

Equilibrium theory of two-dimensional simple liquids

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Abstract. Using the Wigner-Kirkwood expansion and bare Lennard-Jones (LJ) (12–6) potential, an effective LJ potential is derived, which includes the quantum effects through the expressions of the effective diameter $\bar{\sigma}(T, \lambda)$ and well-depth $\bar{\epsilon}(T, \lambda)$. We use the WCA perturbation theory to calculate the free energy and pressure for the LJ and effective LJ potentials. Simple analytic expressions are given for the reference system and the first order correction calculated. The results are quite good at high density. The quantum effects on the free energy and pressure are also discussed.

Keywords. Helmholtz free energy; equation of state; quantum effects; perturbation theory.

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1. Introduction

The present paper is concerned with the evaluation of equilibrium properties of two-dimensional (2-d) fluids, whose molecules interact via the Lennard-Jones (LJ) (12–6) potential, both in the classical and semiclassical limits. The 2-d LJ (12–6) fluid is often used as a model substance to investigate surface phenomena (Steele 1973, 1974; Dash 1975). While classical fluids have been studied well (Glandt and Fitts 1977, 1978a,b, Henderson 1977; Toxvaerd 1978; Barker *et al* 1981), in the case of quantum fluid, only dilute gas has been studied (Siddon and Schick 1974). However, a dense 2-d quantum fluid has not yet been investigated.

For the semiclassical fluid, we use the Wigner-Kirkwood (wk) expansion method (Wigner 1932, Kirkwood 1933) to develop an effective LJ potential which includes quantum effects. The advantage of this approach is that once the effective pair potential is expressed in the form of the bare potential, the problem can be treated classically.

One of the most successful theory of classical fluids is the perturbation theory proposed by Weeks, Chandler and Andersen (wca) (Weeks *et al* 1971a,b). Success of this theory depends on a correct knowledge of the reference system. Computer simulation values of the radial distribution function (rdf) and thermodynamic properties for the reference system are not available. However, they can be obtained by expanding them about those of the hard disc system, which are available (Henderson 1975, 1977, Chae *et al* 1969; Wood 1970).

The purpose of this paper is two-fold. First, we use the wca perturbation theory to derive analytic expressions for the thermodynamic properties of the 2-d LJ (12–6) fluid. Second, we estimate the quantum effects on the thermodynamic properties of the dense fluid at high temperature.

In §2, we use the wk expansion of the Slater sum and the bare \sqcup (12-6) potential to obtain the effective pair potential, which includes the quantum effects. In §3, we discuss the wca perturbation theory to calculate the free energy and equation of state. In §4, we discuss in detail the reference system. The wca criterion for the diameter d is solved for the 2-d system. Analytic expressions for the pressure and free energy are also reported. Results for both the classical and semiclassical fluids are discussed in §5.

2. Theoretical formalism

We consider a 2-d fluid, whose molecules interact via the (\sqcup) (12-6) potential defined by

$$u(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6], \quad (1)$$

where ε represents the depth of the potential well and σ the diameter of the molecules.

In the semiclassical limit, where the deviation from the classical behaviour is small, the Slater sum W_N can be expressed as (Wigner 1932; Kirkwood 1933)

$$W_N(1, 2, \dots, N) = \exp[-\beta U] \left(1 + \frac{\hbar^2 \beta^2}{24m} \sum_{i=1}^N \{ \beta (\nabla_i U)^2 - 2\nabla_i^2 U \} + O(\hbar^4) \right), \quad (2)$$

where U represents the total potential of the system i.e.

$$U = \sum_{i < j} u(i, j),$$

where $u(i, j)$ is the pair potential between particles i and j . The canonical partition function for the 2-d fluid may be written as

$$Q_N = \frac{1}{N! \lambda^{2N}} \int \dots \int \exp \left[-\beta \sum_{i < j} u^e(i, j) \right] \prod_{i=1}^N d\vec{r}_i, \quad (3)$$

where

$$u^e(i, j) = u(i, j) + \frac{\hbar^2 \beta}{12m} \nabla^2 u(i, j) + O(\hbar^4). \quad (4)$$

The effective pair potential u^e is the function of temperature T and thermal wavelength λ .

