

Perturbative solution to order $\beta\epsilon$ of the Percus-Yevick equation for triangular well potential for $n=2$

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Abstract. The radial distribution function for a fluid in which the molecules interact *via* a triangular well potential is considered. Expanding the radial distribution function in powers of $\beta\epsilon$, where ϵ is the depth of the potential and $\beta = 1/k_B T$ the first-order terms are calculated analytically using the Percus-Yevick theory in the Baxter's formulation. The first-order terms in the direct correlation function $c(r)$ are also calculated. The first- and second-order terms in the free energy obtained from the energy equation of state are calculated and compared with other calculations.

Keywords. Triangular well potential; Percus-Yevick approximation; Baxter's formulation; radial distribution function; correlation functions; Monte-Carlo simulation.

1. Introduction

Of great importance in the equilibrium theory of classical fluids is the radial distribution function $g(r)$ defined by (Hill 1956)

$$g(r_{12}) = \frac{V^2 \int \dots \int \exp(-\beta\Phi) d\mathbf{r}_3 \dots d\mathbf{r}_N}{\int \dots \int \exp(-\beta\Phi) d\mathbf{r}_1 \dots d\mathbf{r}_N}, \quad (1)$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, \mathbf{r}_i is the position vector of the i th particle and $\beta = 1/k_B T$ where k_B is the Boltzmann constant and T is the temperature. In addition V is the volume and Φ is the total potential energy of the system. A knowledge of the radial distribution function gives an insight into the structure and thermodynamic properties of the liquid. If the potential energy Φ results solely from the additive contributions of a pair potential $u(r)$ *i.e.*

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{1 \leq i < j \leq N} u(r_{ij}), \quad (2)$$

then the thermodynamic properties can be calculated either from

$$\frac{pV}{Nk_B T} = 1 - \frac{2\pi\rho}{3k_B T} \int_0^{\infty} \frac{du}{dr} g(r) r^2 dr, \quad (3)$$

$$U = \frac{3}{2} Nk_B T + 2\pi N\rho \int_0^{\infty} u(r) g(r) r^2 dr, \quad (4)$$

or

$$\frac{1}{k_B T} \left(\frac{\partial P}{\partial \rho} \right)_T = 1 - 4\pi\rho \int_0^{\infty} r^2 c(r) dr. \quad (5)$$

In (5) $c(r)$ is the direct correlation function defined through the Ornstein-Zernicke relation

$$h(r_{12}) = c(r_{12}) + \rho \int h(r_{13}) c(r_{23}) d\mathbf{r}_3, \quad (6)$$

and $h(r_{12}) = g(r_{12}) - 1$ is the total correlation function. Equations (3), (4) and (5) are called the pressure, energy and compressibility equations respectively. In order to calculate radial distribution function from (6) a closure relation is needed and in the present paper we consider the Percus-Yevick (PY) approximation (Percus and Yevick 1958) given by

$$c(r) = f(r) y(r), \quad (7)$$

where $f(r) = \exp[-\beta u(r)] - 1,$ (8)

and $y(r) = g(r) \exp[\beta u(r)].$ (9)

The function $y(r)$ is continuous although $g(r)$ and $u(r)$ are not. In this paper we consider the triangular well potential given by

$$u(r) = \begin{cases} \frac{n\epsilon}{n-1} \left(\frac{r}{n\sigma} - 1 \right) & \begin{matrix} r < \sigma \\ \sigma < r < n\sigma \\ r \geq n\sigma \end{matrix} \end{cases}, \quad (10)$$

and consider the case for $n = 2$. Monte-Carlo simulations were done for this potential by Card and Walkley (1974) and Smith *et al* (1975) have reported results for the radial distribution function and the thermodynamic properties using Barker-Henderson (BH) perturbation theory (Barker and Henderson 1976).

The energy equation can be integrated to get the Helmholtz free energy and for the case of the triangular well potential gives

$$\begin{aligned} \frac{A}{Nk_B T} &= \int_0^{\beta\epsilon} \frac{U}{N\epsilon} d(\beta\epsilon) \\ &= \frac{A_0}{Nk_B T} + 2\pi\rho \int_0^{\beta\epsilon} d(\beta\epsilon) \int_1^2 r^2 u^*(r) g(r) dr, \end{aligned} \quad (11)$$

where $u^*(r) = u(r)/\epsilon$ and A_0 is the hard sphere free energy which according to Caranhan and Starling's (1969) equation of state is given by

$$\begin{aligned} \frac{A_0}{Nk_B T} &= \frac{A^{hd}}{Nk_B T} + \int_0^\eta \left(\frac{\beta p}{\rho} - 1 \right) \frac{d\eta'}{\eta'} \\ &= \frac{3}{2} \ln \lambda - 1 + \ln \rho + \frac{\eta(4-3\eta)}{(1-\eta)^2}, \end{aligned} \quad (12)$$

where $\lambda = h^2/2\pi mk_B T$, m is the molecular mass and h is the planck's constant.

