

## First order quantum correction to the free energy of simple liquids

S K DATTA

Department of Physics, Jalpaiguri Govt. Engg. College, Jalpaiguri 735 102, India

MS received 14 November 1984; revised 10 June 1985

**Abstract.** Using the perturbation theory of Weeks *et al* the first order quantum correction to the free energy of a simple fluid characterised by a double Yukawa potential function has been expressed in a simple closed analytical form which allows numerical calculation simply on a desk calculator.

**Keywords.** Quantum correction; double Yukawa potential; radial distribution function; perturbation theory.

PACS No. 61-20

### 1. Introduction

The derivation of equilibrium properties of simple dense fluids in closed analytical form has gained much importance after the work of Verlet and Weis (1972a, b). Recently the thermodynamics and structure of simple fluids in a fully analytic form have been derived (Datta 1983) where the perturbation theory of Weeks *et al* (1971) (hereafter termed wca) has been utilised and the simple fluids characterized by a double Yukawa (DY) potential function (suggested by Foiles and Ashcroft 1981) with parameters adjusted to fit closely a Lennard–Jones (LJ) potential function. The DY potential is given by

$$\phi_{\text{DY}}(r) = \frac{E}{r/\sigma} \{ \exp[-a(r/\sigma - 1)] - \exp[-b(r/\sigma - 1)] \}, \quad (1)$$

where  $E = 2.0199\epsilon$ ,  $a = 14.735$ ,  $b = 2.6793$ , and  $\epsilon$  and  $\sigma$  are the parameters of the LJ potential.

In the present paper we derive a closed-form analytical expression for the first order quantum correction to the free energy of a simple fluid characterised by the DY potential function utilising the wca perturbation theory. It is well known that the  $\hbar^2$  correction to the free energy for an analytic potential is given by

$$\beta f = \beta f^{\text{cl}} + \frac{\hbar^2 \rho}{(k_B T)^2 24\pi m} \int_0^\infty \nabla^2 \phi(r) g^{\text{cl}}(r) r^2 dr + \dots, \quad (2)$$

where  $m$  is the mass of an atom and  $g^{\text{cl}}(r)$  is the radial distribution function (RDF) of the classical system (*i.e.*  $\hbar \rightarrow 0$ ,  $m \rightarrow \infty$ )  $\beta = 1/k_B T$ ,  $k_B$  the Boltzmann constant and  $T$  the absolute temperature.

In WCA perturbation theory the pair potential  $\phi(r)$  is divided as

$$\phi(r) = \phi_0(r) + \phi_1(r), \quad (3)$$

where  $\phi_0(r)$  and  $\phi_1(r)$  are the reference (repulsive) part and the perturbation (attractive) part respectively of the pair potential. These are given by

$$\begin{aligned} \phi_0(r) &= \phi(r) + \varepsilon & r \leq r_m, \\ &= 0 & r > r_m, \end{aligned} \quad (4)$$

$$\begin{aligned} \phi_1(r) &= -\varepsilon & r \leq r_m, \\ &= \phi(r) & r > r_m, \quad r_m = 2^{1/6}\sigma. \end{aligned} \quad (5)$$

We now proceed to calculate separately the contributions of the reference part and the attractive part of the potential to the integral in (2).

## 2. Calculation of the reference part contribution

To calculate the contribution of the reference part to the integral in (2) we approximate the RDF of the actual fluid by that of the reference fluid system *i.e.* we assume  $g^{cl}(r) \rightarrow g_0(r)$  which is valid at the high density range of the fluid. With this choice the form of the integral in (2) may be rewritten as

$$I_{\text{ref}} = \int_0^\infty \nabla^2 \phi_0(r) g^{cl}(r) r^2 dr \rightarrow \int_0^\infty \nabla^2 \phi_0(r) g_0(r) r^2 dr, \quad (6)$$

Again the WCA approximation for the RDF  $g_0(r)$  is given by

$$g_0(r) = Y_d(r) \exp[-\beta\phi_0(r)], \quad (7)$$

where  $Y_d(r)$  is the reduced pair correlation function of a hard sphere fluid of diameter  $d$ . It is defined as

$$Y_d(r) = g_d(r) \exp[\beta\phi_d(r)], \quad (8)$$

$g_d(r)$  being the hard sphere  $g(r)$  and  $d$  is chosen so that

$$\int_0^\infty Y_d(r) \{ \exp[-\beta\phi_0(r)] - \exp[-\beta\phi_d(r)] \} dr = 0. \quad (9)$$