We use (4) and the \sqcup potential to obtain the effective pair potential in the form of the \sqcup potential. For the 2-d fluid, (4) can be written as

$$u^e(R) = 4\varepsilon[(R^{-12} - R^{-6}) + \alpha(4R^{-14} - R^{-8})], \quad (5)$$

where

$\alpha = 3\hbar^2 \beta / m\sigma^2$ and $R = r/\sigma$. The effective pair potential can be written in the form of the \sqcup potential by simply replacing $\sigma \rightarrow \hat{\sigma}(T, \lambda)$ and $\varepsilon \rightarrow \hat{\varepsilon}(T, \lambda)$ in (1). In order to derive the expressions for $\hat{\sigma}$, we assume that $\hat{\sigma} = \hat{\sigma}/\sigma$ be the value of R at which $u^e(R)$ is zero i.e. $u^e(\hat{\sigma}) = 0$. Solving (5) for $\hat{\sigma}$, we get

$$\hat{\sigma} = (1 + 3\alpha \hat{\sigma}^{-2})^{1/6}. \quad (6)$$

Equation (6) can be solved by iterative process to obtain $\hat{\sigma}$. To a first approximation we obtain

$$\hat{\sigma} = (1 + X)^{1/6}, \quad (7)$$

where

$$X = 3\alpha = 3\pi^{*2}/4\pi^2 T^* \tag{8}$$

Here $T^* = kT/\epsilon$ is the reduced temperature and $\pi^* = \hbar/\sigma(m\epsilon)^{1/2}$ is the quantum-mechanical parameter. Then the position of the minimum of $u^e(R)$ is shifted from $2^{1/6}$ to $2^{1/6}\hat{\sigma}$. The minimum value of $u^e(R)$ is found to be $-\hat{\epsilon}$, where

$$\hat{\epsilon} = \tilde{\epsilon}/\epsilon = [1 + 2X - (2^{2/3}/3)X(1 + X)^{-1/3}]/(1 + X)^2 \tag{9}$$

Thus the effective pair potential is expressed in the form of the \mathcal{L} potential, where $\tilde{\sigma}$ and $\tilde{\epsilon}$ are functions of T^* and π^* . The values of $\tilde{\sigma}$ and $\tilde{\epsilon}$ for the 2-d fluid Ne with $\pi^* = 0.593$ (de Boer and Bird 1954; Singh and Sinha 1981) are reported in table 1 for various isotherms $T^* = 2.0, 1.5, 1.25, 1.0$ and 0.8 . $\tilde{\sigma}$ increases with decrease of temperature while $\tilde{\epsilon}$ decreases when temperature decreases. We find that the quantum effects make the effective pair potential, both shallower and longer-ranged.

We use this theory to calculate the thermodynamic properties, such as the free energy and pressure of a dense fluid in the semiclassical limit. We consider the reduced density and reduced temperature of a classical \mathcal{L} fluid to be given by

$$\rho^* = \rho\sigma^2, T^* = kT/\epsilon,$$

Then we replace $\rho^* \rightarrow \rho^* \hat{\sigma}^2$ and $T^* \rightarrow T^*/\hat{\epsilon}$. The classical values of the thermodynamic properties at the reduced density $\rho^* \hat{\sigma}^2$ and reduced temperature $T^*/\hat{\epsilon}$ will be the thermodynamic properties of the semiclassical fluid at ρ^* and T^* . Thus the free energy and pressure of the semiclassical fluid can be written as

$$A(\rho^*, T^*, \pi^*) = \hat{A}(\rho^* \hat{\sigma}^2, T^*/\hat{\epsilon}), \tag{10}$$

$$P(\rho^*, T^*, \pi^*) = \hat{P}(\rho^* \hat{\sigma}^2, T^*/\hat{\epsilon}), \tag{11}$$

where $\hat{A}(\rho^* \hat{\sigma}^2, T^*/\hat{\epsilon})$ and $\hat{P}(\rho^* \hat{\sigma}^2, T^*/\hat{\epsilon})$ are respectively, the free energy and pressure of the classical fluid at the reduced density $\rho^* \hat{\sigma}^2$ and reduced temperature $T^{e*} \equiv T^*/\hat{\epsilon}$.