In the Baxter's formulation (Baxter 1968) the *PY* integral equation is equivalent to the integral equations

$$rc(r) = - Q'(r) + 2\pi\rho \int_r^{n\sigma} dt Q'(t) Q(t-r), \quad (13)$$

$$rh(r) = - Q'(r) + 2\pi\rho \int_0^{n\sigma} dt (r-t) h(|r-t|) Q(t), \quad (14)$$

where $Q'(r)$ is the derivative of $Q(r)$ and $Q(r) = 0$ for $r \geq n\sigma$.

Hence
$$Q(r) = - \int_r^{n\sigma} Q'(t) dt. \quad (15)$$

The function $Q(r)$ is continuous whereas $Q'(r)$ is not. Further the compressibility is given by

$$\frac{1}{k_B T} \left(\frac{\partial p}{\partial \rho} \right)_T = [\tilde{Q}(0)]^2, \quad (16)$$

and
$$\tilde{Q}(k) = 1 - 2\pi\rho \int_0^{n\sigma} Q(r) \exp(ikr) dr. \quad (17)$$

In the case of hard spheres results were presented by Henderson and Chen (1978) for $Q(r)$ and $y(r)$ which we denote by $Q_0(r)$ and $y_0(r)$. Using $R = r/\sigma$ we have in the region $0 < R < 1$

$$Q'_0(R) = aR + b, \quad (18)$$

$$Q_0(R) = \frac{1}{2} a(R^2 - 1) + b(R - 1), \quad (19)$$

$$y_0(R) = a^2 - 6\eta (a + b)^2 R + \frac{1}{2} \eta a^2 R^2, \quad (20)$$

where $a = (1 + 2\eta)/(1 - \eta)^2, \quad (21)$

$$b = -3\eta/[2(1 - \eta)^2] \quad (22)$$

$$\eta = \pi\rho\sigma^3/6. \quad (23)$$

In the region $1 < R < 2$

$$Ry_0(R) = \sum_{l=0}^2 A_l \exp(m_l R), \quad (24)$$

where m_l are the roots of the equation

$$S(m) = m^3 + \frac{6\eta}{(1 - \eta)} m^2 + \frac{18\eta^2}{(1 - \eta^2)} m - \frac{12\eta(1 + 2\eta)}{(1 - \eta)^2} = 0. \quad (25)$$

The values of m_l are given by Wertheim (1963). For actual numerical calculations we use the following expressions due to Smith and Henderson (1970).

$$m_l = [-2\eta + (2\eta f)^{1/3} (y_+ j^l + y_- j^{-l})]/(1 - \eta), \quad (26)$$

with $f = 3 + 3\eta - 3\eta^2, \quad (27)$

$$y_{\pm} = [1 \pm \{(1 + 2(\eta^2/f)^2)^{1/2}\}]^{1/3}, \quad (28)$$

$$j = \exp [2\pi \sqrt{-1/3}]. \quad (29)$$

It has been noted that for a dense fluid the repulsive forces which are nearly hard sphere interactions dominate the structure and effect of the attractive forces is to provide a uniform background which are of the mean field type. Utilizing this idea several perturbation theories were developed (Barker and Henderson 1976; Anderson *et al* 1976). In these theories the excess free energy is expanded as a power series in a parameter λ multiplying some part of the interaction considered as perturbation, *e.g.* the attractive part; the statistical averages of the terms in the series are then calculated as integrals of the distribution functions of the remaining part of the interaction, the so-called reference system. Motivated by this success we attempted to solve (13) and (14). Our aim is to present analytical expressions for the perturba-

tion terms in the case of the triangular well potential. In § 2 we present the perturbation expansions for the radial distribution function, direct correlation function and $Q(r)$ and present the results for the perturbation terms. In § 3 results for the thermodynamic properties are presented. Henderson and Chen (1975) obtained the solutions for a square well potential. Fulinski and Jedrzejek (1977) obtained perturbative solution of the PY equation for the square mound potential. Chen (1979) made a qualitative investigation of the PY equation by perturbation methods for a general class of intermolecular potentials.

