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Selfconsistent PY2 and CHNC2 approximation. Evaluation of fifth virial coefficients

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Abstract. A selfconsistent approximation has been proposed for the PY2 and CHNC2 theories for the evaluation of the virial coefficients. The theory has been used to calculate the fifth virial coefficients of hard spheres and for a fluid interacting according to the Lennard-Jones 6-12 potential function. The agreement between the exact and the present values is good.

1. Introduction

Verlet (1964) has recently proposed extensions of the well known Percus-Yevick (PY) and convolution hypernetted chain (CHNC) theories, which he calls the PY2 and CHNC2 theories, by taking the second term of the functional Taylor expansion. In this paper we present a selfconsistent approximation to yield better values of the virial coefficients and also to test Verlet's approximation in the second order theories.

2. PY and CHNC theories

Assuming classical statistics and that the potential energy of a system of N particles is pairwise additive, namely

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

where $u(r_{ij})$ is the pair potential function, the equation of state can be calculated with the pressure equation given by

$$\frac{PV}{NkT} = 1 - \frac{2\pi\rho}{3kT} \int_0^\infty g(r) \frac{du}{dr} r^3 dr. \quad (2)$$

Here $g(r)$ is the well known radial distribution function, and $\rho (= N/V)$ is the number density.

The equation of state can also be calculated from the compressibility equation given by

$$\frac{1}{kT} \left(\frac{\partial P}{\partial \rho} \right)_T = 1 - 4\pi\rho \int_0^\infty c(r) r^2 dr. \quad (3)$$

Here $c(r)$ is the direct correlation function defined by

$$h(r_{12}) = c(r_{12}) + \rho \int h(r_{23})c(r_{13}) dr_3 \quad (4)$$

where $h(r)$ is the total correlation function and is related to $g(r)$ by

$$h(r) = g(r) - 1. \quad (5)$$

The Percus–Yevick (Percus and Yevick 1958, Stell 1963) theory is based on the approximation

$$c(r) = f(r)y(r) \quad (6)$$

with

$$f(r) = \exp(-\beta u(r)) - 1 \quad (7)$$

$$y(r) = \exp(\beta u(r))g(r) \quad (8)$$

and

$$\beta = \frac{1}{kT}. \quad (9)$$

The CHNC (Van Leeuwen *et al* 1959, Meeron 1960, Morita 1960) approximation can be written as

$$c(r) = f(r)y(r) + y(r) - 1 - \ln y(r). \quad (10)$$

Percus (1962) has shown that these approximations can be derived by the method of functional Taylor expansion.

3. PY2 and CHNC2 theories

Verlet (1964) has recently proposed extensions of the PY and CHNC theories, which he calls the PY2 and CHNC2 theories, by taking into account the quadratic term in the functional Taylor series expansion.

The PY2 approximation is given by

$$c(r) = f(r)y(r) + \Phi(r) \quad (11)$$

where

$$\begin{aligned} \Phi(1, 2) = & \frac{1}{2}\rho^2 \int c(1, 3)c(1, 4)(g^{(3)}(3, 4, 5) - g(3, 4)) \\ & \times (\delta(2, 5) - \rho c(2, 5)) \, dr_3 \, dr_4 \, dr_5 \\ & - \frac{1}{2}\rho^2 \int c(1, 3)c(1, 4)g(3, 4)(c(2, 3) + c(2, 4)) \, dr_3 \, dr_4. \end{aligned} \quad (12)$$

Here δ is the three dimensional Dirac delta function. Although several approximations for the correction term $\Phi(r)$ are possible we propose to test the approximation of Verlet in order to evaluate the fifth virial coefficients. This approximation has been utilized for calculating the virial coefficients of hard rods and hard cubes by Verlet (1965).