We may expand the pressure in the power of density and obtain an expression for the reduced n th virial coefficient of the semiclassical fluid

$$B_n^*(T^*) = \hat{\sigma}^{2(n-1)} \cdot \hat{B}_n^*(T^{e*}), \tag{12}$$

where $\hat{B}_n^*(T^{e*})$ is the reduced n th virial coefficient of the classical fluid at the reduced temperature T^{e*} .

Table 1. Values of parameters for the two-dimensional \mathcal{L} (12-6) fluid Ne.

T^*	$\hat{\sigma}$	$\hat{\epsilon}$	d_B^*		δ	
			$\pi^* = 0$	$\pi^* = 0.593$	$\pi^* = 0$	$\pi^* = 0.593$
2.00	1.00657	0.97916	0.98833	0.98743	0.00235	0.00237
1.50	1.00872	0.97238	1.00012	0.99899	0.00203	0.00206
1.25	1.01041	0.96701	1.00724	1.00595	0.00184	0.00188
1.00	1.01294	0.95906	1.01566	1.01407	0.00163	0.00167
0.80	1.01604	0.94927	1.02357	1.02174	0.00143	0.00148

3. Perturbation expansion

We use the WCA perturbation theory to calculate the thermodynamic properties of the fluids. We divide the pair potential $\phi(r)$ (which is either $u_{\text{LJ}}(r)$ or $u_{\text{eLJ}}^{\epsilon}(r)$) into two parts

$$\phi(r) = \phi_0(r) + \phi_p(r), \quad (13)$$

where $\phi_0(r)$, which contains the repulsive part of the potential, is treated as a reference and $\phi_p(r)$, which contains the attractive part of the potential, is the perturbation. According to the WCA scheme (Weeks *et al* 1971), we write

$$\begin{aligned} \phi_0(r) &= \phi(r) + \varepsilon, & r < r_m \\ &= 0, & r > r_m \end{aligned} \quad (14)$$

and

$$\begin{aligned} \phi_p(r) &= -\varepsilon & r < r_m \\ &= \phi(r) & r > r_m, \end{aligned} \quad (15)$$

where ε is the depth of the potential at r_m .

Using this division of the potential, the free energy per particle is given by

$$f = f_0 + f_1 + \dots, \quad (16)$$

where f_0 is the free energy per particle of the reference system and f_1 is the first order correction to it. Thus

$$f_1 = \frac{1}{2}\rho \int g_0(r)\phi_p(r)d\bar{r}, \quad (17)$$

where $g_0(r)$ is the radial distribution function (RDF) of the reference system and ρ is the number density.

Other thermodynamic properties can be calculated using (16). Then the equation of state $P/\rho kT \equiv Z$ is given by

$$Z = Z_0 + Z_1 + \dots, \quad (18)$$

where Z_0 is the compressibility factor for the reference system and Z_1 is the first order correction to it. Thus

$$Z_1 = \beta\rho(\partial f_1/\partial\rho)_\beta. \quad (19)$$

The pressure of the 2-d fluid is also given through the virial equation of state (Glandt and Fitts 1977)

$$Z = 1 - \frac{1}{4}\beta\rho \int g(r)r \frac{\partial\phi(r)}{\partial r} d\bar{r}. \quad (20)$$

According to the WCA scheme (Weeks *et al* 1971a), the RDF $g(r)$ of the system is approximated by that of the reference system $g_0(r)$. Then (20) is approximated as

$$Z^A = 1 - \frac{1}{4}\beta\rho \int g_0(r)r \frac{\partial\phi(r)}{\partial r} d\bar{r}. \quad (21)$$

Using (13) in (21) we get

$$Z^A = Z_0 + Z_1, \quad (22)$$

where

$$Z_0 = 1 - \frac{1}{4}\beta\rho \int g_0(r)r \frac{\partial \phi_0(r)}{\partial r} d\bar{r} \quad (23)$$

is the virial equation of state for the reference system and

$$Z_1^A = -\frac{1}{4}\beta\rho \int g_0(r)r \frac{\partial \phi_p(r)}{\partial r} d\bar{r} \quad (24)$$

is the first order correction to the virial equation of state.

