

A Simplified Expression for the Hard-Sphere Dimer Fluid Radial Distribution Function

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Abstract—Recently, in our laboratory a closed form expression for the correlation function of the hard-sphere dimer fluid obtained from Wertheims multidensity Ornstein-Zernike integral equation theory with Percus-Yevick approximation was presented by Kim et al. [2001]. However, it is difficult to apply its expression to perturbation theory and vapor-liquid equilibria calculations, since it is of very complex form. In this work, we present a simplified expression for the first shell of the radial distribution function (RDF) of the hard-sphere dimer fluid using a series expansion of the analytical expression. The expansion is carried out in terms of both the packing fraction and the radial distance. Expressions are also obtained for the coordination number and its first and second derivatives as functions of radial distance and packing fraction. These expressions, which are useful in perturbation theory, are simpler to use than those obtained from the starting equation, while giving good agreement with the original expression results. Then we present an simplified equation of state for the square-well dimer fluid of variable well width (λ) based on Barker-Henderson perturbation theory using its expression for the radial distribution function of the hard-sphere dimer fluid, and test its expression with NVT and Gibbs ensemble Monte Carlo simulation data [Kim et al., 2001].

Key words: Hard Sphere Dimer, Perturbation Theory, Simplified Form, Radial Distribution Function, Integral

INTRODUCTION

In the last few decades, fluids consisting of hard-body fluids have been the subject of a great deal of research, both in theory as well as in computer simulations. One of the reasons is that such fluids have many properties in common with fluids having more realistic intermolecular potentials. Moreover, once the properties of a hard-body fluid have been obtained, those of a more realistic fluid with a similar shape can be obtained through a perturbation theory that uses the hard-body fluid as the reference fluid.

The Ornstein-Zernike (OZ) integral equation theory with the Percus-Yevick (PY) closure approximation is of significant interest because it provides an analytical solution for the radial distribution function (RDF) [Wertheim, 1963; Thiele, 1964; Throop et al., 1965; Baxter, 1968; Smith et al., 1970; Chang et al., 1994], which makes it possible for the equation of state to be formulated in a closed form through perturbation theory [Chang et al., 1994; Tang et al., 1993, 1994].

Hard-sphere chain fluids have been studied extensively by computer simulation and integral equation theories such as the polymer-reference interaction site model theory [Yethiraj et al., 1990, 1992], Chiew's PY theory [Chiew, 1990, 1991] and the multidensity Ornstein-Zernike integral equation theory [Wertheim, 1984, 1986; Kalyuzhnyi et al., 1997; Chang et al., 1995a, b, 1999]. Also, chain fluids with other potentials have been studied [Chang et al., 1998; Yeom et al., 2000]. Chiew's PY theory is an extension of Baxter's spherically associating fluid theory [Baxter, 1968] to fluids containing linear chains with special bond connectivity constraints. Recently an approximate analytical solution of the PY theory for the intermolecular RDF was developed by Tang and Lu [Tang et al.,

1996].

Since Wertheim formulated the multidensity Ornstein-Zernike (MOZ) integral equation theory for anisotropic associating fluids [Wertheim, 1984, 1986], several studies have been done to apply the MOZ theory to hard-sphere chains. Using the polymer Percus-Yevick closure and the ideal-chain approximation, Chang and Sandler [Chang et al., 1995a, b] calculated inter- and intramolecular RDFs for hard-sphere chains, and later Chang and Kim [Chang et al., 1999] obtained analytical expressions for these RDFs. On the other hand, Kim et al. [2001] obtained an analytical expression for the RDF using the MOZ theory for hard sphere dimer (HSD) fluids.

Although much effort has been aimed at obtaining more manageable expressions of the RDF derived by the PY theory, these expressions have limitations in practical application. Even analytical solutions are often too complicated, especially for use in perturbation theories such as those of Barker-Henderson or Weeks-Chandler-Andersen. To derive the equation of state, these theories require integrations and derivations of functions that depend on the RDF and the inter-molecular potential. The resulting pressure expressions for the first and second order perturbation term are always complicated and generally nonanalytical.

Thus, it would be desirable to obtain simpler expressions which have the same results with original analytic solution and have a simple form of pressure equation in perturbation treatment for a more realistic fluid. The aim of this paper is to derive a simple form that allows considerable simplicity in the expression of the first coordination shell of the RDF and that can be used easily in perturbation, While retaining good agreement with results obtained from RDF derived by Kim et al. first of all, the correlation function of the hard-sphere dimer fluid presented by Kim et al. is summarized. We will present a simplified expression for the first shell of the radial distribution function (RDF) of the hard-sphere dimer fluid using a series expansion of the analytical expression in terms of radial distance and

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packing fraction. And then we will derive perturbation expression using it.

