



Calculation of the entropy for hard-sphere from integral equation method

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Abstract. The Ornstein-Zernike integral equation method has been employed for a single-component hard sphere fluid in terms of the Percus-Yevick (PY) and Martynov-Sarkisov (MS) approximations. The virial equation of state, excess chemical potential and free energy have been computed in both approximations. The excess entropy has been obtained with both thermodynamic relation and free energy expression for reduced densities of 0.1 to 0.9. It has been shown that the entropy values from thermodynamic relation in the MS approximation are better than those from the PY approximation, especially for high densities, and presents a reasonable comparison with available data in the literature, while the values from free energy expression in both approximations are not only close to each other, but also comparable to accurate ones.

Keywords: Ornstein-Zernike equation, integral equation, closure relation, hard-sphere potential, excess chemical potential, entropy

1 Introduction

In classical statistical physics the physical systems, such as a liquid can be modeled as a spherical symmetric hard-sphere particle model or Lennard-Jones potentials [1, 2]. Theoretical investigations for the systems can be performed with various methods, such as explicit approaches—Monte-Carlo or Molecular dynamics simulations [1], and implicit approaches represented as an integral equation or a polarizable continuum model methods [3]. An integral equation (IE) approach mentioned here is a mathematical tool we use in our study. As an implicit approach, the IE method does not consider the number of particles in the system which in turn may make a calculation cheap, and a solution of the IE can give directly the correlation functions determining the general structure of the system. A one-component, homogeneous system can be well investigated with the Ornstein-Zernike (OZ) [4] IE theory combined with an appropriate auxiliary equation.

In this work, our purpose is to obtain an excess entropy for single-component hard-sphere fluid using the OZ IE approach combined with the Percus-Yevick [5] (PY) and Martynov-Sarkisov [6] (MS) approximations. To reach it, we will first compute a virial

equation of state and along with it, we will obtain an excess chemical potential for the system at equilibrium using an analytical expression based on the correlation function. Using these two quantities, we will compute the excess entropy employing a thermodynamic relation. We will also compute the excess Helmholtz free energy using the analytical expression based on the correlation function, value of which is equal to the excess entropy, but has a negative sign. We will compare our findings for thermodynamic properties with available data in literature [7, 8]. Note that, to our knowledge, the MS approximation has not been tested for this calculation, yet, even though this problem had been considered in the past [7–9]. Therefore, we believe that our findings in this work can be considered as some contribution to this area.

In Section 2, we will discuss the Ornstein-Zernike theory and thermodynamic properties which we will compute. In Section 3 we present numerical results and their discussions. In Section 4 the conclusion is given.

2 Theory

2.1 The Ornstein-Zernike equation

In statistical mechanics, structural properties for the liquids existing at equilibrium can be obtained in terms of the integral equation formalism [3]. For a single-component homogeneous system, the Ornstein-Zernike integral equation can be written in the form

$$h(r) = c(r) + \rho \int c(|\mathbf{r} - \mathbf{r}'|)h(\mathbf{r}')d\mathbf{r}' \quad (1)$$

where $h(r)$ and $c(r)$ are the total and direct correlation functions, respectively, and ρ is the density of the system.

In equation (1), the two correlation functions are unknown, therefore, it cannot be solved directly. To solve this OZ equation (1), we need another equation that is solved together with the OZ equation (1) in a self-consistent way. This required equation is called a *closure equation (relation)* which may be written in the form

$$h(r) = \exp[-\beta u(r) + \gamma(r) - B(r)] - 1, \quad (2)$$

where $u(r)$ is a pair potential for particles in the system; $\gamma(r) = h(r) - c(r)$ is an indirect correlation function; $B(r)$ is a bridge function; $\beta = 1/k_{\text{B}}T$ where k_{B} is the Boltzmann's constant and T is a temperature of the system. The radial distribution function g can be defined as $g(r) = h(r) + 1$ as well.