4. Thermodynamic properties of the reference system

The thermodynamic properties for the 2-d fluid with the reference potential (14) are not available. We use the WCA approximation (Weeks *et al* 1971) and write RDF $g_0(r)$ for the reference system as

$$\hat{g}_0(r) = \exp[-\beta\phi_0(r)]Y_{hd}(r/d), \quad (25)$$

where $Y_{hd}(r/d)$ is the function for the hard-disc system.

We use (25) to calculate the RDF of the reference fluid. For $r > d$, the Monte Carlo results (Chae *et al* 1969; Wood 1970) of $Y_{hd}(r/d)$ are used. It may, however, be noted that one needs to know $Y_{hd}(r/d)$ for $r \leq d$ i.e. inside the hard core. There are no machine simulation results for it. Chae *et al* (1969) gave the following expression from the solution of the modified Born-Green-Yvon (BDYN) integral equation

$$Y_{hd}(r/d) = g_{hd}(1) \exp \left[2(\rho d^2)g_{hd}(1) \left\{ \cos^{-1}(r/2d) - \frac{1}{4}(r/d)(4 - (r/d)^2)^{1/2} - \frac{\pi}{3} + \frac{\sqrt{3}}{4} \right\} \right] \quad \text{for } r \leq d. \quad (26)$$

We use (26) for the value of $Y_{hd}(r/d)$ for $r \leq d$ in our calculations.

The WCA criterion is followed (Weeks *et al* 1971) to determine d . Thus the hard-disc diameter can be determined from the condition

$$\int_0^\infty \{ \exp[-\beta\phi_0(r)] - \exp[-\beta u_{hd}(r)] \} Y_{hd}(r/d) r dr = 0. \quad (27)$$

We follow the method of Verlet and Weis (1972a, b) to obtain an expression of d and it is found that

$$d = d_B \left(1 + \frac{\sigma_1}{2\sigma_0} \delta \right), \quad (28)$$

where,

$$d_B = \int_0^\infty (1 - \exp[-\beta\phi_0(r)]) dr, \quad (29)$$

$$\delta = \int_0^\infty \left(\frac{r}{d_B} - 1 \right)^2 \frac{d}{dr} \{ \exp[-\beta\phi_0(r)] \} dr. \quad (30)$$

d_b and δ are functions of the temperature only and are identical to those of the 3-d system. For the 2-d system σ_0 and σ_1 are derived using the modified BGYM expression of $Y_{hd}(r)$ for $r < d$. They are given in Appendix ((A.5) and (A.6)).

The values of d_b^* and δ for classical fluid ($\pi^* = 0$) and Ne ($\pi^* = 0.593$) are given in table 1 for the isotherms $T^* = 2.0, 1.5, 1.25, 1.0$ and 0.8 . We find that the quantum effects decrease d_b^* and increase δ . Since δ is a very small factor, the hard disc diameter d^* given by (28) decreases with increase of quantum parameter π^* .

When $g_0(r)$, the RDF of the reference system of (23), is approximated by $\hat{g}_0(r)$ defined by (25), the virial pressure of the reference system becomes equal to the pressure obtained by differentiating the free energy. Then the equation of state of the reference system is given by

$$\hat{Z}_0 = 1 + 2\eta \int_0^\infty dr \frac{r^2}{d^2} Y_{hd}(r/d) \delta \phi_0(r), \quad (31)$$

where

$$\delta \phi_0(r) = \frac{d}{dr} \{ \exp[-\beta \phi_0(r)] \}.$$

Equation (31) can be evaluated to give

$$\hat{Z}_0 = Z_{hd}(\eta) + 2\delta \Delta Z, \quad (32)$$

where Z_{hd} is the compressibility factor for the hard-disc fluid and

$$\Delta Z = \eta \left(\frac{\tau_2}{2} - \frac{\sigma_1}{2\sigma_0} \tau_1 \right). \quad (33)$$

τ_1 and τ_2 are functions of η and are given in Appendix ((A.9) and (A.10)). The equation of state for the hard-disc fluid is given by (Henderson 1975)

$$Z_{hd} = (1 + \eta^2/8)/(1 - \eta)^2, \quad (34)$$

where $\eta = \pi \rho d^2/4$. This provides good results at low and intermediate densities but is not so good at higher density. It has been further modified as (Glandt and Fitts 1977).

$$Z_{hd} = \frac{1 + 0.128\eta^2}{(1 - \eta)^2} - \frac{0.043\eta^3}{(1 - \eta)^3}, \quad (35)$$

which closely agrees with the machine simulation results at all densities. The main contribution to \hat{Z}_0 comes from Z_{hd} which is calculated using (35). The correction term which is multiplied by the very small factor δ , plays only a little role.

