

Thermodynamics and structure of simple dense fluids

S K DATTA

Department of Physics, Jalpaiguri Government Engineering College,
Jalpaiguri 735 102, India

MS received 20 August 1982; revised 7 February 1983

Abstract. The perturbation theory of Weeks, Chandler and Anderson (WCA) has been employed to calculate the free energy and compressibility factor of simple dense fluids characterised by a double Yukawa potential. The structure factor has been calculated in the random phase approximation together with the WCA prescription for the division of the pair potential. The calculated values are in excellent agreement with experimental results.

Keywords. Thermodynamics; perturbation theory; direct correlation function; Verlet-Weis method; radial distribution function; structure factor.

1. Introduction

The perturbation theory of simple liquids developed by Weeks *et al* (1971) provides the most successful description of the structural and equilibrium properties. Weeks *et al* (1971) showed that the fluid structure in the dense state is primarily determined by the repulsive core and a suitable choice of the temperature and density dependent hard core diameter takes into account the soft part of the repulsion also. Verlet and Weis (1972) formulated this simple and highly successful first order perturbation theory in a fully analytic form which allows the numerical computation of thermodynamic properties on a desk calculator. However, unlike the thermodynamic properties which can be expressed in closed analytic form, the main difficulty associated with a real intermolecular pair potential of the form of a Lennard-Jones (LJ) potential in the structure factor calculations is that closed analytical expressions cannot be obtained. This is overcome by the use of a Double Yukawa (DY) potential function.

Foiles and Ashcroft (1981) have shown that a DY potential provides a good physical representation for pair potentials in molecular fluids. These authors have shown that by judicious selection of parameters this potential can have very nearly the same form as LJ potential in the physically important range of separations and can therefore lead to essentially the same associated thermodynamic properties. In the present work we shall use the perturbation theory developed by Weeks *et al* (1971, hereafter referred to as WCA) to calculate the thermodynamic and structural properties of the simple liquids characterised by a DY potential. In § 2 we derive closed analytical expressions for the free energy and the virial pressure of a DY fluid and compare the calculated results with the Monte Carlo results for a LJ fluid. In § 3 we derive an expression for the static structure factor of a DY fluid. Our derivations are based on a random phase approximation (RPA) together with the WCA prescription for the division of the pair potential. The RPA treats the attractive part

of the intermolecular potential as a perturbation to the structure arising from short range repulsive forces. The effects of the latter are included *via* a Blip function expansion about a hard sphere reference liquid. We calculate $S(k)$ for a simple liquid argon and compare this with the experimental results.

2. Thermodynamics of a DY fluid

We approximate the LJ potential by a DY potential of the form

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

$$x = r/s$$

Foiles and Ashcroft (1981) have found that the set of parameters $E = 2.0199 \epsilon$, $s = \sigma$, $a = 14.735$ and $b = 2.6793$ may be a good choice for the matching of the DY and LJ potentials. Here σ and ϵ are the parameters of the LJ potential.

We now calculate the free energy of the fluid using the WCA perturbation theory. In the WCA perturbation theory the pair potential is divided into two parts

$$\phi(r) = \phi_0(r) + \phi_1(r), \quad (2)$$

where $\phi_0(r)$ is the reference part and $\phi_1(r)$ is the perturbation potential, $\phi_0(r)$ includes all the rapidly varying repulsive forces and $\phi_1(r)$ all the smoother attractive tail. These are given by

$$\begin{aligned} \phi_0(r) &= \phi(r) - \phi(r_m) = \phi(r) + \epsilon & r < r_m \\ &= 0 & r > r_m \\ \phi_1(r) &= \phi(r_m) = -\epsilon & r < r_m \\ &= \phi(r) & r > r_m \end{aligned} \quad (3)$$

$-\epsilon$ and r_m are the values of the potential minima and the separation distance at which $\phi(r)$ is a minimum *i.e.*

$$\left. \frac{\partial \phi}{\partial r} \right|_{r=r_m} = 0, \quad -\epsilon = \phi(r_m). \quad (4)$$

Verlet and Weis (1972, referred to as vw) gave analytical representation for the free energy in the WCA perturbation theory. The free energy per particle in WCA theory is given by

$$\beta f = \beta f_0 + \beta f_1 = \beta f_0 + \frac{1}{2} \rho \beta \int \phi_1(r) g_0(r) \vec{dr} \quad (5)$$