Equation (12) contains a triple distribution function $g^{(3)}(3, 4, 5)$ and hence is not selfcontained. However Verlet has proposed the approximation

$$\begin{aligned} & \exp\{\beta(u(1, 3) + u(2, 3))\}g^{(3)}(1, 2, 3) \\ & = g(1, 2) + \rho \int (g^{(3)}(1, 2, 4) - g(1, 2))c(3, 4) \, dr_4. \end{aligned} \quad (13)$$

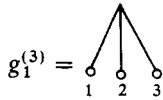
In terms of the density expansion

$$g^{(3)}(1, 2, 3) = g(1, 2)g(2, 3)g(1, 3) \left(\sum_{n=0}^{\infty} \rho^n g_n^{(3)}(1, 2, 3) \right). \quad (14)$$

Here

$$g_0^{(3)} = 1 \quad (15)$$

and



The CHNC2 approximation may be written as

$$c(r) = f(r)y(r) + y(r) - 1 - \ln y(r) + \psi(r) \quad (16)$$

where

$$\psi(r) = \Phi(1, 2) - \frac{1}{2}(h(1, 2) - c(1, 2))^2. \quad (17)$$

We use Verlet's approximation to eliminate $g^{(3)}(3, 4, 5)$ by the following expression:

$$\begin{aligned} & \ln g^{(3)}(1, 2, 3) - g(1, 2) + \beta(u(1, 3) + u(2, 3)) \\ &= \rho \int \left(\frac{g^{(3)}(1, 2, 4)}{g(1, 2)} - 1 \right) c(3, 4) \, dr_4. \end{aligned} \quad (18)$$

If an expansion in terms of density is made then equations (14) and (15) are valid. Oden *et al* (1966) have given the first two terms in the expansion of $\psi(r)$ and $\Phi(r)$

$$\begin{aligned} \psi(r) = & \frac{1}{2}\rho^2 \left(\text{triangle with all three diagonals} \right) + \frac{1}{2}\rho^3 \left(4 \left(\text{triangle with two diagonals} \right) + 4 \left(\text{triangle with one diagonal} \right) + 2 \left(\text{triangle with no diagonals} \right) \right. \\ & \left. + \left(\text{square with one diagonal} \right) + \left(\text{square with two diagonals} \right) + \left(\text{square with three diagonals} \right) + \left(\text{square with four diagonals} \right) \right) \end{aligned} \quad (19)$$

and

$$\Phi(r) = \psi(r) + \frac{1}{2}\rho^2 \left(\text{triangle with all three diagonals} \right) + \frac{1}{2}\rho^3 \left(2 \left(\text{square with one diagonal} \right) + 4 \left(\text{square with two diagonals} \right) \right). \quad (20)$$

The fourth virial coefficients are exact in both the PY2 and CHNC2 cases but is not the case from fifth virial coefficient onwards. The resulting fifth virial coefficients in both the cases, calculated both from the pressure and compressibility equations, are given below

3.1. PY2

$$\begin{aligned} B_5(p) = & -\frac{2}{5} \left(\text{pentagon} \right) - 2 \left(\text{pentagon with one diagonal} + \text{pentagon with two diagonals} \right) - \frac{1}{3} \left(\text{pentagon with three diagonals} + \text{pentagon with four diagonals} \right) \\ & - \left(\text{pentagon with five diagonals} + \text{pentagon with six diagonals} \right) - \frac{1}{6} \left(3 \left(\text{pentagon with one diagonal} + \text{pentagon with two diagonals} \right) \right. \\ & \left. - \frac{1}{36} \left(\text{pentagon with one diagonal} + 3 \left(\text{pentagon with two diagonals} \right) \right) - \frac{1}{24} \left(2 \left(\text{pentagon with three diagonals} + \text{pentagon with four diagonals} \right) \right) \end{aligned} \quad (21)$$

$$\begin{aligned}
 B_5(c) = & -\frac{2}{5} \text{[pentagon]} - 2 \left(\text{[pentagon with 1 diagonal]} + \text{[pentagon with 2 diagonals]} \right) - \frac{3}{10} \left(\text{[pentagon with 3 diagonals]} + \text{[pentagon with 4 diagonals]} \right) \\
 & - \frac{4}{5} \left(\text{[pentagon with 3 diagonals]} + \text{[pentagon with 4 diagonals]} \right) - \frac{1}{10} \left(3 \text{[pentagon with 4 diagonals]} + \text{[pentagon with 5 diagonals]} \right). \tag{22}
 \end{aligned}$$