2. Perturbation expansions

We solve (13) and (14) by expanding the radial distribution function, direct correlation function and $Q(r)$ in powers of $\beta\epsilon$. We use the reduced units ($R = r/\sigma$, $\rho = N\sigma^3/V$)

$$y(R) = y_0(R) + \beta\epsilon y_1(R) + \dots, \tag{30}$$

$$c(R) = \begin{cases} -y_0(R) - \beta\epsilon y_1(R) - \dots & 0 < R < 1 \\ -\beta\epsilon (R-2) y_0(R) - \dots & 1 < R < 2, \\ 0 & R \geq 2 \end{cases} \tag{31}$$

$$g(R) = \begin{cases} 0 & 0 < R < 1 \\ y_0(R) + \beta\epsilon [y_1(R) - (R-2) y_0(R)] + \dots & 1 < R < 2, \\ y_0(R) + \beta\epsilon y_1(R) + \dots & R \geq 2 \end{cases} \tag{32}$$

$$Q(R) = \begin{cases} Q_0(R) + \beta\epsilon Q_1(R) + \dots & 0 < R < 1 \\ \beta\epsilon Q_1(R) + \dots & 1 < R < 2 \\ 0 & R \geq 2. \end{cases} \tag{33}$$

Our interest in the present paper is to obtain the first order terms analytically in the PY theory. In the limit $\beta\epsilon \rightarrow 0$ the results reduce to that for the hard sphere system. We present the results for $Q_1(R)$ and $y_1(R)$ in the region $0 < R < 2$ for triangular well potential.

2.1 Expressions for $Q_1(R)$

Substituting (30) to (33) in (13) and (14) we get

$$\begin{aligned} -Ry_1(R) = & -Q_1'(R) + 12\eta \int_R^1 Q_0'(t) Q_1(t-R) dt \\ & + 12\eta \int_R^{R+1} Q_1'(t) Q_0(t-R) dt, \end{aligned} \tag{34}$$

$$Q_1'(R) = 12\eta \int_{R+1}^2 (R-t)y_0(t-R)Q_1(t)dt - 12\eta \int_0^2 (R-t)Q_1(t)dt, \quad (35)$$

in the region $0 < R < 1$ and

$$Ry_0(R) = -Q_1'(R) + 12\eta \int_R^2 Q_1'(t)Q_0(t-R)dt, \quad (36)$$

$$\begin{aligned} R[y_1(R) + Y_0(R)] &= -Q_1'(R) - 12\eta \int_0^2 (R-t)Q_1(t)dt \\ &\quad + 12\eta \int_0^{R-1} (R-t)Y_0(R-t)Q_1(t)dt + 12\eta \int_0^{R-1} (R-t)[Y_0(R-t) \\ &\quad + y_1(R-t)]Q_0(t)dt, \end{aligned} \quad (37)$$

in the range $1 < R < 2$. In (36) and (37)

$$Y_0(R) = -(R-2)y_0(R). \quad (38)$$

In order to obtain $Q_1(R)$ and $y_1(R)$ we must solve these coupled integrodifferential equations. The simplest of these is (36). Substituting $RY_0(R) = H(R)$ and $Q_1'(R) = f(R)$, equation (36) becomes

$$Q_1'(R) = -RY_0(R) + 12\eta \int_R^2 Q_1'(t)Q_0(t-R)dt. \quad (39)$$

Differentiation (39) three times we get

$$\begin{aligned} \mathcal{L}'[f] &= f'''(R) - \frac{6\eta}{(1-\eta)}f''(R) + \frac{18\eta^2}{(1-\eta)^2}f'(R) \\ &\quad + \frac{12\eta(1+2\eta)}{(1-\eta)^2}f(R) = -H'''(R). \end{aligned} \quad (40)$$

$$\text{Thus } D(m) = m^2 - \frac{6\eta}{(1-\eta)}m^2 + \frac{18\eta^2}{(1-\eta)^2}m + \frac{12\eta(1+2\eta)}{(1-\eta)^2} = 0. \quad (41)$$

$$\text{Since } D(-m) = -S(m), \quad (42)$$

the solution for the homogeneous equation is

$$f(R) = \sum_{l=0}^2 B_l \exp(-m_l R). \quad (43)$$

Including the particular integral we get for $1 < R < 2$

$$Q_1'(R) = \sum_{l=0}^2 B_l \exp(-m_l R) - \sum_{l=0}^2 \frac{A_l m_l^2}{D(m_l)} G_l \exp(m_l R) + \sum_{l=0}^2 \frac{A_l m_l^3}{D(m_l)} R \exp(m_l R), \tag{44}$$

where $G_l = 2m_l - 3 + m_l \frac{D'(m_l)}{D(m_l)}$. (45)

The B_l are determined by the condition that

$$Q_1'(2) = -H(2), \tag{46}$$

$$Q_1''(2) = -H'(2) - 12\eta Q_1'(2) Q_0(0), \tag{47}$$

$$Q_1'''(2) = -H''(2) + 12\eta Q_1'(2) Q_0'(0) - 12\eta Q_1''(2) Q_0(0). \tag{48}$$