ANALYTICAL SOLUTION AND INTEGRATION FORM OF THE HARD-DIMER RDF

Kim et al. [2001a, b] presented a closed form expression for the correlation function of a hard-sphere dimer fluid obtained from Wertheim's multidensity Ornstein-Zernike integral equation theory with Percus-Yevick approximation.

The RDF of hard-sphere dimer fluids in the first shell is given by

$$g^{HSD}(r) = \frac{1}{r} \sum_{i=1}^4 \frac{N_2(s_i)}{M_1(s_i)} e^{s_i(r-1)} \quad (1)$$

where

$$N_2(s) = 2(1+2\eta) + (6+15\eta)s + 8(1+2\eta)s^2 + 4(1+2\eta)s^3 \quad (2)$$

$$M(s) = -48\eta(1+2\eta) - 24\eta(2+7\eta)s + 144\eta^2s^2 + 48\eta(1-\eta)s^3 + 8(1-\eta)s^4 \quad (3)$$

and $M_1(s) = \partial M / \partial s$. The quantities s_i are zeros of $M(s)$.

They utilized Tang and Lu's Hilbert transform result for the integral of the RDF

$$\int_1^\lambda g^{HSD}(x) x^2 dx = - \left. \frac{d\hat{G}(s)}{ds} \right|_{s=0} + \text{Res}_{\{\hat{G}(s)\}} \left[\hat{G}(s) \frac{\lambda s - 1}{s^2} e^{\lambda s} \right] \quad (4)$$

where $\hat{G}(s)$ is the Laplace transform of $rg(r)$,

$$\hat{G}(s) = \int_1^\infty x g^{HSD}(x) e^{-sx} dx = \frac{N_2(s)}{M(s)} e^{-s} \quad (5)$$

and Res represents the summation of residues produced by all singularities in function $\hat{G}(s)$. Substituting Eq. (5) into Eq. (4) and noting that

$$\left. \frac{d\hat{G}(s)}{ds} \right|_{s=0} = - \frac{1}{24\eta} \quad (6)$$

yields

$$\begin{aligned} \int_1^\lambda g^{HSD}(x) x^2 dx &= \frac{1}{24\eta} + \text{Res}_{\{M(s)\}} \left[\frac{N_2(s)(\lambda s - 1)}{M(s)s^2} e^{(\lambda-1)s} \right] \\ &= \frac{1}{24\eta} + \sum_{i=1}^4 \frac{N_2(s_i)(\lambda s_i - 1)}{M_1(s_i)s_i^2} e^{(\lambda-1)s_i} \end{aligned} \quad (7)$$

A SIMPLIFIED EXPRESSION FOR THE FIRST COORDINATION SHELL OF THE HARD-DIMER RDF

To simplify the expression for the first coordination shell of the RDF, we might think of expanding it in power series of the radial distance x around $x=1$. However, this expansion converges rather slowly and as many as 15 terms are needed to achieve good accuracy with the analytical solution. This is due to the fact that the PY solution of the RDF has a peak at a reduced distance $x < 1$. It seems more advisable to expand $g(x)$ around $x=1.5$, which corresponds to the middle of the first shell and is particularly convenient when the resulting expression of the RDF is to be used in a perturbation theory for the square-well fluid with range $\lambda=1.5$. In this case, the number of terms of the expansion is reduced.

Instead of expanding RDF itself, we expanded the integral of RDF

$$I(\lambda, \eta) = \int_1^\lambda g(x) x^2 dx \quad (8)$$

as follows

$$I(\lambda, \eta) = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} I_{nm} \frac{(\lambda-1.5)^n}{(1-\eta)^{n+1}} \eta^m \quad (9)$$

which plays an important role in perturbation theories for the square-well fluid.

At $m=8$ and $n=8$, AAD% of $I(\lambda, \eta)$ is 9.632×10^{-3}

The expansion on $I(\lambda, \eta)$ instead of the expansion on $g(x)$ itself is because the expansion on $I(\lambda, \eta)$ is more useful and convenient than the expansion on $g(x)$ itself in the perturbation theory. In order to reduce the low rate of convergence, we define the denominator form of $I(\lambda, \eta)$ expansion as the above form.

From Eq. (9), the RDF is readily obtained in the form

$$g(x) = \frac{1}{x^2} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} I_{nm} \frac{n(x-1.5)^{n-1}}{(1-\eta)^{n+1}} \eta^m \quad (10)$$

I_{nm} is the correlation parameter, given by Table 1.