3.2. CHNC2

$$\begin{aligned}
 B_5(p) = & -\frac{2}{5} \text{[pentagon]} - 2 \left(\text{[pentagon with 1 diagonal]} + \text{[pentagon with 2 diagonals]} \right) - \frac{1}{3} \left(\text{[pentagon with 3 diagonals]} + \text{[pentagon with 4 diagonals]} \right) \\
 & - \left(\text{[pentagon with 3 diagonals]} + \text{[pentagon with 4 diagonals]} \right) - \frac{1}{6} \left(3 \text{[pentagon with 4 diagonals]} + \text{[pentagon with 5 diagonals]} \right) \\
 & - \frac{1}{24} \left(2 \text{[pentagon with 5 diagonals]} \right) \tag{23}
 \end{aligned}$$

$$\begin{aligned}
 B_5(c) = & -\frac{2}{5} \text{[pentagon]} - 2 \left(\text{[pentagon with 1 diagonal]} + \text{[pentagon with 2 diagonals]} \right) - \frac{1}{3} \left(\text{[pentagon with 3 diagonals]} + \text{[pentagon with 4 diagonals]} \right) \\
 & - \frac{9}{10} \left(\text{[pentagon with 3 diagonals]} + \text{[pentagon with 4 diagonals]} \right) - \frac{1}{10} \left(3 \text{[pentagon with 4 diagonals]} + \text{[pentagon with 5 diagonals]} \right). \tag{24}
 \end{aligned}$$

4. Selfconsistent approximation

Because of the approximations involved in the PY2 and CHNC2 theories the fifth virial coefficients are not consistent as calculated from equations (2) and (3). We now propose an approximation for achieving selfconsistency in the virial coefficients calculated either from the pressure equation or from the compressibility equation. The equation may be written as

$$c(r) = f(r)y(r) + (1 - m)(y(r) - 1 - \ln y(r)) + \Phi(r) - \frac{1 - m}{2} (h(1, 2) - c(1, 2))^2 \tag{25}$$

where m is a parameter. When $m = 1$ equation (25) reduces to PY2 while with $m = 0$ we get CHNC2. Similar selfconsistent approximations (SCA) were suggested for the first order theories by Rowlinson (1965), Lado (1967), Hurst (1966), Rushbrooke and Hutchinson (1961), Hutchinson and Rushbrooke (1963) and Watts and Henderson (1969).

By a linear combination of functions Stell (1969) obtained a different SC2 approximation given by

$$c(r) = e(r)y(r) - 1 - \theta \ln y(r) - (1 - \theta)(y(r) - 1) + \frac{1}{2}(1 - \theta)(h(r) - c(r))^2 + \Phi(r) \tag{26}$$

where

$$e(r) = \exp(-\beta u(r)). \tag{27}$$

The parameter m is chosen in equation (25) so that it reduces to the PY2 and CHNC2 approximations at the two extremes namely $m = 1$ and 0 respectively. Since both the PY2 and CHNC2 theories yield results which are exact up to the fourth virial coefficient.

equation (25) has been tested for the evaluation of fifth virial coefficients. The resulting expressions for the fifth virial coefficients calculated according to the pressure and compressibility equations are given below

4.1. SCA

$$\begin{aligned}
 B_5(p) = & -\frac{2}{5} \text{pentagon} - 2 \left(\text{pentagon with one diagonal} + \text{pentagon with two diagonals} \right) - \frac{1}{3} \left(\text{pentagon with three diagonals} + \text{pentagon with four diagonals} \right) \\
 & - \left(\text{pentagon with five diagonals} + \text{pentagon with six diagonals} \right) - \frac{1}{6} \left(3 \text{pentagon with seven diagonals} + \text{pentagon with eight diagonals} \right) \\
 & - \frac{1}{24} \left(2 \text{pentagon with nine diagonals} + \text{pentagon with ten diagonals} \right) - \frac{1}{36} m \left(\text{pentagon with eleven diagonals} + 3 \text{pentagon with twelve diagonals} \right) \quad (28)
 \end{aligned}$$

$$\begin{aligned}
 B_5(c) = & -\frac{2}{5} \text{pentagon} - 2 \left(\text{pentagon with one diagonal} + \text{pentagon with two diagonals} \right) - \frac{10-m}{30} \left(\text{pentagon with three diagonals} + \text{pentagon with four diagonals} \right) \\
 & - \frac{9-m}{10} \left(\text{pentagon with five diagonals} + \text{pentagon with six diagonals} \right) - \frac{1}{10} \left(3 \text{pentagon with seven diagonals} + \text{pentagon with eight diagonals} \right). \quad (29)
 \end{aligned}$$

The condition

$$B_5(p) = B_5(c) \quad (30)$$

has been used to evaluate m .