$\beta = 1/k_B T$, k_B is the Boltzmann constant. Here f_0 and $g_0(r)$ are respectively the free energy and the pair correlation function of the reference system. vw have shown that the free energy of reference system f_0 is related to that of the hard sphere (HS) system by

$$\beta f_0 = \beta f_{\text{HS}}^{\text{ex}} + 4 \beta \delta \Delta f, \quad (6)$$

where
$$\beta \Delta f = \frac{3\eta^2 (1 + 1.759 \eta - 5.249 \eta^3)}{(1 - \eta)^3}, \quad (7)$$

$$\eta = \frac{\pi \rho^* c^3}{6}, \quad c = \frac{d}{\sigma}, \quad \rho^* = \rho \sigma^3, \quad (8)$$

and
$$\beta f_{\text{HS}}^{\text{ex}} = \frac{\eta (4 - 3\eta)}{(1 - \eta)^2} \quad (9)$$

δ is a function of temperature and has been calculated by vw. WCA approximate the reference pair correlation function

$$g_0(r) \text{ by } g_0(r) \simeq \exp[-\beta \phi_0(r)] Y_d(r) \quad (10)$$

$Y_d(r)$ is the reduced pair correlation function of a reference fluid of hard spheres of diameter d where d is determined by the WCA criterion

$$\int_0^\infty Y_d(r) [\exp[-\beta \phi_0(r)] - \exp[-\beta \phi_{\text{HS}}(r)]] \overleftarrow{dr} = 0. \quad (11)$$

With the above restriction and the fact that $Y_d(r) = g_d(r)$ for $r > d$ the first order term in the free energy reduces to (Hansen and McDonald, 1976)

$$\beta f_1 = 2\pi \rho \beta \int_d^\infty \phi_1(r) g_d(r) r^2 dr \quad (12)$$

We calculate this first order contribution using the Percus and Yevick (1958) approximation for the hard sphere radial distribution function $g_d(r)$.

We note that in the case of a DY fluid βf_1 is given by

$$\begin{aligned} \beta f_1 = & -2\pi \rho \beta \epsilon \int_{d_w}^{r_m} g_d^{\text{PY}}\left(\frac{r}{d_w}, \eta_w\right) r^2 dr \\ & + 2\pi \rho \beta E \int_{d_w}^\infty \left[\frac{\exp[-a(r/\sigma-1)] - \exp[-b(r/\sigma-1)]}{r/\sigma} \right] g_d^{\text{PY}}\left(\frac{r}{d_w}, \eta_w\right) r^2 dr \end{aligned}$$

$$-2\pi\rho\beta E \int_{d_w}^{r_m} \left[\frac{\exp[-a(r/\sigma-1)] - \exp[-b(r/\sigma-1)]}{r/\sigma} \right] g_d^{\text{PY}} \left(\frac{r}{d_w}, \eta_w \right) r^2 dr \quad (13)$$

where $E = 2.0199 \epsilon$, $d_w^3 = d^3 \frac{\eta_w}{\eta}$, $\eta_w = \eta \left(1 - \frac{\eta}{16} \right)$

In equation (13) the first integral is given by Verlet and Weis (1972) as

$$I_1 = -12\eta_w\beta\epsilon \left[\frac{A}{2}(x_m^2-1) + \frac{B}{3}(x_m^3-1) + \frac{C}{4}(x_m^4-1) \right] \quad (14)$$

where $A = a_0 - a_1 + \frac{a_2}{2}$, $B = a_1 - a_2$, $C = \frac{a_2}{2}$

$$a_0 = \frac{1 + \eta_w/2}{(1 - \eta_w)^2}, \quad a_1 = \frac{1 - 5\eta_w - 5\eta_w^2}{(1 - \eta_w)^3} \quad (15)$$

$$a_2 = -\frac{3\eta_w(2 - 4\eta_w - 7\eta_w^2)}{(1 - \eta_w)^4}, \quad x_m = \frac{r_m}{d_w}.$$

It is interesting to note that one can obtain this integral directly from the work of Thiele (1963). This is given by

$$I_1 = -12\eta_w\beta\epsilon \left[\frac{(\eta_w - 4)(\eta_w^2 + 2)}{24(1 + 2\eta_w)^2} + \frac{1}{3}x_m^3 \right]. \quad (16)$$

The expression is very simple and gives more or less good results at intermediate and high densities. In the present calculations we have, however, used the more commonly used expression given by (14). The second integral can be written as

$$I_2 = \frac{12\eta_w\beta E}{c_w} [e^a G(ac_w) - e^b G(bc_w)] \quad (17)$$

where $c_w = d_w/\sigma$.

