

## SHORT COMMUNICATIONS

### SELF-CONSISTENT APPROXIMATION AND FIFTH VIRIAL COEFFICIENTS FOR A SQUARE WELL POTENTIAL

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[Manuscript received 27 March 1973]

#### Abstract

A proposed self-consistent approximation for the second-order Percus-Yevick and convoluted hypernetted chain theories is used to calculate the fifth virial coefficients for a square well potential. The results are in good agreement with the exact values.

Percus (1962, 1964) has shown that the integral equation for the radial distribution function from both the Percus-Yevick (PY; Percus and Yevick 1958; Stell 1963) and convoluted hypernetted chain (CHNC; van Leeuwen *et al.* 1959; Meeron 1960; Morita 1960) theories of the fluid state can be obtained by expansion in a functional Taylor series with truncation at the first-order term. This method is based essentially on a consideration of the behaviour of the  $n$ th order distribution function in the presence of an external field which is ultimately taken to be that of an added molecule. Verlet (1964) has extended the method to the second-order terms in the expansions and the improved PY 2 and CHNC 2 theories that result give consistent values of the fourth virial coefficient when computed from either the pressure equation or the compressibility equation. In the present note we consider a self-consistent approximation to both theories which yields consistent values of the fifth virial coefficient.

It is assumed in classical statistical mechanics that the total potential energy  $U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  of a system of  $N$  particles can be expressed as a sum of the two-body interactions as

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

and the equation of state of the system can be calculated either from the pressure equation

$$pV/NkT = 1 - (2\pi\rho/3kT) \int_0^\infty g(r) (du/dr) r^3 dr \quad (2)$$

or from the compressibility equation

$$(kT)^{-1}(\partial p/\partial \rho)_T = 1 - 4\pi\rho \int_0^\infty C(r) r^2 dr. \quad (3)$$

Here  $g(r)$  is the radial distribution function,  $\rho = N/V$  is the number density, and  $C(r)$  is the direct correlation function, which is related to the pair correlation function

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$h(r) = g(r) - 1$  by the Ornstein-Zernike equation

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

The PY 2 and CHNC 2 extensions proposed by Verlet (1964) are given respectively by

$$C(r) = f(r)y(r) + \Phi(r) \quad (5a)$$

and

$$C(r) = f(r)y(r) - 1 - \ln y(r) + y(r) + \Psi(r). \quad (5b)$$

Oden *et al.* (1966) have given the first two terms in the density expansions of  $\Psi(r)$  and  $\Phi(r)$ , while the diagram contributions and the resulting fifth virial coefficients for the PY 2 and CHNC 2 theories calculated from equations (2) and (3) have been obtained by Kim *et al.* (1966).

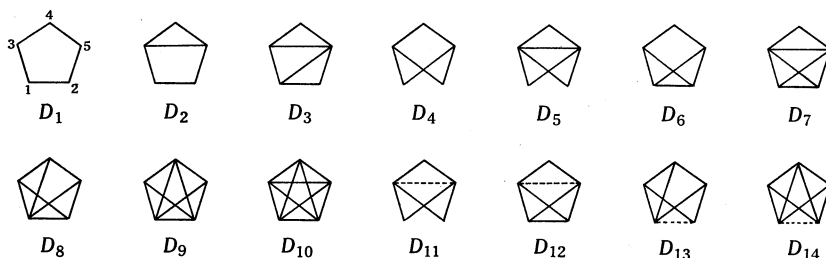


Fig. 1.—Definitions of the  $D_n$  ( $n = 1 \dots 14$ ) terms appearing in equations (8) and (9). Each diagram represents a multiple integral, with a full line between two points  $i$  and  $j$  denoting a factor  $f(r_{ij}) = \exp\{-\beta u(r_{ij})\} - 1$  in the integrand and a dashed line denoting a factor  $r_{ij} \partial\{f(r_{ij})\}/\partial r_{ij}$ .

An exact distribution function  $g(r)$ , if it were known, would yield consistent virial coefficients of all order calculated from either equations (2) or (3). Since the PY 2 and CHNC 2 theories only give exact fourth virial coefficients, in order to obtain consistent fifth virial coefficients some kind of self-consistent approximation for  $C(r)$  must be introduced. Such an approximation has been given by Gopala Rao and Narasimha (1972) and takes the form

$$C(r) = f(r)y(r) + (1-m)\{y(r) - 1 - \ln y(r)\} + \Phi(r) - \frac{1}{2}(1-m)\{h(r_{12}) - C(r_{12})\}^2. \quad (6)$$

Equation (6) reduces to the PY 2 approximation for  $m = 1$  and to the CHNC 2 approximation for  $m = 0$ . Similar self-consistent approximations were suggested for the first-order theories (see e.g. Rushbrooke and Hutchinson 1961; Rowlinson 1965). Stell (1969) has proposed an alternative self-consistent approximation to the second-order theories, which may be written as

$$C(r) = \exp\{-\beta u(r)\} y(r) - 1 - \theta \ln y(r) - (1-\theta)\{y(r) - 1\} + \frac{1}{2}(1-\theta)\{h(r) - C(r)\}^2 + \Phi(r), \quad (7)$$

where  $\theta$  is a parameter.

With the approximation (6), the fifth virial coefficients  $B_5$  calculated from the pressure equation (2) and the compressibility equation (3) are found to be respectively

$$B_5^{(p)} = -\frac{2}{5}D_1 - 2(D_2 + D_3) - \frac{1}{3}(D_4 + D_5) - (D_6 + D_7) - \frac{1}{6}(3D_8 + D_9) - \frac{1}{24}(2D_{13} + D_{14}) - \frac{1}{36}m(D_{11} + 3D_{12}) \quad (8a)$$

and

$$B_5^{(c)} = -\frac{2}{5}D_1 - 2(D_2 + D_3) - \frac{1}{30}(10-m)(D_4 + D_5) - \frac{1}{10}(9-m)(D_6 + D_7) - \frac{1}{10}(3D_8 + D_9), \quad (8b)$$

where the diagrams representing the terms  $D_n$  ( $n = 1 \dots 14$ ) are illustrated in Figure 1.