We note that

$$\frac{d^2\phi_0}{dr^2} \exp[-\beta\phi_0] = -\frac{1}{\beta} \frac{d}{dr} [\delta\phi_0(r)] - \frac{d\phi_0}{dr} \delta_{\phi_0}(r) \quad (10)$$

where the sharp peaked function

$$\delta_{\phi_0}(r) = \frac{d}{dr} \{ \exp[-\beta\phi_0(r)] \} \quad (11)$$

behaves like a delta function around  $r = d$ . The integral in (6) may then be separated as

$$I_{\text{ref}} = \int_0^\infty \left( \frac{d^2\phi_0}{dr^2} + \frac{2}{r} \frac{d\phi_0}{dr} \right) Y_d(r) \exp[-\beta\phi_0(r)] r^2 dr$$

$$\begin{aligned}
 &= -\frac{2d}{\beta} \int_0^\infty (r/d) Y_d(r/d) \delta_{\phi_0}(r) dr - \frac{d^2}{\beta} \int_0^\infty (r/d)^2 Y_d(r/d) \frac{d}{dr} [\delta_{\phi_0}(r)] dr \\
 &\quad - d^2 \int_0^\infty (r/d)^2 Y_d(r/d) \frac{d\phi_0}{dr} \delta_{\phi_0}(r) dr.
 \end{aligned}
 \tag{12}$$

We now expand  $(r/d) Y_d(r/d)$  and  $(r/d)^2 Y_d(r/d)$  around  $r = d$  as

$$(r/d) Y_d(r/d) = \alpha_0 + \alpha_1(r/d - 1) + \frac{\alpha_2}{2}(r/d - 1)^2 + \dots
 \tag{13}$$

$$(r/d)^2 Y_d(r/d) = \sigma_0 + \sigma_1(r/d - 1) + \frac{\sigma_2}{2}(r/d - 1)^2 + \dots
 \tag{14}$$

where in the Percus and Yevick 1958 (hereafter termed PY) approximation the parameters  $\alpha_0, \alpha_1, \alpha_2, \sigma_0, \sigma_1$  and  $\sigma_2$  are given by

$$\begin{aligned}
 \alpha_0 &= \frac{1 + \eta/2}{(1 - \eta)^2}, & \alpha_1 &= \frac{1 - 5\eta - 5\eta^2}{(1 - \eta)^3}, & \alpha_2 &= \frac{-3\eta(2 - 4\eta - 7\eta^2)}{(1 - \eta)^4} \\
 \sigma_0 &= \alpha_0, & \sigma_1 &= \alpha_1 + \alpha_0, & \sigma_2 &= 2\alpha_1 + \alpha_2.
 \end{aligned}
 \tag{15}$$

We again expand  $d\phi_0/dr$  in a Taylor series around its value at  $r = d$  as

$$\frac{d\phi_0}{dr} = \phi'_0(d) + (r - d)\phi''_0(d) + \frac{1}{2}(r - d)^2\phi'''_0(d) + \dots,
 \tag{16}$$

where  $\phi'_0(d), \phi''_0(d)$  and  $\phi'''_0(d)$  are respectively the first, second and the third derivatives of  $\phi_0(r)$  at  $r = d$ . Finally with the hard sphere diameter  $d$  determined by the WCA criterion (9), using the expansions of  $(r/d) Y_d(r/d)$  and  $(r/d)^2 Y_d(r/d)$  and utilising the properties of delta function it can be very easily shown that the integral in (12) reduces to

$$\begin{aligned}
 I_{\text{ref}} &= d \left[ dk_B T g'_d(d) - g_d(d) d\phi'_0(d) - \frac{\delta}{2} \left\{ \sigma_0 d^3 \phi'''_0(d) + \sigma_1 d^2 \phi''_0(d) \right. \right. \\
 &\quad \left. \left. + \left( \sigma_2 - \frac{\sigma_1^2}{\sigma_0} \right) d\phi'_0(d) \right\} - k_B T \delta \alpha_2 \left\{ 1 + \frac{\sigma_1}{2\sigma_0} \right\} \right],
 \end{aligned}
 \tag{17}$$

where  $g_d(d)$  and  $g'_d(d)$  are respectively the value and the derivative of hard sphere  $g_d(r)$  evaluated at  $r$  slightly greater than  $d$ .  $\delta$  the function of temperature alone is defined as (Verlet and Weis 1972a).

$$\delta = \frac{d}{d_B} \int_0^\infty \left( \frac{r}{d} - 1 \right)^2 \delta_{\phi_0}(r) dr \simeq \int_0^\infty \left( \frac{r}{d_B} - 1 \right)^2 \delta\phi_0(r) dr,
 \tag{18}$$

where

$$d_B = \int_0^\infty \{ 1 - \exp[-\beta\phi_0(r)] \} dr.
 \tag{19}$$

In the above derivation we have assumed that all terms involving  $\delta^n, n \geq 2$  are negligibly small. The contribution of the last term in (17) involving  $\delta$  is however extremely small.