$G(z)$ is the Laplace transform of $rg_d^{\text{PY}} \left(\frac{r}{d_w}, \eta_w \right)$ and is given by Wertheim (1964)

as

$$G(z) = \frac{zL(z)}{12\eta_w [L(z) + S(z)e^a]} \quad (18)$$

with $L(z) = 12\eta_w \left[\left(1 + \frac{\eta_w}{2} \right) z + (1 + 2\eta_w) \right]$ (19)

and $S(z) = (1 - \eta_w)^2 z^3 + 6\eta_w (1 - \eta_w) z^2 + 18\eta_w^2 z - 12\eta_w (1 + 2\eta_w).$ (20)

The third integral I_3 can be written as

$$I_3 = - \frac{12\eta_w \beta E}{c_w} [F(a) - F(b)],$$
 (21)

where $F(z) = \frac{A}{zc_w} [\exp(z(1 - c_w)) - \exp(z(1 - x_m c_w))]$

$$+ \frac{B}{zc_w} \left[\left(1 + \frac{1}{zc_w} \right) \exp(z(1 - c_w)) - \exp(z(1 - x_m c_w)) \left(x_m + \frac{1}{zc_w} \right) \right]$$

$$+ \frac{C}{zc_w} \left\{ \left[1 + \frac{2}{zc_w} + \frac{2}{(zc_w)^2} \right] \exp[z(1 - c_w)] - \left\{ x_m^2 + \frac{2x_m}{zc_w} + \frac{2}{(zc_w)^2} \right\} \exp[z(1 - x_m c_w)] \right\}$$
 (22)

with A, B and C being given by equation (15). The compressibility factor can be obtained by the numerical differentiation of the excess free energy. However using the virial equation of state vw has shown that

$$p/\rho k_B T = Z_0 + Z_1$$
 (23)

where $Z_0 = \frac{1 + 2\eta + 3\eta^2}{(1 - \eta)^2} + 4\eta \delta \left(\frac{\tau_2}{2} - \frac{\tau_1 \sigma_1}{2\sigma_0} \right)$ (24)

is the compressibility factor of the reference system

$$Z_1 = \frac{1}{1 - 3L} \left(\eta_w \frac{\partial \beta f_1}{\partial \eta_w} - 3L \xi_2 \right)$$
 (25)

with $d_w \frac{\partial \beta f_1}{\partial d_w} = -3\xi_2, L = \frac{\eta_w}{d_w} \frac{\partial d_w}{\partial \eta_w} = \lambda - \frac{\eta}{48} \left(1 - \frac{\eta}{8} \right)^{-1}$

$$\lambda = \delta \eta_w \frac{\partial}{\partial \eta_w} \left(\frac{\sigma_1}{2\sigma_0} \right)$$
 (26)

and $\xi_2 = - \frac{2\pi\rho}{3k_B T} \int_0^\infty r^3 \frac{d\phi_1(r)}{dr} g_d^{\text{py}} \left(\frac{r}{d_w}, \eta_w \right) dr.$ (27)

In the present case of a DY fluid ξ_2 is given by

$$\xi_2 = - \frac{4 \eta_w \beta E}{c_w} [M(a) - M(b)], \quad (28)$$

where $M(z) = [z c_w G'(z c_w) - G(z c_w)] e^z$

$$\begin{aligned} & - \left(\frac{A}{z c_w} + A' \right) [\exp(z(1 - c_w)) - \exp(z(1 - x_m c_w))] \\ & - \left(\frac{B}{z c_w} + B' \right) \left[\left(1 + \frac{1}{z c_w} \right) \exp[z(1 - c_w)] \right. \\ & \quad \left. - \left(x_m + \frac{1}{z c_w} \right) \exp[z(1 - x_m c_w)] \right] \\ & - \left(\frac{C}{z c_w} + C' \right) \left[\left\{ 1 + \frac{2}{z c_w} + \frac{2}{(z c_w)^2} \right\} \exp[z(1 - c_w)] \right. \\ & \quad \left. - \left\{ x_m^2 + \frac{2 x_m}{z c_w} + \frac{2}{(z c_w)^2} \right\} \exp[z(1 - x_m c_w)] \right] \end{aligned} \quad (29)$$