APPLICATION TO PERTURBATION THEORIES OF SQUARE-WELL FLUIDS OF VARIABLE WIDTH

In perturbation theory the Helmholtz free energy of the system is expanded in the inverse temperature around that of a reference

Table 1. Parameters I_{nm} involved in Eq. (9) up to $n=8$, $m=8$

n	m								
	0	1	2	3	4	5	6	7	8
0	0.50151	0.84636	−0.96198	0.46857	−13.6613	46.4631	−98.7908	111.451	−45.4170
1	1.64849	−0.02511	−7.45037	−0.85329	6.85938	12.1549	−41.1000	113.130	−98.7401
2	1.60498	−3.93626	−5.62713	−4.34775	157.401	−550.036	1149.83	−1351.87	628.560
3	0.68559	−3.08019	−0.93061	62.1987	−270.001	805.062	−1579.18	1569.11	−578.236
4	0.12554	−0.58117	4.77797	−6.07342	−15.3681	34.3968	−173.848	448.769	−322.394
5	0.01064	0.10059	4.18765	−47.9975	237.273	−766.056	1548.57	−1650.11	691.227
6	−0.00319	0.34058	−5.11619	41.0545	−209.873	651.797	−1124.95	972.125	−324.113
7	0.00082	−0.03047	0.66734	−6.41021	31.1024	−69.1859	50.3279	29.0152	−39.2324
8	0.00085	−0.05197	1.02276	−9.44811	49.3776	−153.710	275.959	−259.597	98.3267

system whose thermodynamic structural properties are known. The second-order expansion of the Helmholtz free energy is of the form

$$\frac{A^{ex}}{Nk_B T} = \frac{A_0^{ex}}{Nk_B T} + \frac{1}{T^*} \frac{A_1}{Nk_B T} + \frac{1}{T^{*2}} \frac{A_2}{Nk_B T} \quad (11)$$

where A^{ex} is the Helmholtz free energy in excess of that of an ideal gas at the same temperature and number density and A_0^{ex} is the excess Helmholtz free energy of the reference system. A_1 and A_2 are the first- and the second-order perturbation terms for the Helmholtz free energy, respectively. N is the number of molecules, k_B is the Boltzmann constant, T is temperature, and T^* is the reduced temperature ($T^* = k_B T / \epsilon$). A_1 and A_2 are derived from knowledge of the equation of state and the RDF of the reference fluid.

For the reference equation of state we employ TPT, given by

$$\frac{A^{ex,HSD}}{Nk_B T} = \frac{A^{ex,HS}}{Nk_B T} - \ln g^{HS}(\sigma^+) \quad (12)$$

where the superscript HSD denotes the hard-sphere dimer fluid and $g^{HS}(\sigma^+)$ is the contact value of RDF of the hard sphere fluid. If the Carnahan-Starling equation of state is used for hard-sphere excess Helmholtz free energy and for the contact value of the RDF, the compressibility factor is given by

$$Z^{HSD} = 1 + \frac{4\eta(2-\eta)}{(1-\eta)^3} - \frac{\eta(\frac{5}{2}-\eta)}{(1-\eta)(1-\frac{\eta}{2})} \quad (13)$$

The first-order perturbation term for square-well dimer fluid around the reference hard-sphere dimer fluid is given by

$$\frac{A_1^{DIM}}{Nk_B T} = -8\pi\rho\sigma^3 I^{HSD} \quad (14)$$

$$I^{HSD} = \int_1^\lambda g^{HSD}(r) r^2 dr \quad (15)$$

In the previous section we obtained a simplified expression for the I^{HSD} of hard-sphere dimer fluids.

The second-order perturbation term can be formed from the Barker-Henderson perturbation theory as

$$\frac{A_2^{DIM}}{Nk_B T} = -4\pi\rho\sigma^3 \frac{\partial \rho}{\partial p^{HSD}} \frac{\partial(\eta I^{HSD})}{\partial \eta} \quad (16)$$

The compressibility factors are obtained by differentiating the corresponding Helmholtz free energy term with respect to η ,

$$Z^{SWD} = Z^{HSD} + \frac{Z_1^{DIM}}{T^*} + \frac{Z_2^{DIM}}{T^{*2}} \quad (17)$$

$$Z_1^{DIM} = -24\eta \frac{\partial(\eta I)}{\partial \eta} \quad (18)$$

$$Z_2^{DIM} = -12\eta \frac{\partial}{\partial \eta} \left(\frac{\partial \rho}{\partial p^{HSD}} \frac{\partial(\eta I^{HSD})}{\partial \eta} \right) \quad (19)$$

