



# A comprehensive comparison between thermodynamic perturbation theory and first-order mean spherical approximation: Based on discrete potentials with hard core



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## ABSTRACT

Using the *TL* (Tang and Lu, 1993) method, Ornstein-Zernike integral equation is solved perturbatively under the mean spherical approximation (*MSA*) for fluid with potential consisting of a hard sphere plus square-well plus square-shoulder (*HS + SW + SS*) to obtain first-order analytic expressions of radial distribution function (*RDF*), second-order direct correlation function, and semi-analytic expressions for common thermodynamic properties. A comprehensive comparison between the first-order *MSA* and high temperature series expansion (*HTSE*) to third-, fifth- and seventh-order is performed over a wide parameter range for both a *HS + SW* and the *HS + SW + SS* model fluids by using corresponding "exact" Monte Carlo results as a reference; although the *HTSE* is carried out up to seventh-order, and not to the first order as the first-order *MSA* the comparison is considered fair from a calculation complexity perspective. It is found that the performance of the first-order *MSA* is dramatically model-dependent: as target potentials go from the *HS + SW* to the *HS + SW + SS*, (i) there is a dramatic dropping of performance of the first-order *MSA* expressions in calculating the thermodynamic properties, especially both the excess internal energy and constant volume excess heat capacity of the *HS + SW + SS* model cannot be predicted even qualitatively correctly. (ii) One tendency is noticed that the first-order *MSA* gets more reliable with increasing temperatures in dealing with the pressure, excess Helmholtz free energy, excess enthalpy and excess chemical potential. (iii) Concerning the *RDF*, the first-order *MSA* is not as disappointing as it displays in the cases of thermodynamics. (iv) In the case of the *HS + SW* model, the first-order *MSA* solution is shown to be quantitatively correct in calculating the pressure and excess chemical potential even if the reduced temperatures are as low as 0.8. On the other hand, the seventh-order *HTSE* is less model-dependent; in most cases of the *HS + SW* and the *HS + SW + SS* models, the seventh-order *HTSE* improves the fifth- and third-order *HTSE* in both thermodynamic properties and *RDF*, and the improvements are very demonstrable in both the excess internal energy and constant volume excess heat capacity; for very limited cases, the seventh-order *HTSE* improves the fifth-order *HTSE* only within lower density domain and even shows a bit of inadaptation over higher density domain.

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## 1. Introduction

Radial distribution function (*RDF*)  $g(r)$  plays two important roles in representing the structure of fluid and relating bulk thermodynamic properties to microscopic molecular interactions, and investigation of  $g(r)$  and thermodynamic properties of liquid and solid substances has always been a crucial field [1]. The bulk structural and thermodynamic properties are not only fundamental to phase equilibrium calculations of bulk fluid, but also a basic precondition

for constructing the grand potential functional approximation, the most basic element in a classical density functional theory (*DFT*) approach. Although the bulk Helmholtz free energy and bulk second-order direct correlation function  $c(r)$  are well known for a long time to play important roles in constructing the free energy functional approximation [2], in a recent publication [3], one of the present authors illustrates that direct incorporation of the *RDF* information into the functional approximation improves obviously the validity of the latter. Efficient ways to find the fluid  $g(r)$  with reliable accuracy and with less calculation include (i) a so-called Ornstein-Zernike (*OZ*) integral equation [4], which relates a total correlation function denoted by  $h(r)=g(r)-1$  to the  $c(r)$ ; in

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this approach, accuracy of the *RDF* depends on the bridge function approximation used. (ii) Via Percus' test particle method [5]. Here one solves for the equilibrium density profiles in the presence of an external potential that represents a test bulk particle located at the origin. It can be shown that these profiles, when normalized by the bulk density, are the *RDF*. In this approach, the accuracy of the *RDF* depends on the grand potential functional approximation, whose minimization gives the Euler–Lagrange equations used to calculate the inhomogeneous equilibrium density profiles. (iii) A coupling parameter series expansion (*CPSE*) [6], whose higher-order truncation could be easily achieved using numerical solution of the *OZ* integral equation. Analytic expression of the *RDF* is of significance as it can, by help of the *OZ* integral equation, give analytic expression of the  $c(r)$ , and can, by help of integrating the molecular potential function weighted by the *RDF*, give analytic expressions of excess internal energy  $U_{ex}$ , excess Helmholtz free energy  $F_{ex}$ , and other thermodynamic quantities. Approximate and analytic methods are given enough attention in statistical mechanics community [7]. Analytically solving the *OZ* integral equation under certain bridge function approximation is reliable and common approach to acquire analytic *RDF* and  $c(r)$  [4].

Tang and Lu (*TL*) propose a method to solve the *OZ* integral equation for both pure fluids and mixtures [8] with potential consisting of a hard core repulsion with an arbitrary tail under a Percus–Yevick (*PY*) approximation or a mean spherical approximation (*MSA*) by combining the perturbation theory with the application of the Hilbert transform. They find that each perturbation term can be solved analytically through the Hilbert transform with operations in the  $k$ -space or  $s$ -space, representing the Fourier and Laplace transforms, respectively. It is found that the first-order *MSA* solution dominates in the thermodynamics and structures of the hard sphere (*HS*)+Yukawa and *HS* + square well (*HS* + *SW*) model fluids, and is found rather successful to approximate the full *MSA* solution. Note that these studies would have been much more cumbersome had they been performed by the full *MSA* solution.