A , B and C being given by (15) and

$$A' = \frac{a_2}{2}, B' = a_0 - a_1 - a_2, C' = a_1 + a_2 \quad (30)$$

$$G'(z c_w) = \frac{d}{ds} [G(s)]_{s = z c_w} \quad (31)$$

$G(s)$ being given by (18) and a_0 , a_1 and a_2 are given by (15). The use of the DY potential model thus renders the evaluation of the integral I in an analytically exact form unlike the LJ potential model where the integrals I_1^n have been approximated. We have calculated the free energy and the pressure of the DY fluid at different temperatures and densities using the above derivations. These are presented in tables 1 and 2. We compare these with the Monte-Carlo results for the LJ fluid and the variational calculations of Foiles and Ascroft (1981). The WCA results are found to be better than the variational results.

3. Structure factor of the DY fluid

The calculation of the static structure factor is based on a RPA for the Ornstein and Zernike (OZ) direct correlation function (DCF) $C(r)$ of the liquid. The RPA sets

$$C(r) = C_0(r) - \beta \phi_1(r) \quad (32)$$

Table 1. Free energy βf as a function of reduced temperature and density: for a LJ fluid from computer simulations (LJ-Sim); for a DY fluid calculated using WCA theory (DY-WCA); for a DY fluid calculated variationally with the virial hard sphere entropy (DY-var).

$k_B T/\epsilon$	$\rho\sigma^3$	LJ-Sim	DY-WCA	DY-var
2.74	0.6	-0.34	-0.30	-0.21
	0.7	0.01	0.02	0.16
	0.8	0.43	0.44	0.59
	0.9	0.93	0.99	1.12
	1.0	1.59	1.68	1.78
1.35	0.6	-1.77	-1.72	-1.62
	0.7	-1.65	-1.61	-1.48
	0.8	-1.41	-1.36	-1.23
	0.9	-1.02	-0.94	-0.83
	1.0	-0.72	-0.61	-0.56
1.15	0.6	-2.29	-2.24	-2.12
	0.7	-2.25	-2.22	-2.08
	0.8	-2.06	-2.06	-1.92
	0.9	-1.79	-1.69	-1.59
0.75	0.6	-4.24	-4.16	-4.05
	0.7	-4.53	-4.53	-4.38
	0.8	-4.69	-4.66	-4.52
	0.9	—	-4.55	-4.46

Table 2. Compressibility factor $p/\rho k_B T$ as a function of reduced temperature and density. The column headings have the same meaning as those in table 1.

$k_B T/\epsilon$	$\rho\sigma^3$	LJ-Sim	DY-WCA	DY-VAR
2.74	0.65	2.22	2.23	2.37
	0.75	3.05	3.14	3.24
	0.85	4.38	4.55	4.49
	0.95	6.15	6.64	6.22
1.35	0.10	0.72	0.77	0.78
	0.20	0.50	0.53	0.56
	0.30	0.35	0.32	0.38
	0.40	0.27	0.17	0.28
	0.50	0.30	0.19	0.34
	0.55	0.41	0.28	0.45
	0.65	0.80	0.74	0.91
	0.75	1.73	1.74	1.82
	0.85	3.37	3.55	3.36
0.95	6.32	6.65	5.78	
1.00	0.65	-0.25	-0.26	-0.30
	0.75	0.58	0.46	0.54
	0.85	2.27	2.48	2.20
	0.90	3.50	4.02	3.43
0.72	0.85	0.25	0.48	0.16
	0.90	1.60	2.28	1.55

where $C_0(r)$ is the DCF of the reference fluid of interaction potential $\phi_0(r)$. The structure factor $S(k)$ is related to