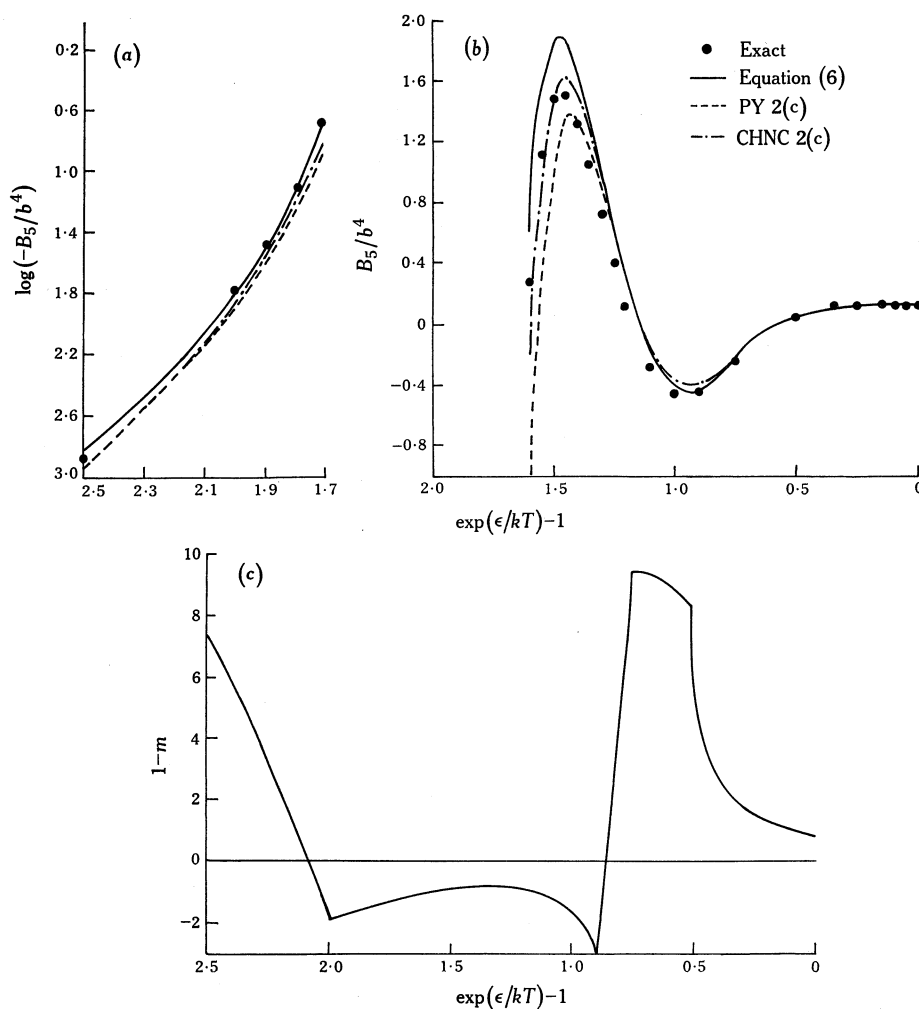


Fig. 2.—Variation with  $\exp(\epsilon/kT) - 1$  of (a) the logarithm of the fifth virial coefficient  $B_5$  at low temperatures, as calculated from the exact expression (9), the self-consistent approximation (6), and the PY 2 and CHNC 2 compressibility equations, (b) the fifth virial coefficient at higher temperatures from the same calculations, and (c) the parameter  $m$  occurring in equation (6).

The condition  $B_5^{(p)} = B_5^{(c)}$  has been used to evaluate the parameter  $m$ . The fifth virial coefficient for a rigid sphere potential function was found to be given by  $0.1109 b^4$  ( $b = \frac{2}{3}\pi\sigma^3$ ), which compares very well with the exact value  $0.1103 \pm 0.0005 b^4$ .

Equation (6) has also been applied in the evaluation of the fifth virial coefficients for a square well potential defined by

$$\begin{aligned} u(r) &= \infty & \text{for } r < \sigma, \\ &= -\varepsilon & \sigma < r < \lambda\sigma, \\ &= 0 & r > \lambda\sigma. \end{aligned}$$

The value of the parameter  $\lambda$  has been taken to be 1.5 and the corresponding diagram contributions from Barker and Henderson (1967) have been used. The resulting fifth virial coefficients from the self-consistent approximation (6) are compared in Figures 2(a) and 2(b) with the PY 2(c) and CHNC 2(c) values from the compressibility equation and the exact values calculated from the equation

$$B_5^{(c)} = -\frac{2}{5}D_1 - 2(D_2 + D_3) - \frac{1}{3}(D_4 + D_5) - (D_6 + D_7) - \frac{1}{6}(3D_8 + 2D_9) - \frac{1}{30}D_{10}, \quad (9)$$

with the  $D_n$  defined in Figure 1. Although the PY 2 and CHNC 2 results only agree well with the exact values at high and low temperatures respectively, as has been found in previous work (Khan 1964; Rowlinson 1969; Gopala Rao and Narasimha Swamy 1971), equation (6) gives a good approximation over the entire temperature range. The variation of the parameter  $m$  with temperature is shown in Figure 2(c).

### Acknowledgment

One of us (K.N.S.) is grateful to the Council of Scientific and Industrial Research, India, for the award of a Research Fellowship during the tenure of which this work was performed.

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