An inter-particle interaction potential for the hard-sphere with a diameter σ can be written in the form [2]

$$u(r) = \begin{cases} 0, & r \geq \sigma \\ \infty, & r < \sigma. \end{cases} \quad (3)$$

The bridge functions we use in this work can be given in the forms:

$$B(r) = \begin{cases} \ln(1 + \gamma) - \gamma, & \text{(PY) [5]} \\ \sqrt{1 + 2\gamma} - \gamma - 1, & \text{(MS) [6].} \end{cases}$$

2.2 Thermodynamic quantities

Once we solve the OZ equation (1), we can have the correlation functions with which we can compute thermodynamic properties for the system.

2.2.1 Virial equation of state

For the hard-sphere system, the virial equation of state can be written in the form [2]

$$\frac{\beta p}{\rho} = 1 + \frac{2\pi}{3} \rho \sigma^3 g(\sigma), \quad (4)$$

where $g(\sigma)$ is the contact value of the radial distribution function at (σ) .

2.2.2 An excess chemical potential

The excess (e) chemical potential $\beta\mu^e$ can be computed with a following approximated analytical expression

$$\begin{aligned} \beta\mu^e \approx & \rho \int \left(\frac{1}{2} h(r)^2 - c(r) - \frac{1}{2} h(r)c(r) \right) dr \\ & + \rho \int \left(B(r) + \frac{2}{3} h(r)B(r) \right) dr. \end{aligned} \quad (5)$$

Note that this expression does not depend on an explicit form of the bridge function. Therefore, we can use it for both approximations in this work. A derivation of this expression can be found in Ref. [10].

2.2.3 An excess entropy

For the hard-sphere system in which internal energy is zero, the excess entropy S^e/Nk_B can be computed as the following thermodynamic relation [2]

$$\frac{S^e}{Nk_B} = \frac{\beta p}{\rho} - \beta\mu^e - 1. \quad (6)$$

In evaluating the expression (6), we use previously obtained values for the pressure and excess chemical potential.

2.2.4 An excess Helmholtz free energy

The excess Helmholtz free energy can be computed with an analytical expression based on the correlation function which can be derived from the Kirkwood charging formula

[10]. For one-component bulk fluid consisting of particle N with density ρ , it can be given in the form

$$\begin{aligned}
 \frac{\beta A^e}{N} &= \frac{\rho}{2} \int d\mathbf{r} \left(\frac{1}{2} h^2 - c \right) \\
 &+ \frac{1}{2} \frac{1}{8\pi^3} \int d\mathbf{k} \left[\hat{c} + \frac{1}{\rho} \ln |1 - \rho \hat{c}| \right] \\
 &+ \frac{\rho}{2} \int d\mathbf{r} gB \\
 &- \frac{\rho}{2} \frac{1}{8\pi^3} \int_0^1 d\nu \int d\mathbf{k} B(\hat{\gamma}(\mu \hat{h})) \hat{h}.
 \end{aligned} \tag{7}$$

The indirect correlation function in the momentum space k in an formula (7) is given as

$$\hat{\gamma}(\nu \hat{h}) = \frac{\rho(\nu \hat{h})^2}{1 + \rho(\nu \hat{h})}. \tag{8}$$

3 Results and discussion

In this work we have done calculations for reduced densities: $\rho\sigma^3 = 0.1$ to 0.9 . For high density, such as, when $\rho\sigma^3 \sim 0.9$, the hard-sphere system behaves like a fluid [1]. We use the Picard iteration method to solve the OZ equation, in which the OZ equation (1) is solved in the Fourier space while the closure equation (2) is solved in a coordinate space. A number of grid points in length interval of $[0, 16\sigma]$ is 2^{15} . The numerical calculation has been done with an in-house Matlab [11] code. The numerical tolerance for a root-mean-squared residual of the indirect correlation functions of successive iterations was set at 10^{-8} .