$$\tilde{C}(k) = \int \vec{dr} \exp(i \vec{k} \cdot \vec{r}) C(r)$$

through the OZ relation

$$S(k)^{-1} = 1 - \rho \tilde{C}(k) \quad (33)$$

Now we adopt the WCA division of the potential described earlier. In order to calculate $C_0(r)$, the DCF of the repulsive reference fluid, following Jacobs and Andersen (1975) we approximate $C_0(r)$ by the sum of $C_{\text{HS}}(r)$, the DCF of the HS fluid at the same temperature and density and the Blip function $B(r)$ as

$$C_0(r) \simeq C_{\text{HS}}(r) + B(r) \quad (34)$$

$$\text{where } B(r) = Y_{\text{HS}}(r) [\exp(-\beta \phi_0(r)) - \exp(-\beta \phi_{\text{HS}}(r))] \quad (35)$$

$$\text{with } Y_{\text{HS}}(r) = \exp[\beta \phi_{\text{HS}}(r)] g_{\text{HS}}(r)$$

and as mentioned earlier the HS diameter d is determined at each temperature and density by the WCA requirement

$$\int B(r) \vec{dr} = \int Y_{\text{HS}}(r) [\exp(-\beta \phi_0(r)) - \exp[-\beta \phi_{\text{HS}}(r)]] \vec{dr} = 0 \quad (36)$$

Thus combining (32) and (34) and taking the Fourier transform (FT) we have

$$\tilde{C}(k) = \tilde{C}_{\text{HS}}(k) + \tilde{B}(k) - \beta \tilde{\phi}_1(k) \quad (37)$$

We utilise the analytical result for the DCF of the HS system. If we adopt the PY approximation (Thiele 1963) then

$$\begin{aligned} -C_{\text{HS}}(r) &= \alpha + \beta_1 (r/d) + \gamma (r/d)^3 & r < d \\ &= 0 & r \geq d \end{aligned} \quad (38)$$

where the coefficients are given by

$$\alpha = \frac{(1+2\eta)^2}{(1-\eta)^4}, \beta_1 = -6\eta \frac{(1+\eta/2)^2}{(1-\eta)^4}, \gamma = \eta \frac{\alpha}{2} \quad (39)$$

and $\eta = \pi \rho d^3/6$ is the packing fraction.

The FT of (38) is given by

$$\begin{aligned} \rho \tilde{C}_{\text{HS}}(k) = & -\frac{24\eta}{(kd)^6} \{ a (kd)^3 (\sin kd - kd \cos kd) \\ & + \beta_1 (kd)^2 [2kd \sin kd - (k^2 d^2 - 2) \cos kd - 2] \\ & + \gamma [(4k^3 d^3 - 24kd) \sin kd - (k^4 d^4 - 12k^2 d^2 \\ & + 24) \cos kd + 24] \} \end{aligned} \quad (40)$$

The FT of the attractive perturbation $\phi_1(r)$ for a DY fluid is given by

$$\begin{aligned} \frac{\tilde{\phi}_1(k)}{\pi \epsilon \sigma^3} = & \frac{4}{k^3 \sigma^3} [kr_m \cos kr_m - \sin kr_m] \\ & + \frac{4 \times 2.0199}{k\sigma} \left[\frac{\exp[-a(r_m/\sigma - 1)]}{a^2} (k\sigma \cos kr_m \right. \\ & + a \sin kr_m) \left(1 + \frac{k^2 \sigma^2}{a^2} \right)^{-1} \Big] - \frac{4 \times 2.0199}{k\sigma} \left[\frac{\exp[-b(r_m/\sigma - 1)]}{b^2} \right. \\ & \left. (k\sigma \cos kr_m + b \sin kr_m) \left(1 + \frac{k^2 \sigma^2}{b^2} \right)^{-1} \right]. \end{aligned} \quad (41)$$

The FT of the Blip function $B(r)$ can be obtained from a recent work of Mayer *et al* (1980). These authors have shown that

$$\tilde{B}(k) = 4\pi \sum_{n=0}^{\infty} \frac{(-1)^n}{(n+2)!} (kd)^n j_0^{(n)}(kd) \times \left(\frac{dC_-}{K_-^{n+1}} - \frac{dC_+}{K_+^{n+1}} \right) \quad (42)$$

where $dC_- = d^3 g_d(d_+) \exp[-\beta \phi_0(d)]$

$$dC_+ = d^3 g_d(d_+) \{ \exp[-\beta \phi_0(d)] - 1 \}$$

$$K_- = -\beta d \phi'_0(d) + Y + 2 \quad (43)$$

$$K_+ = -\beta d \phi'_0(d) \frac{\exp[-\beta \phi_0(d)]}{\exp[-\beta \phi_0(d)] - 1} + Y + 2$$