Integrating (44) we get

$$Q_1(R) = - \sum_{l=0}^2 \frac{B_l}{m_l} \exp(-m_l R) + \sum_{l=0}^2 K_l \exp(m_l R) - \sum_{l=0}^2 L_l R \exp(m_l R) + M, \tag{49}$$

where the constant of integration M is determined by the condition

$$Q_1(2) = 0, \tag{50}$$

$$K_l = \frac{-A_l m_l}{D(m_l)} (G_l + 1), \tag{51}$$

and $L_l = \frac{-A_l m_l^2}{D(m_l)}$. (52)

We now consider (35) to get

$$Q_1'(R) = 12\eta [-PR + Q - \Psi(R)] \tag{53}$$

$$\text{where } \Psi(R) = \int_{R+1}^2 (t-R) y_0(t-R) Q_1(t) dt, \quad (54)$$

$$P = \int_0^2 Q_1(t) dt, \quad (55)$$

$$Q = \int_0^2 t Q_1(t) dt. \quad (56)$$

Substituting the known results of $y_0(R)$ and $Q_1(R)$ in (54) we get

$$\begin{aligned} \Psi(R) = & A + \sum_{l=0}^2 b_l \exp(-m_l R) + R \sum_{l=0}^2 c_l \exp(-m_l R) \\ & + \sum_{l=0}^2 d_l \exp(m_l R) + R \sum_{l=0}^2 e_l \exp(m_l R), \end{aligned} \quad (57)$$

$$\text{where } A = -M \sum_{l=0}^2 \frac{A_l \exp(m_l)}{m_l}, \quad (58)$$

$$\begin{aligned} b_l = & \frac{MA_l \exp(2m_l)}{m_l} - \frac{A_l B_l}{m_l} + \sum_{k=0}^2 \frac{A_l K_k}{(m_l + m_k)} \exp[2(m_l + m_k)] \\ & + \sum_{k=0}^2 \frac{A_l L_k}{(m_l + m_k)^2} \exp[2(m_l + m_k)] - 2 \sum_{k=0}^2 \frac{A_l L_k}{(m_l + m_k)} \exp[2(m_l + m_k)] \\ & - \sum_{k \neq l=0}^2 \left\{ \frac{A_l B_k}{m_k(m_l - m_k)} \exp[2(m_l - m_k)] - \frac{A_k B_l \exp(m_k - m_l)}{m_l(m_k - m_l)} \right\} \end{aligned} \quad (59)$$

$$c_l = (A_l B_l / m_l), \quad (60)$$

$$\begin{aligned} d_l = & - \sum_{k=0}^2 \frac{A_k K_l}{(m_l + m_k)} \exp(m_l + m_k) + \sum_{k=0}^2 \frac{A_k L_l}{(m_l + m_k)} \exp(m_l + m_k) \\ & - \sum_{k=0}^2 \frac{A_k L_l}{(m_l + m_k)^2} \exp(m_l + m_k), \end{aligned} \quad (61)$$

$$e_l = \sum_{k=0}^2 \frac{A_k L_l}{(m_l + m_k)} \exp(m_l + m_k). \tag{62}$$

Integration of (53) gives

$$Q_1(R) = 12\eta \left[-\frac{1}{2} PR^2 + QR - \Phi(R) \right] + N \tag{63}$$

for $0 < R < 1$ where

$$\begin{aligned} \Phi(R) = & AR - \sum_{l=0}^2 \left(\frac{b_l}{m_l} + \frac{c_l}{m_l^2} \right) \exp(-m_l R) - R \sum_{l=0}^2 \frac{c_l}{m_l} \exp(-m_l R) \\ & + \sum_{l=0}^2 \left(\frac{d_l}{m_l} - \frac{e_l}{m_l^2} \right) \exp(m_l R) + R \sum_{l=0}^2 \frac{e_l}{m_l} \exp(m_l R), \end{aligned} \tag{64}$$

and N is the constant of integration and is determined by requiring that $Q_1(R)$ be continuous at $R = 1$. Results of the calculation for $Q_1(R)$ for $\rho = 0.7$ and 0.9 are shown in figure 1. As noted already $Q_1(R)$ is continuous whereas $Q_1'(R)$ has a small discontinuity at $R = 1$.

