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Structure of discrete-potential fluids interacting via two piece-wise constant potentials with a hard-core

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ABSTRACT

The structure of fluids whose molecules interact via potentials with a hard-core plus two piece-wise constant sections of different widths and heights has been studied by the perturbation theory based on the power series of an inverse temperature. The perturbation theory based on the reference system which incorporates both the repulsive and attractive potentials predicts accurate radial distribution function and direct correlation function of the discrete-potential fluids for the whole density regions. In particular, it is the most successful for the square-shoulder plus square-shoulder fluid and shifted square-shoulder fluid with a purely repulsive potential rather than the square-well plus square-well fluids with an attractive potential. It is found that the present theory predicts a more accurate structure than the rational-function approximation and conventional integral equations such as Percus–Yevick and hypernetted-chain theories in most of the cases.

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1. Introduction

During the last decades, the structure and thermodynamic properties of fluids that are expressed as a hard-core plus two piece-wise constant sections of different widths and heights have recently received a considerable amount of attention even though of their relative simplicity [1–10]. The structure and thermodynamics of these fluids can be quite distinct from those of simple fluids. They show various phase diagrams such as a liquid–liquid transition and the formation of different hexatic and crystal phases depending on the values of the widths and heights of both, the barrier and the well. These discrete potentials have been used as simple models to study properties of continuous potential systems and are similar to model potentials for complex fluids such as colloids, protein solutions, star polymers, and resemble pair potentials proposed for water. However, studies of the structural properties of discrete-potential fluids from theoretical are scarce [4,6–9], even though their phase diagram and the thermodynamic properties have been thoroughly examined and are relatively well understood.

Recently, many authors [6,11–16] have introduced the perturbation theory (PT), which is based on the power series of an inverse temperature, for studying the structure and thermodynamics of model fluids with both the repulsive and the attractive potentials. The similar PTs, which is based on the coupling parameter expansion, i.e., λ-expansion, have been applied by several authors for investigating the structure and thermodynamics of model fluids with an attractive perturbative potential [17–19]. The main difference between two theories is the definition of the perturbative potentials. In the λ-expansion, the perturbative potential is defined as $\zeta\beta u_{pert}(r)$, where ζ is a coupling parameter. Thus, the PT based on the power series of an inverse temperature corresponds to the λ-expansion at $\zeta = 1$. Although the thermodynamic PTs are not as versatile as the conventional integral equation theories, they usually give rise to simpler expressions for the equations of state and provide strategies to help the implementation of the theories [20,21]. In the PT, the perturbative potential is typically treated within a thermodynamic hard-sphere perturbed theory. This perturbation approach is only justified for weak perturbation. When the tail of the pair potential of a system is very deep, there is a great need to go beyond this PT. The PT based on the hard-sphere reference system fails at low density and temperature [22,23]. While the PT based on the reference system which incorporates both the repulsive and attractive potentials reduces the discrepancy between the PT based on the hard-sphere reference system and the simulated data at low density and temperature. It is known that the PT based on the high-temperature reference system predicts an accurate radial distribution function (RDF) and direct correlation function (DCF) of an attractive hard-core Yukawa fluid [23]. The conventional FMSA (first-order mean-spherical approximation) theory of Tang and Lu [6,11,16] fails in the region of low temperature even though it provides an analytical solution of Ornstein–Zernike (OZ) relation.

The aim of this paper is to employ the PT based on the inverse temperature expansion for a more systematic study of the structural properties of fluids characterized by a discrete potential with a hard-core plus different combinations of a repulsive shoulder and an attractive well. For this, we consider a more complex situation that the interparticle potential is a sum of more than two discrete potentials.

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We develop the thermodynamic PT, which is based on the reference system which incorporates both the repulsive and attractive potentials, for studying the structure of the fluid interacting via two piece-wise discrete potentials [4,5,7–10]. The higher-order perturbation terms arising from the power series of an inverse temperature have been calculated by invoking the properties of the integral equation and OZ relation [19]. In Section 3, we investigate their RDFs and DCFs at various ranges, and compare our results with the available computer simulations and other approximations. Through these studies, we show that the PT based on the high-temperature reference system provides an accurate structure of discrete potential fluids for the whole density regions. Finally, in the Conclusions section we include a brief discussion on the strengths and weakness of the present theory and the future applications.