$g_d(d_+)$ is the value of the HS RDF at $r = d + 0$

$$Y = [\partial \ln g_d(r) / \partial \ln r]_{r=d+0} \quad (44)$$

and in the PY approximation these are given by

$$g_d(d_+) = \frac{1 + \frac{1}{2}\eta_w}{(1 - \eta_w)^2}, \quad Y = -\frac{(1 + \frac{1}{2}\eta_w)(1 - \eta_w)}{9/2\eta_w(1 + \eta_w)} \quad (45)$$

$j_0(kr) = \sin kr/cr$ and $j_0^{(n)}(kr)$ is the n th derivative of $j_0(kr)$.

The first order term in $\tilde{B}(k)$ vanishes because of (36) which implies that $\tilde{B}(0)=0$ and the next term gives a good approximation to the whole series.

A different type of approach for the calculation of $\tilde{B}(k)$ can be utilised in the light of Hoshino's work (1980). We can assume $B(r)$ to be given by

$$\begin{aligned} B(r) &= P \exp [\delta_1 (r/d - 1)] \quad r < d \\ &= -Q \exp [-\epsilon_1 (r/d - 1)] \quad r > d \end{aligned} \quad (46)$$

where P , Q , δ_1 and ϵ_1 are non-dimensional positive parameters. Then substituting this form of $B(r)$ in (34) and using (i) the continuity of $g_0(r) - C_0(r)$; (ii) the continuity of the first derivative of $g_0(r) - C_0(r)$ and; (iii) the WCA requirement (36), one can write following Hoshino (1980)

$$\tilde{B}(k) = \tilde{B}_-(k) + \tilde{B}_+(k) \quad (47)$$

where

$$\begin{aligned} \rho \tilde{B}_-(k) &= 4\pi\rho \int_{-\infty}^d r^2 B(r) \frac{\sin kr}{kr} dr \\ &= \frac{24\eta P}{kd [\delta_1^2 + (kd)^2]} \left[\delta_1 \sin kd - kd \cos kd \right. \\ &\quad \left. - \frac{\delta_1^2 \sin kd - 2\delta_1 kd \cos kd - (kd)^2 \sin kd}{\delta_1^2 + (kd)^2} \right] \end{aligned} \quad (48)$$

and

$$\begin{aligned} \rho \tilde{B}_+(k) &= 4\pi\rho \int_d^{\infty} r^2 B(r) \frac{\sin kr}{kr} dr \\ &= -\frac{24\eta Q}{kd [\epsilon_1^2 + (kd)^2]} \left[\epsilon_1 \sin kd + kd \cos kd \right. \\ &\quad \left. + \frac{\epsilon_1^2 \sin kd + 2\epsilon_1 kd \cos kd - (kd)^2 \sin kd}{\epsilon_1^2 + (kd)^2} \right]. \end{aligned} \quad (49)$$

The parameters P, Q, δ_1 and ϵ_1 are related to the α, β_1 and γ parameters in $C_{\text{HS}}(r)$ of (38) as, with $P < Q$

$$P + Q = \alpha + \beta_1 + \gamma \quad (51)$$

$$P\delta_1 - Q\epsilon_1 = \beta_1 + 3\gamma \quad (52)$$

and
$$P\left(\frac{1}{\delta_1} - \frac{2}{\delta_1^2} + \frac{2}{\delta_1^3}\right) = Q\left(\frac{1}{\epsilon_1} + \frac{2}{\epsilon_1^2} + \frac{2}{\epsilon_1^3}\right) \quad (53)$$

substituting the value of $\tilde{B}(k)$ from either (42) or (47) in (37) and using (33), (40) and (41) we obtain the analytical expression for the static structure factor of simple liquids. The contribution of $\tilde{B}(k)$ in the low k side is very small and can be neglected. Also the low k expansion of $\tilde{\phi}_1(k)$ is given with $a = 14.735, b = 2.6793, r_m = 2^{1/6} \sigma$ as