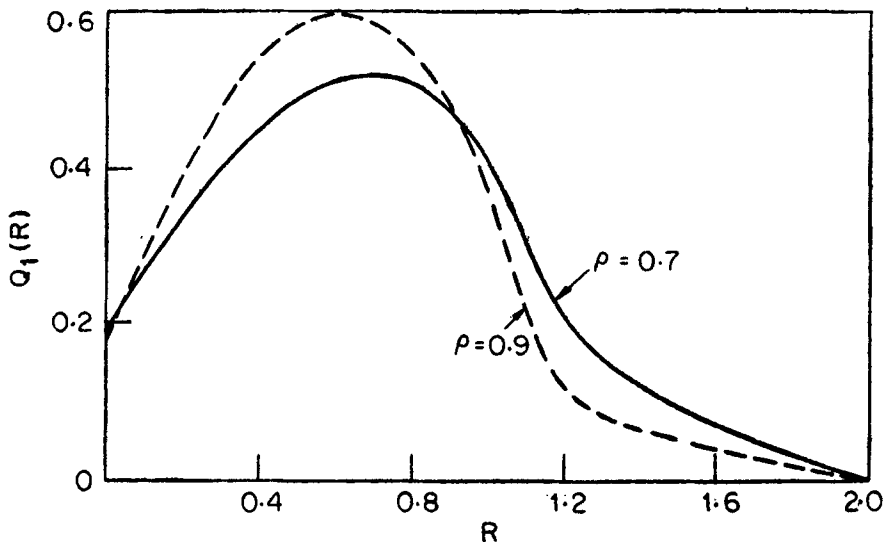


Figure 1. Plot of $Q_1(R)$ vs R for triangular well potential for $n = 2$ in the PY theory.

2.2 Expressions for $y_1(R)$

We start with (36) to obtain $y_1(R)$ in the region

$1 < R < 2$. Defining

$$T(R) = Ry_1(R), \quad (65)$$

$$v(R) = RY_0(R), \quad (66)$$

$$t(R) = Ry_0(R), \quad (67)$$

and using $R - t = z$ we get after differentiating three times

$$\begin{aligned} \mathcal{L}[T] &= T'''(R) + \frac{6\eta}{(1-\eta)} T''(R) + \frac{18\eta^2}{(1-\eta)^2} T'(R) \\ &\quad - \frac{12\eta(1+2\eta)}{(1-\eta)^2} T(R) = \sum_{l=0}^2 M_{1l} \exp(-m_l R) \\ &\quad + \sum_{l=0}^2 M_{2l} R \exp(-m_l R) + \sum_{l=0}^2 M_{3l} \exp(m_l R) \\ &\quad + R \sum_{l=0}^2 M_{4l} \exp(m_l R) + R^2 \sum_{l=0}^2 M_{5l} \exp(m_l R), \end{aligned} \quad (68)$$

where $M_{1l} = V_{1l} + B_l m_l^3, \quad (69)$

$$M_{2l} = V_{2l}, \quad (70)$$

$$M_{3l} = V_{3l} - K_l m_l^4 + 4L_l m_l^3 + B_1 A_l + B_2 A_l m_l + B_3 A_l m_l^2, \quad (71)$$

$$M_{4l} = V_{4l} + L_l m_l^4, \quad (72)$$

$$M_{5l} = V_{5l}, \quad (73)$$

$$\begin{aligned} V_{1l} &= 12\eta \left\{ - \sum_{k=0}^2 \frac{A_k p_l}{(m_l + m_k)} \exp(m_l + m_k) + \sum_{k=0}^2 \frac{A_k q_l}{(m_l + m_k)} \exp(m_l + m_k) \right. \\ &\quad \left. - \sum_{k=0}^2 \frac{A_k q_l}{(m_l + m_k)^2} \exp(m_l + m_k) \right\}, \end{aligned} \quad (74)$$

$$V_{2l} = 12\eta \left[- \sum_{k=0}^2 \frac{A_k q_l}{(m_l + m_k)} \exp(m_l + m_k) \right], \quad (75)$$

$$\begin{aligned} V_{3l} = 12\eta & \left\{ \sum_{k=0}^2 \frac{A_l p_k}{(m_l + m_k)} + \sum_{k=0}^2 \frac{A_l q_k}{(m_l + m_k)^2} - A_l r_l + \sum_{k \neq l=0}^2 \frac{A_l r_k}{(m_l - m_k)} \right. \\ & - \sum_{k \neq l=0}^2 \frac{A_k r_l}{(m_k - m_l)} \exp(m_k - m_l) + \frac{A_l j_l}{2} + \sum_{k \neq l=0}^2 \frac{A_l j_k}{(m_l - m_k)^2} \\ & \left. + \sum_{k \neq l=0}^2 \frac{A_k j_l}{(m_k - m_l)} \exp(m_k - m_l) - \sum_{k \neq l=0}^2 \frac{A_k j_l}{(m_k - m_l)^2} \exp(m_k - m_l) \right\}, \quad (76) \end{aligned}$$