Using the relation

$$\beta f_0 = \int_0^\eta (\hat{Z}_0 - 1) \frac{d\rho}{\rho}, \quad (36)$$

the excess free energy of the reference system is given by

$$\beta f_0 = \beta f_{hd}^{ex} + 2\delta \beta \Delta f, \quad (37)$$

where

$$\beta f_{hd}^{ex} = \int_0^\eta (Z_{hd} - 1) \frac{d\eta}{\eta} \quad (38)$$

is the excess free energy of the hard disc fluid and

$$\beta \Delta f = \int_0^\eta \Delta Z \frac{d\eta}{\eta} - \delta^{-1} \int_0^\eta (\hat{Z}_0 - 1) \frac{\partial \log d}{\partial \eta} d\eta. \quad (39)$$

Using (35) and (38), the expression for f_{hd}^{ex} is given by

$$\begin{aligned} \beta f_{hd}^{ex} = & -1.1925 - 0.743 \ln(1 - \eta) - 0.043(1 - \eta) \\ & + \frac{1.257}{(1 - \eta)} - \frac{0.0215}{(1 - \eta)^2}. \end{aligned} \quad (40)$$

The explicit expression for Δf is given in the Appendix (A.13).

Using (17) and (25), the first order correction to the free energy is given by

$$\begin{aligned} \hat{f}_1 = & \pi \rho \int_d^\infty dr r \phi_p(r) Y_{hd}(r/d) \\ = & \pi \rho \left[\int_d^\infty dr r \phi(r) Y_{hd}(r/d) \right. \\ & \left. - \int_d^{r_m} (\phi(r) + \varepsilon) Y_{hd}(r/d) \right]. \end{aligned} \quad (41)$$

These integrals can be evaluated numerically using the Monte Carlo values (Chae *et al* 1969, Wood 1970) of $Y_{hd}(X)$.

The first order correction to the compressibility factor is calculated by

$$\hat{Z}_1 = \beta \rho (\partial \hat{f}_1 / \partial \rho)_\beta, \quad (42)$$

5. Thermodynamic properties of LJ fluids

5.1 Classical system

In this section we consider the classical fluid whose molecules interact via the LJ potential. The compressibility factor for the fluid is calculated using (18) and (22). Both these equations include the same compressibility factor ((32)) of the reference system but have different expressions for the first order perturbation correction. The values of \hat{Z} and \hat{Z}^A obtained using (18) and (22) respectively are reported in table 2 and compared with Monte Carlo results. Comparison shows a superiority of \hat{Z} over \hat{Z}^A , particularly in the high density region.

5.2 Semiclassical system

This section is concerned with the evaluation of thermodynamic properties of the semiclassical fluid, such as Ne, where the quantum effect is small but not negligible (see, for example, Hansen and Weis 1969).

We have calculated the compressibility factor and excess free energy per particle for the 2-d fluid Ne at different temperatures and densities using (18) and (16) respectively. The compressibility factor and free energy per particle for the reference system are obtained from (32) and (37) respectively.

Table 2. Equation of state Z for classical two-dimensional LJ (12-6) fluid.