$$Z_1^{DIM} = -24 \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} I_{nm} [1+m+(n-m)\eta] \eta^{m+1} \frac{(\lambda-1.5)^n}{(1-\eta)^{n+2}} \quad (20)$$

$$Z_2^{DIM} = -12k_B T \eta \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} I_{nm} \left\{ \left(\frac{\partial \rho}{\partial p^{HSD}} \right) [-1-3n+m^2(1-\eta)-n^2(1+\eta)] \right.$$

$$\left. + 2m(1+n\eta) + \frac{2+3n+n^2}{1-\eta} \right\} + \frac{\partial}{\partial \eta} \left(\frac{\partial \eta}{\partial p^{HSD}} \right) [1+m+(n-m)\eta] \eta \left\{ \frac{(\lambda-1.5)^n}{(1-\eta)^{n+2}} \eta^m \right\} \quad (21)$$

The excess chemical potential can be obtained in an analytic form from the usual thermodynamic relations.

$$\frac{\mu^{ex}}{k_B T} = \frac{A^{ex}}{Nk_B T} + \frac{pV}{Nk_B T} \quad (22)$$

CONCLUSION

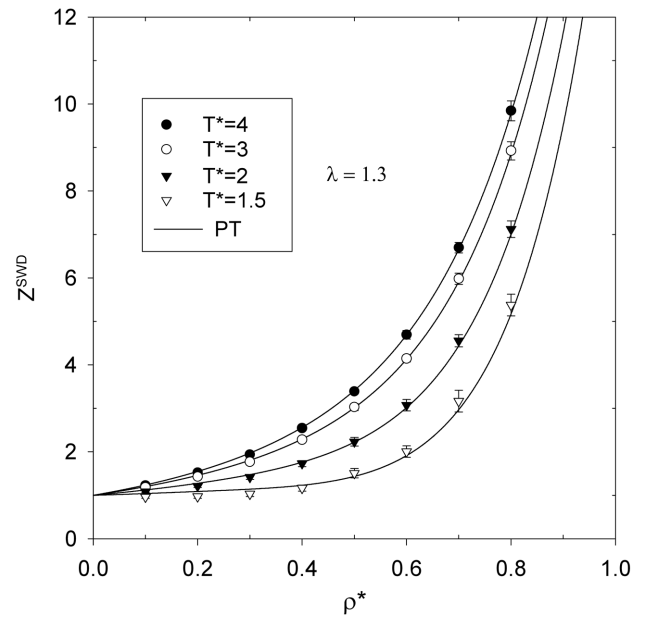


Fig. 1. Compressibility factors of square-well dimer fluids ($\lambda=1.3$). The symbols are simulation data [Kim et al., 2001].

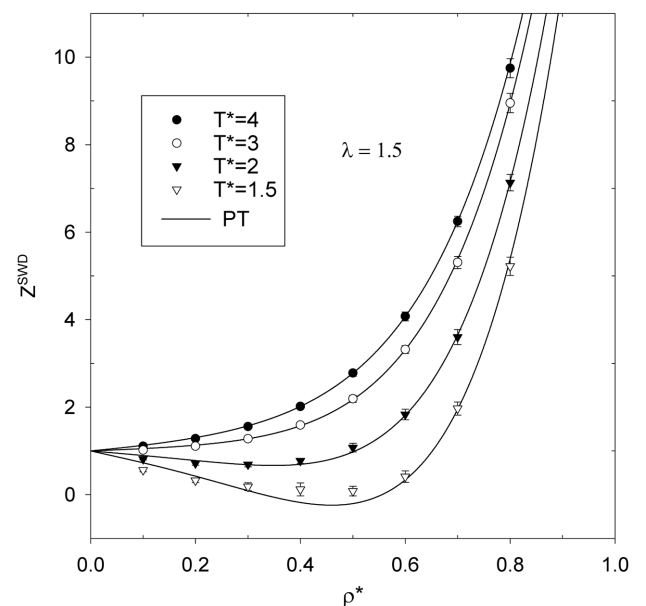


Fig. 2. Compressibility factors of square-well dimer fluids ($\lambda=1.5$). The symbols are simulation data [Kim et al., 2001].