In the *TL* method, there are three of the most encountered functions in the solution— $g(r)$ ,  $c(r)$ , and a factorization function, which are internally convoluted. At the initial stage, the first-order *MSA* solution is not fully completed as the studies were all targeting  $g(r)$  and ignoring the two other functions. By applying the Hilbert transform, the first-order factorization and  $c(r)$  are analytically obtained [9,10], with emphasis on the *MSA* for the *HS* + Yukawa and *HS* + *SW* fluids. The *TL* method is elaborated upon further, and a new approach for analytic Laplace inversion to obtain explicit  $g(r)$  expression in a compact and consistent manner is proposed [11]; the proposed approach can yield  $g(r)$  values directly in any number of shells corresponding to any  $r$  values and provide an extraordinary contrast with analytic efforts reported in literature [12–17], all of which are confined to a limited number of shells and to the system of hard spheres, and whose extension to a large number of shells is prohibitive in practice.

The *TL* method had been applied to several typical model potentials [8,9,11,18,19], including the hard sphere, sticky hard sphere, *HS* + Yukawa, *HS* + *SW*, Lennard–Jones and Kihara; in these works, the authors focus on the  $g(r)$  and several of the thermodynamic properties. Due to lack of comprehensive comparison between the first-order analytic expressions and computer simulations, it is still unclear how far and how precise the first-order *MSA* solution accords with the “exact” simulation results.

Potential models consisting of a *HS* repulsion at close inter-particle separation accounting for the essential impenetrability of the particles, an attractive well at short distances arising from the polymer-induced depletion attraction, plus a soft repulsion at larger distances (inhibiting the vapor–liquid transition which would take place if only the attractive well were present) can serve to

model the effective interactions in solution of colloidal particles in the presence of nonadsorbing polymers or electrolyte solutions. In some alkali metals [20] and alloys [21], the effective interionic pair potentials have a similar form, to some extent. It has been found that fluids with potential models having this general shape may be in an inhomogeneous state with particles arranged in clusters or stripes [22] at low enough temperatures. These kinds of patterns have been observed [23] experimentally and also have been found [24] in computer simulations. The simplest model potential, which has the above mentioned general shape, is the so-called *HS* + *SW* + square shoulder (*SS*) potential. The *HS* + *SW* + *SS* model reduces to the *HS* + *SW* model by adjusting the parameters of the former model. Because of its simplicity, the *HS* + *SW* model has served as models of a wide variety of physical systems including, e.g., *He*, *Ne*, *Ar*, *H<sub>2</sub>*, *CO<sub>2</sub>*, *CH<sub>4</sub>*, *C<sub>2</sub>H<sub>6</sub>*, *n*-pentane, and *n*-butane, and to capture the essential features of the interactions found in colloidal systems; moreover, simulation study had confirmed the presence in the *HS* + *SW* system of the Yang–Yang anomaly expected and experimentally found for asymmetric fluids [25]. Aim of the present work is to apply the *TL* method to solve the *OZ* integral equation for a single component fluid interacting through the *HS* + *SW* + *SS* potential. The first-order *MSA* analytic expressions for  $g(r)$ ,  $c(r)$ , and semi-analytic expressions for common thermodynamic properties such as compressibility factor  $Z$ ,  $U_{ex}$ ,  $F_{ex}$ , constant volume excess heat capacity  $C_V^{ex}$ , excess chemical potential  $\mu_{ex}^*$ , and excess enthalpy  $H_{ex}$  are obtained and compared with corresponding simulation data available in literature and results based on the *CPSE* to third-, fifth-order and a high temperature series expansion (*HTSE*) to seventh-order. The *HS* + *SW* + *SS* fluid is a particular case of the so-called discrete potential fluids (*DPF*), which have been extensively used within the context of both simple and complex fluids. The structural and thermodynamic properties of the *DPF* as a function of the interaction range have been recently studied within the context of the *OZ* integral equation theory and computer simulations [26].

Structure of the present paper is organized as follows: in Section 2 application of the *TL* method to the *HS* + *SW* + *SS* model is briefly summarized and the obtained analytic expressions are presented; Comparisons with the simulation results and the *CPSE* to third-, fifth-order and the *HTSE* to seventh-order are presented and analyzed in Section 3. Our conclusions are summarized in Section 4. In Appendix A and B, some expressions, which are essential to the calculation of basic formulae in the text, and the solving procedure and final expression for  $c(r)$  are recorded.

## 2. Theoretical method

### 2.1. Analytic and semi-analytic expressions of the first order *MSA* solution for the *HS*+*SW*+*SS* model

The *HS* + *SW* + *SS* model potential is of following form:

$$u(r) = \begin{cases} \infty, & r/\sigma < 1 \\ -\varepsilon, & 1 < r/\sigma < \lambda_1 \\ \alpha\varepsilon, & \lambda_1 < r/\sigma < \lambda_2 \\ 0, & r/\sigma > \lambda_2 \end{cases}, \quad (1)$$

where,  $\sigma$  is diameter of the *HS*, and used as length unit throughout the paper;  $\varepsilon$  is energy parameter,  $\lambda_1$  and  $\lambda_2$  are potential range parameters, and  $\alpha$  measures the relative strength of the *SW* and *SS*. By defining  $u_1(r)$  and  $u_2(r)$ :

$$u_1(r) = \begin{cases} \infty, & r/\sigma < 1 \\ -\varepsilon - \alpha\varepsilon, & 1 < r/\sigma < \lambda_1 \\ 0, & r/\sigma > \lambda_1 \end{cases}, \quad (2)$$

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