$$V_{4l} = 12\eta \left[A_l r_l - A_l j_l - \sum_{k \neq l=0}^2 \frac{A_k j_l}{(m_k - m_l)} \exp(m_k - m_l) \right], \quad (77)$$

$$V_{5l} = 12\eta \frac{A_l j_l}{2}, \quad (78)$$

$$p_l = -12\eta (b_l m_l^2 - 2c_l m_l), \quad (79)$$

$$q_l = -12\eta c_l m_l^2, \quad (80)$$

$$r_l = -12\eta (d_l m_l^2 + 2e_l m_l), \quad (81)$$

$$j_l = -12\eta e_l m_l^2, \quad (82)$$

$$B_1 = 12\eta Q_1''(0) + \frac{18\eta^2}{(1-\eta)^2}, \quad (83)$$

$$B_2 = 12\eta Q_1'(0) + \frac{12\eta}{(1-\eta)}, \quad (84)$$

$$B_3 = 12\eta Q_1(0) + 3. \quad (85)$$

In (68) we used the fact

$$\begin{aligned} \mathcal{L}[t] = t'''(R) + \frac{6\eta}{(1-\eta)} t''(R) + \frac{18\eta^2}{(1-\eta)^2} t'(R) \\ - \frac{12\eta(1+2\eta)}{(1-\eta)^2} t(R) = 0. \quad (86) \end{aligned}$$

The solution of the homogeneous part of (68) is

$$T(R) = \sum_{l=0}^2 a_l \exp(m_l R) \quad (87)$$

and including the particular integral gives for $y_1(R)$ in the region $1 < R < 2$

$$\begin{aligned} T(R) &= \sum_{l=0}^2 y_{1l} \exp(-m_l R) + R \sum_{l=0}^2 y_{2l} \exp(-m_l R) \\ &+ \sum_{l=0}^2 y_{3l} \exp(m_l R) + R \sum_{l=0}^2 y_{4l} \exp(m_l R) \\ &+ R^2 \sum_{l=0}^2 y_{5l} \exp(m_l R) + R^3 \sum_{l=0}^2 y_{6l} \exp(m_l R), \end{aligned} \quad (88)$$

where

$$y_{1l} = - \left[\frac{M_{1l}}{D(m_l)} + \frac{M_{2l}}{D(m_l)} \frac{D'(m_l)}{D(m_l)} \right], \quad (89)$$

$$y_{2l} = - M_{2l}/D(m_l), \quad (90)$$

$$y_{3l} = a_l, \quad (91)$$

$$y_{4l} = \frac{M_{3l}}{S'(m_l)} - \frac{M_{4l} S''(m_l)}{2S'(m_l) S'(m_l)} - \frac{2 M_{5l}}{[S'(m_l)]^2} + \frac{M_{5l} [S''(m_l)]^2}{2 [S'(m_l)]^3}, \quad (92)$$

$$y_{5l} = \frac{M_{4l}}{2 S'(m_l)} - \frac{M_{5l} S''(m_l)}{2 [S'(m_l)]^2}, \quad (93)$$

$$y_{6l} = M_{5l}/[3 S'(m_l)]. \quad (94)$$

The a_l are determined from the conditions

$$T(1) = -V(1) - Q_1'(1) - 12 \eta (P - Q), \quad (95)$$

$$\begin{aligned} T'(1) &= -V'(1) - Q_1''(1) - 12 \eta P + 12 \eta t(1) Q_1(0) \\ &+ 12 \eta Q_0(0) [V(1) + T(1)], \end{aligned} \quad (96)$$

$$\begin{aligned} T''(1) &= -V''(1) - Q_1'''(1) + 12 \eta t(1) Q_1'(0) + 12 \eta t'(1) Q_1(0) \\ &+ 12 \eta Q_0'(0) [V(1) + T(1)] + 12 \eta Q_0(0) [V'(1) + T'(1)]. \end{aligned} \quad (97)$$

These conditions ensure the continuity of $y_1(R)$ and its first two derivatives at $R = 1$. In the region $0 < R < 1$, $y_1(R)$ can be calculated using (34). Since the thermodynamic properties do not depend on $y_1(R)$ in this region the integrations were done numerically. Results for $y_1(R)$ are shown in figure 3 for the two densities $\rho = 0.7$ and 0.9 . In figures 2 and 4 results for $c_1(R)$ and $g_1(R)$ are shown.