In 1 we have compared the values of the equation of states (EOS) and excess chemical potential obtained from both the PY and MS approximations with available data in Ref. [7], which was obtained in terms of the Carnahan and Starling (CS) EOS calculation [8]. We note that the CS data [8] can be considered as ‘exact’ values [7]. For higher densities, values for both quantities from the PY approximation are lower than those from the MS approximation. The MS values are quite close to those obtained in Ref. [8].

2 presents our findings for an excess entropy S^e/Nk_B obtained with an equations (6) and (7) ($S^e/Nk_B = -\beta A^e/N$) from both approximations and their comparisons with those of Refs. [7] and [8]. As expected, the largest deviations come from the PY results (column 2) here, especially for high density, since values for both the PY pressure and excess chemical potential are lower (1). Values (columns 4 and 5) obtained in both approximations using the Kirkwood charging technique are not only close to each other, but also comparable to accurate values shown in last column. Values from Ref. [7] are obtained with the help of the hybrid-bridge function, which enables better values than ours.

Table 1. The $\beta p/\rho$ and $\beta\mu^e$ as a function of $\rho\sigma^3$.

$\rho\sigma^3$	$\beta p/\rho$			$\beta\mu^e$		
	PY	MS	Ref. [8]	PY	MS	Ref. [8]
0.1	1.24	1.24	1.2397	0.46	0.46	0.4637
0.2	1.55	1.55		1.03	1.03	
0.3	1.95	1.96	1.9667	1.72	1.73	1.7468
0.4	2.48	2.50		2.58	2.62	
0.5	3.17	3.23	3.2624	3.67	3.77	3.8068
0.6	4.09	4.23		5.09	5.27	
0.7	5.32	5.61	5.7102	7.00	7.32	7.3593
0.8	7.00	7.58	7.7497	9.70	10.2	10.1525
0.9	9.33	10.4	10.7461	13.7	14.3	14.1052

Table 2. An excess entropy S^e/Nk_B

$\rho\sigma^3$	S^e/Nk_B (6)		$-\beta A^e/N$ (7)		Ref. [7]	Ref. [8]
	PY	MS	PY	MS		
0.1	-0.22	-0.22	0.22	0.22	-0.2240	-0.2241
0.2	-0.48	-0.48	0.47	0.47		
0.3	-0.77	-0.77	0.75	0.75	-0.7790	-0.7801
0.4	-1.10	-1.12	1.08	1.09		
0.5	-1.50	-1.53	1.47	1.49	-1.5414	-1.5444
0.6	-2.00	-2.04	1.94	1.97		
0.7	-2.68	-2.71	2.54	2.61	-2.6851	-2.6491
0.8	-3.70	-3.60	3.34	3.43	-3.3824	-3.4028
0.9	-5.39	-4.87	4.49	4.58	-4.3555	-4.3591

When using thermodynamic relation (6), based on the results shown in 1 and 2 we note that the MS approximation makes better calculations than the PY does. A reason why this happens might be related to the fact that a correlation function from the MS approximation is better than those from the PY approximation [12, 13]. Finally, note that our results obtained are independent of the number of grid points and the length interval employed.

4 Conclusion

In this work, we have implemented the Ornstein-Zernike integral equation theory with the Percus-Yevick and Martynov-Sarkisov bridge functions for a single-component hard-sphere system. Analytical expressions based on correlation functions which have been obtained as a solution of the integral equation for an excess chemical potential and an excess Helmholtz free energy have been tested. An excess entropy has been computed with help of thermodynamic relation and excess free energy expression obtained from the Kirkwood charging technique, and has been compared available accurate data. When thermodynamic relation is used, it has been shown that

the Martynov-Sarkisov approximation does work better than the Percus-Yevick approximation in which the integral equation can have a closed-form solution [9], and its values are close to accurate data. In both approximations, for excess entropy an excess free energy expression presents comparable values to accurate ones. Note that it is better to use well-approximated bridge functions, such as hybrid or pressure-consistent bridge approximations [7] to obtain well-consistent data from the integral equation method.

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