2. Theoretical background

We consider the system which interacting via potentials with a hard-core plus two piece-wise constant sections of different widths and heights.

$$
\begin{aligned}
u(r,\epsilon) &= \infty, & r < \sigma \\
&= \epsilon_1, & \sigma < r < \lambda_1 \sigma \\
&= \epsilon_2, & \lambda_1 \sigma < r < \lambda_2 \sigma \\
&= 0, & r > \lambda_2 \sigma
\end{aligned}
\tag{1}
$$

where σ denotes the hard-sphere diameter, λ the potential range in units of the particle diameter, and ϵ_i the potential depth. Following the thermodynamic PT based on the high-temperature reference system, the interparticle potential can be divided into $u_{ref}(r)$, the reference system potential, and $u_{pert}(r,\epsilon)$ the perturbation part such as

$$
u(r,\epsilon) = u_{ref}(r) + u_{pert}(r,\epsilon).
\tag{2}
$$

Then, the potential for the reference system becomes

$$
\begin{aligned}
u_{ref}(r) &= \infty, & r < \sigma \\
&= \epsilon_1, & \sigma < r < \lambda_1 \sigma \\
&= \epsilon_{ref}, & \lambda_1 \sigma < r < \lambda_2 \sigma \\
&= 0, & r > \lambda_2 \sigma
\end{aligned}
\tag{3}
$$

where the subscript 'ref' denotes the reference system. While the perturbative potential $u_{pert}(r,\epsilon)$ is given by

$$
\begin{aligned}
u_{pert}(r,\epsilon) &= 0, & r < \sigma \\
&= \epsilon_1, & \sigma < r < \lambda_1 \sigma \\
&= \epsilon A(r), & \lambda_1 \sigma < r < \lambda_2 \sigma \\
&= 0, & r > \lambda_2 \sigma
\end{aligned}
\tag{4}
$$

where $A(r)$ is a simple function representing the potential shape. For example, the square-well type takes $A(r) = -1$ for $\lambda_1 \sigma < r < \lambda_2 \sigma$. For the square-shoulder type, it takes $A(r) = 1$ for $\lambda_1 \sigma < r < \lambda_2 \sigma$.

Following an inverse temperature approach, we expand the RDF $g(r,\epsilon)$ and DCF $c(r,\epsilon)$ in the power series of an inverse temperature

$$
g(r,\epsilon) = g_{ref}(r) + (\beta\epsilon)\left(\frac{\partial g(r,\epsilon)}{\partial \beta\epsilon}\right)_{\beta\epsilon=0} + \frac{(\beta\epsilon)^2}{2!}\left(\frac{\partial^2 g(r,\epsilon)}{\partial(\beta\epsilon)^2}\right)_{\beta\epsilon=0} + \cdots
\tag{5}
$$

$$
c(r,\epsilon) = c_{ref}(r) + (\beta\epsilon)\left(\frac{\partial c(r,\epsilon)}{\partial \beta\epsilon}\right)_{\beta\epsilon=0} + \frac{(\beta\epsilon)^2}{2!}\left(\frac{\partial^2 c(r,\epsilon)}{\partial(\beta\epsilon)^2}\right)_{\beta\epsilon=0} + \cdots
\tag{6}
$$

where $g_{ref}(r)$ and $c_{ref}(r)$, which are presumably known, denote the RDF and DCF of the reference system, respectively. In the liquid state theory, the closure relation is given by

$$
c(r,\epsilon) = exp\left[-\beta u_{ref}(r) + \beta\epsilon A(r) + y(r,\epsilon) + B(r,\epsilon)\right] - y(r,\epsilon) - 1
\tag{7}
$$

where $y(r,\epsilon) = h(r,\epsilon) - c(r,\epsilon)$ is the indirect correlation function and $h(r,\epsilon)$ the total correlation function denoted by $h(r,\epsilon) = g(r,\epsilon) - 1$. The bridge function $B(r,\epsilon)$ is a sum of infinite series of the bridge diagram and also a function of ϵ. The relationship between $g(r,\epsilon)$ and $c(r,\epsilon)$ which is given by the OZ relation

$$
h(r,\epsilon) = c(r,\epsilon) + \rho\int d\vec{s}\ c(s,\epsilon)h\left(|\vec{r}-\vec{s}|,\epsilon\right)
\tag{8}
$$

where ρ is the particle density.