3. Thermodynamic properties

By substituting the perturbation expansion for the radial distribution function given by (32) into (11) we get the perturbation expansion for the Helmholtz free energy as

$$A = A_0 + \beta\epsilon A_1 + (\beta\epsilon)^2 A_2 + \dots, \tag{98}$$

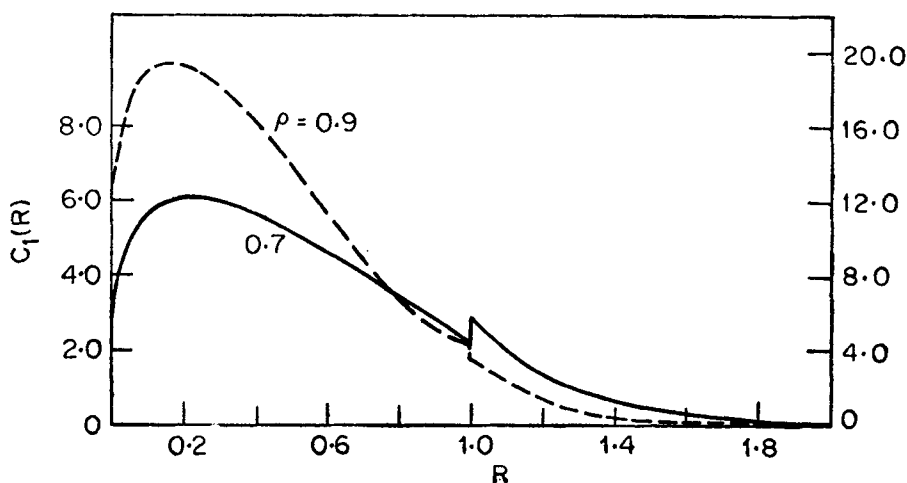


Figure 2. Plot of $C_1(R)$ vs R .

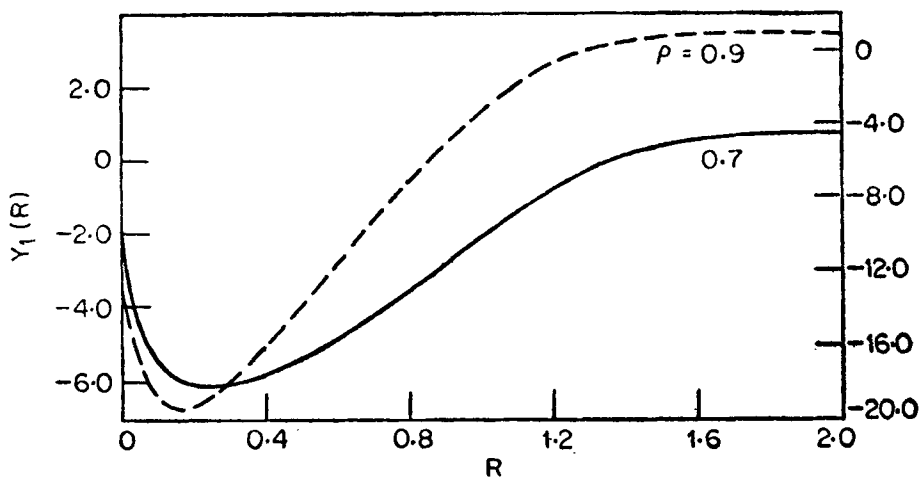


Figure 3. Plot of $Y_1(R)$ vs R .

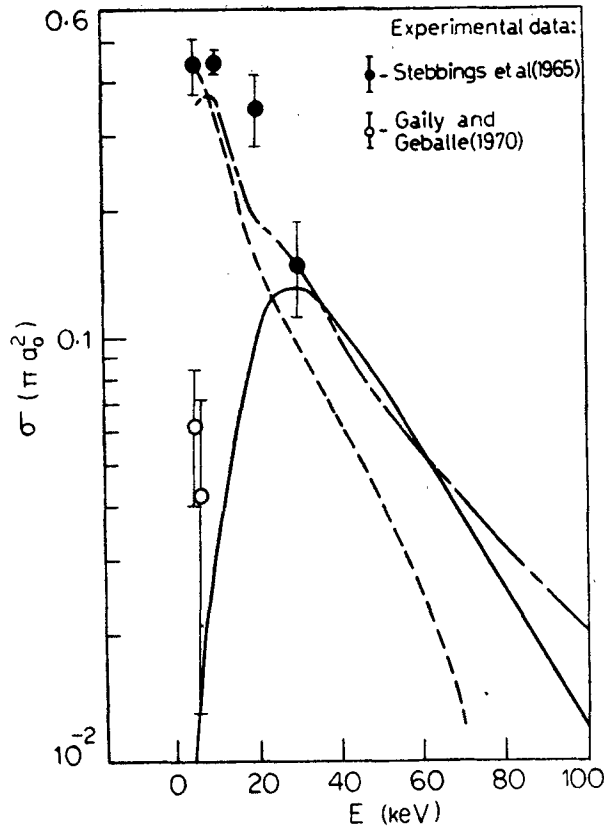


Figure 4. Plot of $g_1(R)$ vs R . Open circles represent PY $g_0(R)$ at $\rho = 0.7$ ● and —, —, —, — represent $g(R)$ values from MC and PY theory respectively at $\rho = 0.707$ and $k_B T/\epsilon = 1.5$. Other details as in figure 1. ▲ represents $g_1(R)$ results from Smith *et al* at $\rho = 0.7$.