In the PY approximation the values of  $g_d(d)$  and  $g'_d(d)$  are given by (Lebowitz 1964)

$$g_d(d) = \sigma_0 = \frac{1 + \eta/2}{(1 - \eta)^2} \quad \text{and} \quad g'_d(d) = -\frac{9\eta(1 + \eta)}{2(1 - \eta)^3}. \quad (20)$$

The value of  $g_d(d)$  can however be correctly determined from the semi-empirical hard sphere equation of state obtained by Carnahan and Starling (1969) while the values of  $g'_d(d)$ ,  $\sigma_1$  and  $\sigma_2$  can be accurately obtained from the semi-empirical hard sphere RDF derived by vw (1972a, b).

### 3. Calculation of the attractive contribution

The contribution of the attractive part of the PY potential to the integral in (2) can be readily expressed in a closed form manner. Using the fact that  $Y_d(r) = g_d(r)$  for  $r > d$ , our desired integral reduces to [Hansen and McDonald 1976]

$$I_{\text{att}} = E \int_{r_m}^{\infty} (r/\sigma) g_d(r) \{a^2 \exp[-a(r/\sigma - 1)] - b^2 \exp[-b(r/\sigma - 1)]\} dr \quad (21)$$

and in the PY approximation this can be expressed as

$$I_{\text{att}} = E\sigma c^2 [a^2 \exp[a] \{G(ac) - F(a)\} - b^2 \exp[b] \{G(bc) - F(b)\}], \quad (22)$$

where  $G(z)$  is the Laplace transform of  $rg_d^{\text{PY}}(r)$  already derived by Wertheim (1964) and is given by

$$G(z) = \frac{zL(z)}{12\eta\{L(z) + S(z) \exp[z]\}}, \quad (23)$$

$$L(z) = [(1 + \eta/2)z + (1 + 2\eta)]12\eta, \quad (24)$$

$$S(z) = (1 - \eta)^2 z^3 + 6\eta(1 - \eta)z^2 + 18\eta^2 z - 12\eta(1 + 2\eta). \quad (25)$$

Again  $F(z)$  is given by

$$\begin{aligned} F(z) = & \frac{A}{zc} \left( \exp[-zc] - \exp[-zcx_m] \right) + \frac{B}{zc} \left[ \left( 1 + \frac{1}{zc} \right) \exp[-zc] \right. \\ & \left. - \left( x_m + \frac{1}{zc} \right) \exp[-zcx_m] \right] + \frac{C}{zc} \left[ \left( 1 + \frac{2}{zc} + \frac{2}{(zc)^2} \right) \exp[-zc] \right. \\ & \left. - \left( x_m^2 + \frac{2x_m}{zc} + \frac{2}{(zc)^2} \right) \exp[-zcx_m] \right] \end{aligned} \quad (26)$$

where  $x_m = r_m/d$ ,  $c = d/\sigma$ ,  $d(\rho, T)$  is the wCA diameter.

$$A = \alpha_0 - \alpha_1 + \frac{\alpha_2}{2}, \quad B = \alpha_1 - \alpha_2 \quad \text{and} \quad C = \alpha_2/2. \quad (27)$$

However to get the correct value of the integral in (21) we can utilise the vw expression for  $g_d(r)$  as given by Jedrijezek and Mansoori (1979).

Finally, the  $h^2$  correction term is given by

$$\frac{h^2}{(k_B T)^2 24 \pi m} (I_{\text{ref}} + I_{\text{att}}). \tag{28}$$

Using the wca perturbation theory we are thus able to obtain the first order quantum correction to the free energy of the simple liquid in a fully analytic form which allows numerical calculation simply on a desk calculator.

Mandel (1972) calculated the integral in (2) using the LJ potential and the wca prescription and found that the wca formalism worked surprisingly well. Since the earlier work was done for the LJ potential, utilising the present closed form analytical expression the values of Laplacian  $\langle \nabla^2 \phi \rangle^*$  (defined as

$$\frac{\epsilon}{\sigma^2} \langle \nabla^2 \phi \rangle^* = 4 \pi \rho \int_0^\infty \nabla^2 \phi(r) g^{cl}(r) r^2 dr$$

have been calculated using both the DY and LJ potentials. All the calculations in this paper have been done using PY values of  $g_d(r, \eta)$ . The calculated values are shown in table 1 along with the results of Mandel and the molecular dynamics (MD) results of Verlet (1967). The contribution of the attractive part of the LJ potential to the integral in (2) being difficult to express analytically has been approximated by the DY attractive part contribution. This replacement however entails very small error.

