 1.4$ . The values of the quantum-mechanical hard-sphere RDF are also given in the figures for comparison. On comparison, we find that the effect of the attractive interaction on the RDF at densities  $\rho d^3 \leq 0.6$  is substantial. This is not surprising, because, at moderate

densities  $\rho d^3 \leq 0.6$ , the attractive forces can play a significant role. It is expected that at high density—near the triple point, the contribution of the attractive tail to the structure of liquids is small.<sup>26,27</sup>

In Table I, we give the values of excess Helmholtz free energy. The results, tabulated, demonstrate the effect of the attractive potential on the excess Helmholtz free energy. Unfortunately

TABLE I. Excess Helmholtz free energy  $\beta f$  ( $\equiv -a/\rho$ ) for a Yukawa-tail fluid in semiclassical limit under different approximations.

$\rho d^3$	$\lambda/d$	$kT/\epsilon$	$\beta f_{hs}$	$\beta f_{HTA}$	$\beta f_{RING}$	$\beta f_2$	$\beta f_{ORPA}$	$\beta f_{ORPA + B_2}$
0.30	0.20	1.4	1.0039	-2.7685	-0.0627	-0.0003	-1.8273	-1.8276
0.60	0.20	1.4	2.7630	-5.6668	-0.1580	-0.0371	-3.0618	-3.0989

computer experiments results are not known in this case, we cannot check the accuracy of our calculation.

## VI. DISCUSSION

The purpose of this paper has been to obtain a set of computationally convenient approximations for the structural and thermodynamic properties of the semiclassical fluids of the nonanalytic potential, using quantum-mechanical hard-sphere system as the reference system and the attractive interaction as the perturbation on this hard-sphere system. The basic physical concept, associated with this approach is, that for a dense fluid, the quantum effects are largely determined by the repulsion due to the hard core and attractive interactions play a minor role. The effect

of perturbation is expressed in terms of the "renormalized potential"  $C(\gamma)$ . The "optimization" condition, which in effect makes the renormalized potential as small as possible, is not considered in this paper. It is well known that an unoptimized theory fails for classical systems. However, the theory developed here may be expected to provide an accurate theory for the semiclassical fluids with the nonanalytic potential. Application of this theory to some real fluids will be discussed in future publication.

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