5. Results and discussion

5.1. Hard spheres

The potential function for hard spheres of diameter σ is

$$u(r) = \begin{cases} \infty & \text{for } r < \sigma \\ 0 & \text{for } r > \sigma. \end{cases} \quad (31)$$

The selfconsistent value of the fifth virial coefficient is given in table 1 and is compared with other values. It is gratifying that this value is in surprisingly good agreement with the exact value. The value of m required to achieve selfconsistency is +0.2245.

Table 1. Fifth virial coefficient for hard spheres†

	$B_5(p)$	$B_5(c)$
Exact		0.1103 ± 0.0005
PV	0.0859	0.1211
PV2	0.1240	0.1074
CHNC	0.1447	0.0493
CHNC2	0.0657	0.1230
SCA	0.1109	0.1109
($m = +0.2245$)		

† in units of $b = \frac{2}{3}\pi\sigma^3$.

5.2. Lennard-Jones 6-12 potential

The potential function is given by

$$u(r) = 4\epsilon \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right\}. \quad (32)$$

The fifth virial coefficients have been calculated for the temperature range $T^*(=kT/\epsilon)$ from 1 to 100 and is shown in figure 1 along with PY2(c) and CHNC2(c) and exact values.

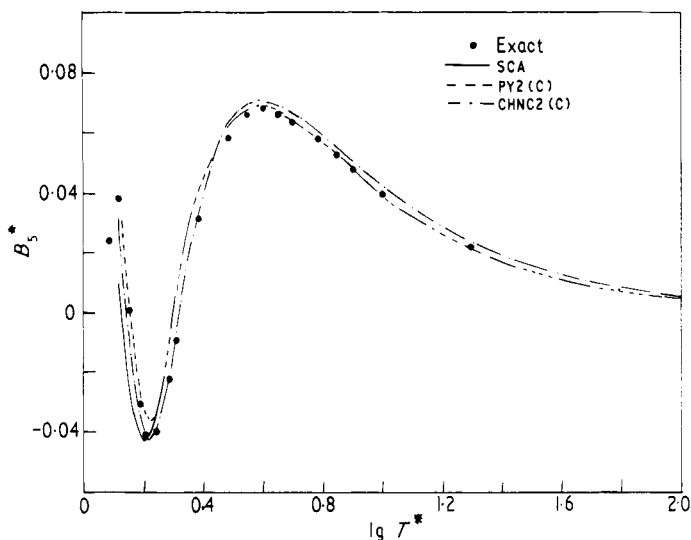


Figure 1. Fifth virial coefficient for the Lennard-Jones 6-12 potential.

It is gratifying to note that the agreement between the SCA and exact values is good. It may be pointed out in this connection that the SCA values are closer to the CHNC2 compressibility values at low temperatures and with PY2 compressibility values at high temperatures. Hence the SCA values are in reasonably good agreement in the entire

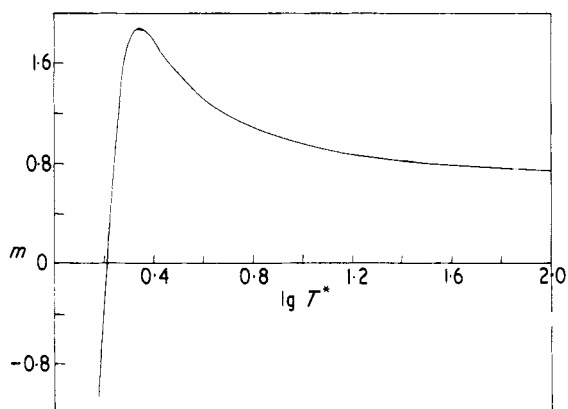


Figure 2. Variation of m with temperature.

temperature range. This is to be expected since the CHNC approximation works well at low temperatures while the PY approximation is good at high temperatures (Khan 1964, Gopala Rao and Swamy 1971). The temperature dependence of the parameter m is shown in figure 2.

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