$$\frac{\tilde{\phi}_1(k)}{\pi \epsilon \sigma^3} = -5.02694 + 1.6872 (k\sigma)^2 - 0.30019 (k\sigma)^4 + 0 (k^6) \quad (54)$$

while that of $\tilde{C}_{\text{HS}}(k)$ is given by

$$\tilde{C}_{\text{HS}}(k) = \tilde{C}_{\text{HS}}(0) + a_{\text{HS}} k^2 + \gamma_{\text{HS}} k^4 + 0 (k^6) \quad (55)$$

with
$$1 - \rho \tilde{C}_{\text{HS}}(0) = \alpha \quad (56)$$

$$a_{\text{HS}} = \frac{\eta d^2 (16 - 11\eta + 4\eta^2)}{20 \rho (1 - \eta)^4} \quad (57)$$

$$\gamma_{\text{HS}} = -\frac{\eta d^4 (80 - 72\eta + 12\eta^2 + 7\eta^3)}{2800 \rho (1 - \eta)^4} \quad (58)$$

Thus $1 - \rho \tilde{C}(0) = 1 - \rho \tilde{C}_{\text{HS}}(0) + \rho \beta \tilde{\phi}_1(k=0)$

$$= \frac{(1 + 2\eta)^2}{(1 - \eta)^4} - 15.7926 \rho \beta \epsilon \sigma^3 \quad (59)$$

The critical points are then given by $\eta_c = 0.1287$

$$\text{i.e. } \rho_c^* = \rho_c \sigma^3 = 0.2457 \left(\frac{d}{\sigma}\right)^3 \simeq 0.24$$

$$T_c^* = \frac{1}{\epsilon \beta_c} = 1.415 \left(\frac{d}{\sigma}\right)^3 \simeq 1.39 \quad (60)$$

We see that these are identical with the values of critical constants calculated by Evans and Sluckin (1981). The absence of the $(k\sigma)^3$ term in (54) shows that $\phi(r)$ does not behave exactly as r^{-6} for large r . We have calculated the structure factor of liquid argon at temperature 148°K and density 0.982 g/cc taking $\sigma = 3.405$ Å and $\epsilon/k_B T = 119.8^\circ\text{K}$ so that this state corresponds to $T^* = 1.2354$ and $\rho^* = 0.84$.

Figure 1 shows the plot of the calculated $S(k)$ values taking into account the Blip function contribution calculated using (42). It is seen that our calculated values are very good throughout except at very low values of k where the measurements are difficult to make (Mikolaj and Pings, 1967).

4. Conclusions

The good agreement of the present calculations with the experimental results shows that the justification for the replacement of the LJ potential by a DY potential is reasonable. By treating the attractive forces in the RPA, the repulsive forces in a Blip function expansion about a hard sphere reference system and using the WCA prescription for the division of the pair potential we are able to obtain the structure and thermodynamics of dense simple fluids in a fully analytic form.

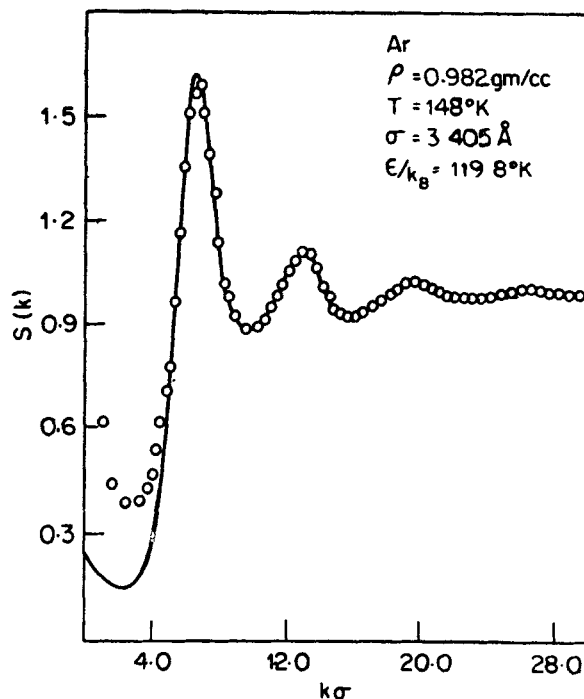


Figure 1. Structure factor of liquid Argon. Solid line—present calculations (RPA-DY) o—experimental results.

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