The wca diameters have been calculated in the way suggested by Meyer *et al* (1980) using PY values of  $Y$  given by

$$Y = \left. \frac{\partial \ln g_d(r, \eta)}{\partial \ln r} \right|_{r=d+0} = - \frac{9\eta(1+\eta)}{2(1-\eta)(1-\eta/2)} \tag{29}$$

**Table 1.** Values of the Laplacian  $\langle \nabla^2 \phi \rangle^*$  as a function of density and temperature.

$\rho^*$	$T^*$	Present work		Work of Mandel	
		DY-WCA	LJ-WCA	LJ-WCA	LJ-MD
0.65	0.900	501	491	496	499
0.65	1.036	542	531	535	552
0.75	0.827	670	658	661	634
0.75	0.881	693	679	682	677
0.75	1.071	771	753	752	739
0.85	0.658	833	820	824	787
0.85	0.719	869	854	856	816
0.85	0.786	907	891	891	854
0.85	0.880	961	941	937	902
0.85	1.128	1093	1065	1055	1032
0.85	1.214	1136	1105	1078	1075
0.85	2.202	1585	1523	1486	1483
0.88	0.940	1095	1070	1062	1027
0.88	1.095	1184	1153	1140	1118

MD, molecular dynamics

The values of  $\delta$  have been taken from the work of vw (1972a, interpolated from table 12 contained therein). Again the same  $d$  and  $\delta$  (calculated for LJ potential) have been utilised also for the DY potential calculations.

An inspection of table 1 shows that the present results for the LJ potential are almost exactly identical to that of Mandel. Some deviations between the two sets of results appear with the rise of temperature. This is evident because with the rise of temperature the contributions of the terms involving

$$\varepsilon_1 = \int_0^\infty \left(\frac{r}{d} - 1\right)^3 \delta_{\phi_0}(r) dr$$

and of higher order terms also become significant. However, most of the deviations between the present result and that of Mandel can be accounted for by including only the first order term in  $\varepsilon_1$ . This term can be obtained in the following way. If we introduce one more term in the vw expression for wCA diameter as

$$d = d_B \left[ 1 + \frac{\sigma_1}{2\sigma_0} \delta + \frac{\sigma_2}{6\sigma_0} \varepsilon_1 \right], \quad (30)$$

then the term involving the first power of  $\varepsilon_1$  is given by

$$-\varepsilon_1 d \left[ \frac{\sigma_0}{6} d^4 \phi_0''''(d) + \frac{\sigma_1}{2} d^3 \phi_0'''(d) + \frac{\sigma_2}{3} d^2 \phi_0''(d) - \frac{\sigma_1 \sigma_2}{6 \sigma_0} d \phi_0'(d) \right] \quad (31)$$

and this must be added to  $I_{ref}$ . Since the quantity  $\phi_0''''(d)$  is of order  $10^5$  while  $\varepsilon_1$  is of order  $10^{-5}$  and increases with temperature this  $\varepsilon_1$  term will contribute significantly at the higher temperatures.

Now coming to the case of small disagreement between the LJ and DY results for  $\langle \nabla^2 \phi \rangle^*$  we note that this happens due to the slight deviation between the values of the higher order derivatives ( $\phi_0'''(d)$ , etc) of the reference parts of the two potentials.

Finally, considering the overall simplicity of the method we conclude that the present analytical route is the most easiest one for estimating the first order quantum correction to the free energy of simple liquids.

## References

- Carnahan N F and Starling K E 1969 *J. Chem. Phys.* **51** 635  
 Datta S K 1983 *Pramana* **20** 313  
 Foiles S M and Ashcroft N W 1981 *J. Chem. Phys.* **75** 3594  
 Hansen J P and McDonald I R 1976 *Theory of simple liquids* (New York: Academic Press) pp. 184  
 Jedrijezek C and Mansoori G A 1979 *Acta Phys. Pol.* **A56** 583  
 Lebowitz J L 1964 *Phys. Rev.* **A133** 895  
 Mandel F 1972 *J. Chem. Phys.* **57** 3929  
 Meyer A, Silbert M and Young W H 1980 *Chem. Phys.* **49** 147  
 Percus J K and Yevick G J 1958 *Phys. Rev.* **110** 1  
 Verlet L and Weis J J 1972a *Phys. Rev.* **A5** 939  
 Verlet L and Weis J J 1972b *Mol. Phys.* **24** 1013  
 Verlet L 1967 *Phys. Rev.* **159** 98  
 Wertheim M S 1964 *J. Math. Phys.* **5** 643  
 Weeks J D, Chandler D and Andersen H C 1971 *J. Chem. Phys.* **54** 5237