All the required derivatives for the RDF and DCF can be obtained from Eqs. (7) and (8) in a self-consistent way under the assumption that the bridge function $B(r,\epsilon)$ is known. However, the bridge function is still unknown. We simply assume that $B(r,\epsilon)$ of the perturbed system, close to $\beta\epsilon = 0$, is the same as that of the reference system; $\partial^n B(r,\epsilon)/\partial(\beta\epsilon)^n = 0$. This assumption had extensively been tested by several authors [17,19]. They have shown that this assumption works well for the square-well fluid with an attractive perturbative potential in most of the cases except for the low temperature. We define the nth partial derivative of $g(r,\epsilon)$ and $c(r,\epsilon)$ with respect to $\beta\epsilon$ as $g^{(n)}(r,\epsilon)$ and $c^{(n)}(r,\epsilon)$. Then, we have the nth-order derivatives $c^{(n)}(r,\epsilon)$, from Eq. (7),

$$
\begin{aligned}
c^{(1)}(r,\epsilon) &= \left[-A(r) + y^{(1)}(r,\epsilon)\right]g(r,\epsilon) - y^{(1)}(r,\epsilon) \\
c^{(2)}(r,\epsilon) &= \left[-A(r) + y^{(1)}(r,\epsilon)\right]^2 g(r,\epsilon) + y^{(2)}(r,\epsilon)[g(r,\epsilon)-1] \\
c^{(3)}(r,\epsilon) &= \left[-A(r) + y^{(1)}(r,\epsilon)\right]^3 g(r,\epsilon) + 3\left[-A(r) + y^{(1)}(r,\epsilon)\right]y^{(2)}(r,\epsilon)g(r,\epsilon) \\
&= +y^{(3)}(r,\epsilon)[g(r,\epsilon)-1] \\
&\quad \cdots
\end{aligned}
\tag{9}
$$

where $g(r,\epsilon) = exp[-\beta u_{ref}(r) + \beta\epsilon A(r) + y(r,\epsilon) + B(r,\epsilon)]$. It becomes $g(r, \epsilon = 0) = g_{ref}(r)$ at $\beta\epsilon = 0$. The nth-order indirect correlation function $y^{(n)}(k,\epsilon) = h^{(n)}(k,\epsilon) - c^{(n)}(k,\epsilon)$ becomes, in Fourier space,

$$
y^{(n)}(k,\epsilon) = \sum_{m=0}^{n}\frac{n!}{m!(n-m)!}c^{(m)}(k,\epsilon)s^{(n-m)}(k,\epsilon) - c^{(n)}(k,\epsilon), n \geq 1
\tag{10}
$$

where $s^{(n)}(k,\epsilon)$ is the nth partial derivative of the structure factor $s(k,\epsilon) = 1/[1 - \rho c(k,\epsilon)]$ with respect to $\beta\epsilon$. Taken together with Eqs. (9) and (10), Eqs. (4) and (5) constitute the PT based on the power series of an inverse temperature for studying the structural properties of fluids interacting via piece-wise constant potentials with a hard-core. One should stress that although we have restricted our study to the two piece-wise constant sections, the present theory can be extended for studying the structure and thermodynamics of fluid with n piece-wise constant sections by applying the present PT successively.

3. Results and discussion

Through this study, the RDF and DCF of the fluids up to sixth-order in terms of an inverse temperature have been calculated, if not pointed out. The reduced quantities have been used: reduced temperature $T^* \equiv k_B T/\varepsilon$ and reduced density $\rho^* \equiv \rho\sigma^3$.

Fig. 1 shows the RDFs of a square-well (SW) fluid with $\lambda = 1.3$ at $T^* = 1.0$. As for the RDF and DCF of the hard-sphere reference system, we have solved the OZ equation with the closure provided by Malijevsky and Labik [24] using the standard iterative method. The structure for the SW potential at $T^* = 1.0$ has been calculated from the PT at $T^* = 2.0$. The PT based on the high-temperature reference system ($T^* = 2.0$) converge more rapidly than the PT based on the hard-sphere reference system. In particular, at intermediate density $\rho^* = 0.4$ the PT is more accurate than the PT based on the hard-sphere reference system. We can check that the present PT is better than the FMSA theory of Tang and Lu [11] and nonperturbative model