A perturbation theory of classical simple fluids

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Abstract The Weeks-Chandler-Andersen (WCA) perturbation theory of classical simple fluid is re-examined using the 'modified' Born-Green-Yvan expression for the function $Y(r)$ of the hard sphere fluid. We calculate the thermodynamic properties of the Lennard-Jones (12-6) fluid. They are found to be in good agreement with the Verlet-Weis, Boublik and Simulation results.

Keywords Perturbation theory, free energy, equation of state

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1. Introduction

Weeks-Chandler-Andersen (WCA) [1] perturbation theory with the semi empirical expression for the hard-sphere radial distribution function (RDF) $g_{HS}(r)$ [2,3] is in error in some applications. This difficulty can be avoided by using a better expression for $g_{HS}(r)$.

In the present work, we are primarily concerned with the WCA theory and the 'modified' Born-Green-Yvan (BGYM) expression for $Y_{HS}(r)$ for $r \leq \ell$, obtained by Chae, Ree and Rec [4]. These values for $Y_{HS}(r)$ are in much better agreement than those of PY-values [5].

2. Theoretical formulation

We consider a system, whose molecules interact via the LJ (12-6) potential

$$u(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right],$$

where $\varepsilon$ and $\sigma$ are constants with units of energy and length, respectively.

Using the division of potential according to the WCA scheme [1], the excess free energy per particle is given by

$$f = f_0 + f_1,$$

where $f_0$ is the excess free energy per particle of the reference system and $f_1$ is the first order perturbation correction to it. Thus

$$f_1 = 2\pi \rho \int_0^\infty g_0(r) u_p(r) r^2 dr,$$

where $g_0(r)$ is the RDF of the reference system.

3. Reference system

The free energy of the reference system is expressed in terms of that of the hard spheres of diameter $d$, which can be determined by the Verlet-Weis method [2, 3].

In the present work, to evaluate $d$, we use the BGYM expression for $Y_{HS}(\ell/d)$, given as [4]

$$Y_{HS}(\ell/d) = g_{HS}(d) \exp \left[ \pi \rho d \right] g_{HS}(d) \left[ \frac{(1/12)(\ell/d)^2}{-(\ell/d)+((1/12))} \right]$$

for $\ell \leq d$. 

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where $g_{HS}(d)$ is the hard sphere RDF at the contact and given by [6]

$$g_{HS}(d) = (1 - \eta / 2) / (1 - \eta)^3. \quad (5)$$

where $\eta = \pi \rho d^3 / 6$ is the packing fraction. Then $d$ is given by

$$d = d_s [1 + (\sigma_1 / 2 \sigma_0) \delta]. \quad (6)$$

where

$$d_s = \frac{\int_0 (1 - \exp[-\beta u_0(r)]) dr}{\int_0 (1 - \exp[-\beta u_0(r)]) dr} \quad (7)$$

and

$$\delta = \int_0 (d/d_s - 1)^2 (d/dr) (\exp[-\beta u_0(r)]) dr \quad (8)$$

and

$$\sigma_1 / 2 \sigma_0 = (1 - (11 / 2) \eta + (17 / 4) \eta^2 + \eta^3) / (1 - \eta)^3. \quad (9)$$

Only $\sigma_1 / 2 \sigma_0$ differs from that derived by Verlet and Weis (VW).

The virial equation of state for the reference system is given by [2, 3]

$$\beta P_s / \rho = Z_0 = Z_{HS} + 4 \delta \Delta Z. \quad (10)$$

where $Z_{HS}$ is the hard sphere compressibility factor and given by [6]

$$Z_{HS} = (1 + \eta + \eta^2 + \eta^3) / (1 - \eta)^3 \quad (11)$$

and $\Delta Z$ is derived using the GYBM expression for $Y_{HS}(r/d)$

$$\Delta Z = -2 \eta^2 (1 - \eta / 2)^2 / (1 - \eta)^9 \quad (12)$$

which differs from that given by Verlet and Weis [2, 3].

With the help of eq. (10), we obtain an expression for the free energy per particle for the reference system

$$\beta f_s = \beta f_{HS}^{el} + 4 \delta \beta \Delta f. \quad (13)$$

where [6]

$$\beta f_{HS}^{el} = \eta (4 - 3 \eta) / (1 - \eta)^2 \quad (14)$$

is the excess free energy of the hard sphere system and

$$\beta \Delta f = (1 / 30) (\eta^2 / (1 - \eta)^3) - (1 / 8) (\eta^2 / (1 - \eta)^4) - (1 / 10) (\eta / (1 - \eta)^5) + (15 / 16) (\eta^2 / (1 - \eta)^5) \quad (15)$$

4. First order perturbation term

In the WCA theory, the RDF $g_0(r)$ of the reference system is approximated as [1]

$$g_0(r) = \exp [-\beta u_0(r)] Y_{HS} (r / d) \quad (16)$$

Substituting eq. (16) in eq. (3), we obtain

$$f_1 = 2\pi \rho \int Y_{HS}(r / d) u_p (r) r^2 dr + O(\delta). \quad (17)$$

In the present calculation, we use the MC [2, 3] and MD [2, 3] values of $g_{HS}(r)$ for $r > d$.

5. Results and discussion

We compare our results of $\beta P / \rho$ and $\beta U / N$ for the LJ (12-6) fluid with VW [2], Boublik [7] and MC [2] values in a range of reduced density $\rho^*$ at $T^* = 1.15$ in Table 1. The agreement is quite good. At low density, Boublik theory [7] is superior to the present theory due to the second order perturbation terms.

Table 1. Values of $\beta P / \rho$ and $\beta U / N$ for the LJ (12-6) fluid at $T^* = 1.15$

<table>
<thead>
<tr>
<th>$\rho^*$</th>
<th>Exact</th>
<th>Present</th>
<th>VW</th>
<th>Boublik</th>
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</table>

Thus we come to the conclusion that the WCA perturbation theory, using the BGYM integral equation for $Y_{HS}(r/d)$ for $r \leq d$, can be employed to calculate the equilibrium properties of simple fluid.

Acknowledgments

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References