T^*	ρ^*	\hat{Z}	\hat{Z}^A	Z_{MC}
2.00	0.60	2.361	2.351	2.301
	0.70	3.133	3.412	3.242
	0.75	3.985	4.215	3.902
	0.80	4.936	5.272	4.759
1.50	0.60	2.053	2.094	2.059
	0.70	2.912	3.226	3.025
	0.75	3.794	4.134	3.800
	0.80	4.886	5.342	4.784
1.25	0.60	1.773	1.861	1.838
	0.70	2.741	3.077	2.762
	0.75	3.571	4.013	3.588
	0.80	4.802	5.333	4.605
1.00	0.50	1.186	0.809	1.112
	0.60	1.314	1.476	1.487
	0.70	2.322	2.702	2.309
	0.75	3.180	3.765	3.127
	0.80	4.576	5.243	4.420
0.80	0.50	0.806	0.339	0.728
	0.60	0.703	0.953	0.957
	0.70	1.759	2.225	1.967
	0.80	2.634	3.377	2.661

We examine the quantum effects on the thermodynamic properties of the reference system and their first order perturbation correction. At high density the quantum effect mainly influences the reference part and its effect on the perturbation correction is small. For example for Ne ($\pi^* = 0.593$) at $T^* = 2.00$, $\rho^* = 0.75$, the quantum corrections to Z_0 and Z_1 are 2.93% and 1.18% respectively. The quantum corrections increase with increase of density and decrease of temperature. In table 3, the compressibility factor \hat{Z} and the excess free energy per particle βf for the 2-d fluid Ne are compared with their classical values obtained under the same approximation. It is found that the quantum effect, which increases the pressure and free energy, increases with increase of density and decrease in temperature.

6. Concluding remarks

Using the wk expansion and bare LJ potential, we have obtained the effective LJ potential, where $\tilde{\sigma}(T^*, \pi^*)$ and $\tilde{\epsilon}(T^*, \pi^*)$ are functions of temperature T and quantum parameter π^* .

We have used the wca perturbation theory to calculate the free energy and pressure for the effective LJ fluids. Approximations have been made to obtain the compressibility factor and free energy for the reference system and first order correction to them. The results for the compressibility factor are shown to be very satisfactory at high density. At low density the agreement is not so good. This is expected mainly due to the slow

Table 3. Equation of state Z and excess free energy per particle βf for the two-dimensional LJ (12-6) fluid.

T^*	ρ^*	Z		βf	
		$\pi^* = 0$	$\pi^* = 0.593$	$\pi^* = 0$	$\pi^* = 0.593$
2.00	0.55	2.105	2.156	0.515	0.542
	0.60	2.361	2.412	0.623	0.654
	0.65	2.613	2.695	0.739	0.776
	0.70	3.133	3.284	0.874	0.920
	0.75	3.985	4.167	1.048	1.105
	0.80	4.936	5.272	1.268	1.337
1.50	0.55	1.873	1.941	0.308	0.348
	0.60	2.053	2.122	0.392	0.438
	0.65	2.280	2.417	0.483	0.536
	0.70	2.913	3.156	0.597	0.664
	0.75	3.794	4.159	0.758	0.842
	0.80	4.886	5.311	0.968	1.074
1.25	0.55	1.661	1.791	0.135	0.205
	0.60	1.773	1.857	0.197	0.254
	0.65	1.991	2.186	0.265	0.332
	0.70	2.742	3.009	0.360	0.446
	0.75	3.571	3.929	0.506	0.613
	0.80	4.802	5.354	0.705	0.842
1.00	0.55	1.313	1.407	-0.135	-0.069
	0.60	1.314	1.430	-0.107	-0.033
	0.65	1.535	1.840	-0.077	0.012
	0.70	2.322	2.710	-0.012	0.105
	0.75	3.180	3.729	0.378	0.252
0.80	0.55	0.841	0.939	-0.482	-0.394
	0.60	0.703	0.875	-0.501	-0.405
	0.65	0.982	1.411	-0.521	-0.400
	0.70	1.759	2.252	-0.497	-0.338
	0.75	2.634	3.469	-0.419	-0.218

convergence of the perturbation series at low density. In retrospect we find that the WCA theory is less successful in 2-d than it is in 3-d, because the WCA theory works well at high density, where molecules are pushed closer together. However, the number of molecules forming a closed packing in 2-d is less than in 3-d. That is why the agreement with the MC results is not so good in 2-d as in 3-d. The results may be improved by using a mixed perturbation scheme; in which the first order term of the free energy is calculated exactly and the remainder of the series is treated using the density expansion of the free energy.