$$\begin{aligned} \text{where } A_1/Nk_B T &= 12\eta \int_1^2 R^2(R-2)y_0(R) dR \\ &= 12\eta \sum_{l=0}^2 A_l \left\{ \frac{2 \exp(2m_l)}{m_l^2} (1-m_l) + \frac{\exp(m_l)(m_l^2-2)}{m_l^2} \right\}, \end{aligned} \quad (99)$$

$$\text{and } A_2/Nk_B T = 6\eta \left[\int_1^2 R^2(R-2)y_1(R)dR - \int_1^2 R^2(R-2)^2y_0(R) dR \right] \quad (100)$$

The pressure is obtained from the thermodynamic identity

$$\frac{P}{\rho k_B T} = \rho \left[\frac{\partial(A/Nk_B T)}{\partial \rho} \right]_T \quad (101)$$

from which we can get the perturbation expansion for the pressure as

$$P = P_0 + \beta\epsilon P_1 + (\beta\epsilon)^2 P_2 + \dots \tag{102}$$

It should be noted that in the energy equation of state A_n (or P_n) will depend on $y_{n-1}(R)$. Results for A_2 are given in figure 5. Since A_1 involves only $y_0(R)$ and since they are already given elsewhere (Swamy and Wankhede 1978) they are not given here.

4. Conclusions

From figure 4 it is seen that the $PY g_i(r)$ values are positive for the values of R considered in the figure and falls down at $R \sim 1.7$ for $\rho = 0.7$. The $g_i(r)$ values obtained are generally less than the $g_0(r)$ values. In the same figure $g_i(r)$ values obtained by Smith *et al* (1975) are given. For comparison the $PY g_0(r)$ and Monte Carlo and $PY g(r)$ at $\rho = 0.707$ and $k_B/T/\epsilon = 1.5$ is also plotted. Throughout the range of R the present $g_i(r)$ values are higher than the results of Smith *et al*. Unfortunately the MC results for $g_i(r)$ are not available. Since at higher densities the structure of the liquid is determined primarily by the repulsive forces one expects that $g_i(r)$ should fall off as the density increases. Since this trend is not observed and since the PY

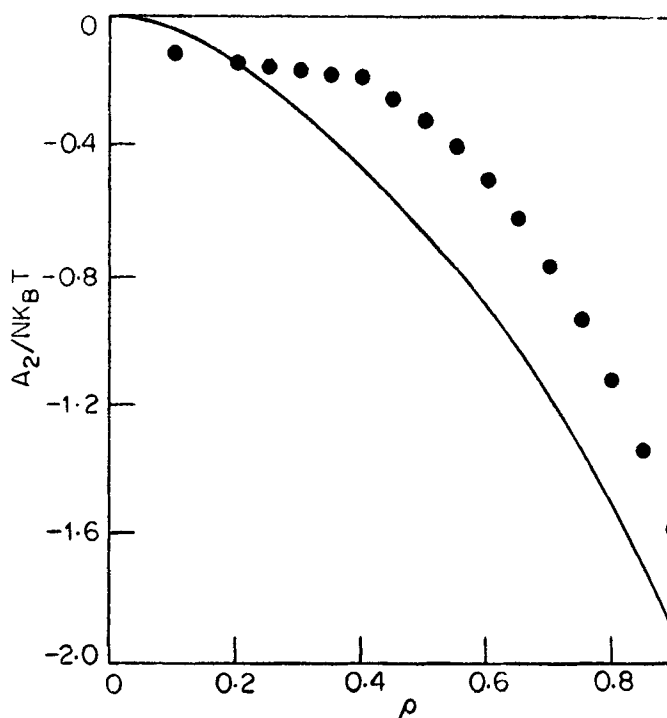


Figure 5. Plot of $A_2/Nk_B T$ vs ρ for the triangular well fluid. The full curve is obtained from the PY theory with the energy equation of state and the points are the results from Smith *et al* (1975).

estimate of $g_1(r)$ is much too large in magnitude we feel that for the triangular well potential the higher order terms are not well described. The second order term in the free energy obtained from the energy equation of state shows good results. However, we feel that this is fortuitous mainly due to cancellation of errors in $y_0(r)$ and $y_1(r)$.

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