We presented a simple form for the first shell of the hard sphere dimer radial distribution function and for the integral I^{HSD} , which plays an important role in perturbation theory. The integral I^{HSD} is fitted with the eighth order of radial distance and packing fraction, respectively, which gives good agreement with the results obtained by original analytic RDF derived by Kim et al. in $1 \leq \lambda \leq 2$. First and second derivative of the I^{HSD} also give good agreement with original expression results. By using the integral I^{HSD} and perturbation theory, we obtained the Helmholtz free energy and compressibility factor for the square-well dimer in the simple form. Fig. 1, Fig. 2 and Fig. 3 show the compressibility factor for the square-well dimer

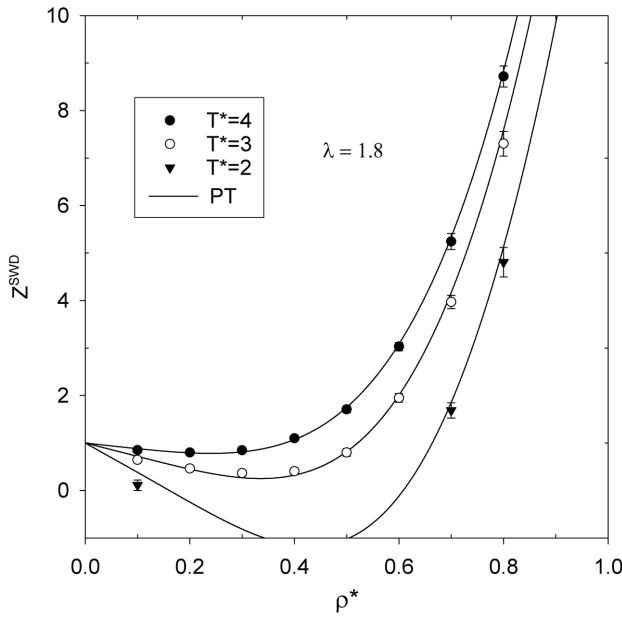


Fig. 3. Compressibility factors of square-well dimer fluids ($\lambda=1.8$). The symbols are simulation data [Kim et al., 2001].

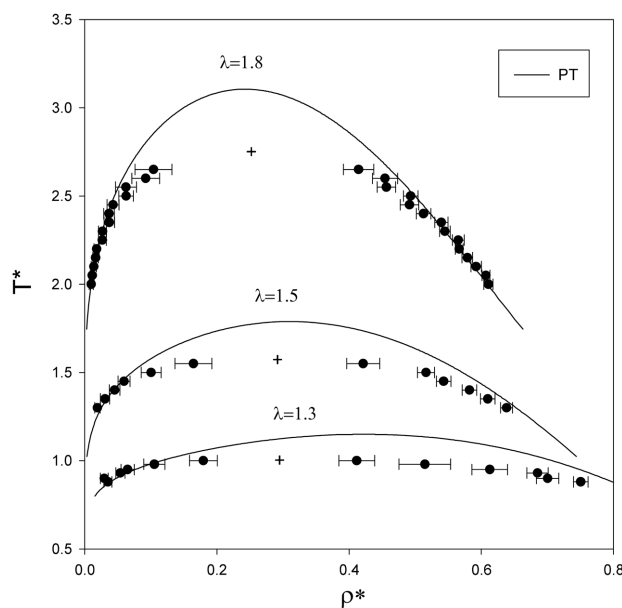


Fig. 4. The vapor-liquid coexisting curves of square-well dimer fluid. The symbols are simulation data [Kim et al., 2001].

that is compared with simulation data [Kim et al., 2001]. Fig. 4 shows the vapor-liquid coexisting curves of square-well dimer fluid.

From these facts we can conclude that by using such a simple expression, complicated and tedious time-consuming calculation can be reduced, while retaining good agreement with the exact expression results.

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NOMENCLATURE

- A : Helmholtz free energy
- A^{ex} : excess Helmholtz free energy
- A^{DIM} : Helmholtz free energy of dimer fluid
- A_0, A_1, A_2 : zero-, first-, second-order contributions to the free energy in perturbation theory
- g^{HS} : radial distribution function of hard sphere
- g^{HSD} : radial distribution function of hard sphere dimer
- I^{HSD} : integral of hard sphere dimer
- I_{nm} : parameters in the expansion of I in power series of the radial distance and packing
- k_B : Boltzmann constant
- N : number of particles
- p^{HSD} : pressure of hard sphere dimer
- Res : summation of residue
- s : zero of $M(s)$
- T : temperature [K]
- T^* : reduced temperature [kT/ϵ]
- V : volume
- Z : compressibility factor
- Z^{HSD} : compressibility factor of hard sphere dimer
- Z_1, Z_2 : first-, second-order contributions to the compressibility factor in perturbation theory
- Z^{SWD} : compressibility factor of square well dimer
- Z^{DIM} : compressibility factor of dimer fluid

Greek Letters

- ϵ : depth of the potential well
- μ^{ex} : excess chemical potential
- η : packing fraction
- λ : radial distance or range of the potential in units of s
- σ : diameter of a hard sphere

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