The effective pair potential, derived here, includes only the first order quantum correction. One can improve the results by including the higher order quantum corrections to define the effective pair potential. However, it is not attempted here. The present theory is expected to be suitable at high temperature, where the quantum effects are small.

Appendix**1 Calculation of σ_0 and σ_1**

Following the method of Verlet and Weis (1972) and using (26), we obtain the following expressions for σ_0 , σ_1 and σ_2

$$\sigma_0 = \frac{\partial}{\partial X} [XY_{hd}(X)]_{X=1} = g_{hd}(1), \quad (\text{A.1})$$

$$\begin{aligned} \sigma_1 &= \frac{\partial^2}{\partial X^2} [XY_{hd}(X)]_{X=1} \\ &\equiv \sigma_0 - \frac{4 \cdot 3^{1/2}}{\pi} \eta \sigma_0^2, \end{aligned} \quad (\text{A.2})$$

$$\begin{aligned} \sigma_2 &= \frac{\partial^3}{\partial X^3} [XY_{hd}(X)]_{X=1} \\ &= -\frac{20 \cdot 3^{1/2}}{3\pi} \eta \sigma_0^2 + \frac{48}{\pi^2} \eta^2 \sigma_0^3. \end{aligned} \quad (\text{A.3})$$

The hard-disc RDF at the core, $g_{hd}(1)$, is obtained using (34) in the relation

$$Z_{hd} = 1 + 2\eta g_{hd}(1). \quad (\text{A.4})$$

Thus we obtain the following expressions

$$\sigma_0 = \left(1 - \frac{7}{16}\eta\right) / (1 - \eta)^2, \quad (\text{A.5})$$

$$\sigma_1 = \sigma_0 \left(\frac{1 - 4.205316\eta + 1.964826\eta^2}{(1 - \eta)^2} \right), \quad (\text{A.6})$$

$$\sigma_2 = -2.940421 \sigma_0^2 \left(\frac{1 - 3.653987\eta + 1.723619\eta^2}{(1 - \eta)^2} \right). \quad (\text{A.7})$$

Since the correction term is small, we have used (34) to derive these coefficients.

2. Calculation of ΔZ

Using a Taylor series expression of $X^2 Y_{hd}(X)$ about $X = 1$, we obtain for the coefficients

$$\tau_0 = \sigma_0, \quad (\text{A.8})$$

$$\tau_1 = \frac{\partial}{\partial X} [X^2 Y_{hd}(X)]_{X=1} = \sigma_0 + \sigma_1 = 2\sigma_0 - \frac{4 \cdot 3^{1/2}}{\pi} \eta \sigma_0^2 \quad (\text{A.9})$$

$$\begin{aligned} \tau_2 &= \frac{\partial^2}{\partial X^2} [X^2 Y_{hd}(X)]_{X=1} = 2\sigma_1 + \sigma_2 \\ &= 2\sigma_0 - \frac{44 \cdot 3^{1/2}}{3\pi} \eta \sigma_0^2 + \frac{48}{\pi^2} \eta^2 \sigma_0^3. \end{aligned} \quad (\text{A.10})$$

Substituting these values in (33), we obtain an expression for ΔZ

$$\Delta Z = -0.735105 \eta^2 \frac{\left(1 - \frac{7}{16} \eta\right)^2}{(1 - \eta)^4}. \quad (\text{A.11})$$

3. Calculation of Δf

Using (28), (32), (33) (A.4), (39) can be written as

$$\beta \Delta f = \int_0^\eta \left[\frac{\tau_2}{2} - \frac{\sigma_1}{2\sigma_0} \tau_1 - 2\eta\sigma_0 \frac{\partial}{\partial \eta} (\sigma_1/2\sigma_0) \right] d\eta. \quad (\text{A.12})$$

Substituting the value of $\sigma_0, \sigma_1, \tau_1$ and τ_2 , it can be solved to give

$$\begin{aligned} \beta \Delta f = & 0.140704 [\ln(1 - \eta) - \eta(1 - 8.948980\eta \\ & + 7.530612\eta^2 - 0.988776\eta^3)/(1 - \eta)^4]. \end{aligned} \quad (\text{A.13})$$

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