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Coupling-parameter expansion in thermodynamic perturbation theory

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An approach to the coupling-parameter expansion in the liquid state theory of simple fluids is presented by combining the ideas of thermodynamic perturbation theory and integral equation theories. This hybrid scheme avoids the problems of the latter in the two phase region. A method to compute the perturbation series to any arbitrary order is developed and applied to square well fluids. Apart from the Helmholtz free energy, the method also gives the radial distribution function and the direct correlation function of the perturbed system. The theory is applied for square well fluids of variable ranges and compared with simulation data. While the convergence of perturbation series and the overall performance of the theory is good, improvements are needed for potentials with shorter ranges. Possible directions for further developments in the coupling-parameter expansion are indicated.

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I. INTRODUCTION

In thermodynamic perturbation theory (TPT) for simple fluids, the interparticle pair potential is split into a reference part $u_{\mathrm{ref}}(r)$ and a perturbation part $u_{\mathrm{pert}}(r)$. All the thermodynamic and structural properties of the reference system, with interparticle potential $u_{\mathrm{ref}}(r)$, are assumed to be known. In earlier approaches [1] to TPT, the properties of the system of interest are obtained in terms of the known properties of the reference system. Thus, the Helmholtz free energy of the system is expressed as an infinite power series involving either $\beta = 1/k_B T$ (where k_B is the Boltzmann constant and T is the temperature) or the coupling parameter ζ, which characterizes the strength of the perturbation. In this expansion, known as high temperature series expansion (HTSE), the first order correction terms depends only on the radial distribution function (RDF) of the reference system. The second order term depends on three particle and four particle distribution functions. An approximation to the second order term is obtained by Barker and Henderson [2]. Higher order correction terms are practically inaccessible as they require still higher order correlation functions. This method gives satisfactory results for long-ranged potentials; however, it becomes quite inaccurate as the range of the potential becomes shorter. For specific potentials (for example, square-well potential) because of their simple forms, methods have been developed which perform better for shorter ranges [3,4]. However, a general theory which accurately predicts thermodynamic properties for short-ranged potentials is lacking.

Zhou [5] developed a new version of TPT to improve its accuracy for short-range potentials. This version, called the coupling-parameter expansion (CPE), relaxes the assumption that the properties of the actual system have to be determined solely in terms of the reference system. As a result, Zhou obtains a new power series expansion for Helmholtz free energy in terms of the coupling parameter ζ. The first term of this expansion coincides with that of HTSE. However, the higher order terms depend upon the derivatives of the RDF with respect to ζ at $\zeta = 0$. The nth order term in the series depends on the nth derivative of $g(\zeta,r)$, i.e., $\partial^n g(\zeta,r)/\partial\zeta^n|_{\zeta=0}$. Zhou proceeds by calculating the derivatives (at $\zeta = 0$) numerically by a finite difference method. Considering an imaginary fluid interacting with potential $u_{\mathrm{ref}}(r) + \zeta u_{\mathrm{pert}}(r)$, the RDF's is computed for some discrete values of ζ close to zero using an integral equation theory (IET) [1]. Zhou has developed this approach including up to fifth order term in the perturbation series [6]. However, the finite difference method is inadequate to obtain higher order derivatives. In fact, to get derivatives higher than third order, numerical procedures are required to smoothen the data sets. Thus, in practice, it is difficult to get derivatives greater than third order and the accuracy of higher order derivatives cannot be ascertained *a priori*.

The present paper is a different approach to the CPE. We assume that the RDF $g(\zeta,r)$ and the direct correlation function (DCF) $c(\zeta,r)$ of the perturbed system can be expressed as a Taylor series in ζ around $\zeta = 0$. Then we derive a system of linear equations connecting the derivatives of $c(\zeta,r)$ in real space and $g(\zeta,r)$ in Fourier space, by using a general closure relation obtained from diagrammatic analysis and the Ornstein-Zernike equation [1]. This coupled sets of equations is easily solved in a self-consistent way to obtain all the required derivatives. Thus, the new method avoids using the finite difference method for obtaining the derivatives of $g(\zeta,r)$. The numerical scheme is simplified and accurate derivatives up to any order can be easily obtained without requiring any smoothing procedures. Another important advantage of the present theory is that it gives both $g(r)$ and $c(r)$ of the actual system, apart from the Helmholtz free energy.

The paper is organized as follows. In Sec. II we discuss the method in detail. In Sec. III we give results of different calculations for square-well fluids and the paper is concluded in Sec. IV.

II. THEORY

We consider a simple classical fluid of particles, at a temperature T, interacting with a spherically symmetric pair

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potential $u(r)$, where r is the interparticle distance. The potential is split into $u_{\mathrm{ref}}(r)$, the reference system potential, and $u_{\mathrm{pert}}(r)$ the perturbation part. It is assumed that the structure (RDF and DCF) and thermodynamic properties of the reference system are known. We denote the RDF, DCF, and the Helmholtz free energy density of the reference fluid as $g_0(r),c_0(r)$, and $f_0(\rho)$, where ρ is the macroscopic density of the homogeneous fluid. A fictitious system with interaction potential defined as

$$u(\zeta,r) = u_{\mathrm{ref}}(r) + \zeta u_{\mathrm{pert}}(r) \tag{1}$$

is considered for the CPE, where ζ is the coupling parameter. The effect of increasing ζ from zero to unity is to gradually switch on the perturbation. We postulate that the RDF and DCF of the system with potential $u(\zeta,r)$ can be written as a MacLaurin series in ζ, that is,

$$c(\zeta,r) = c_0(r) + \zeta\left(\frac{\partial c}{\partial \zeta}\right)_{\zeta=0} + \frac{\zeta^2}{2!}\left(\frac{\partial^2 c}{\partial \zeta^2}\right)_{\zeta=0} + \cdots, \tag{2}$$

$$g(\zeta,r) = g_0(r) + \zeta\left(\frac{\partial g}{\partial \zeta}\right)_{\zeta=0} + \frac{\zeta^2}{2!}\left(\frac{\partial^2 g}{\partial \zeta^2}\right)_{\zeta=0} + \cdots. \tag{3}$$

It is assumed that the series converge for all ζ in [0,1] and the DCF and RDF of the actual system can be obtained by putting $\zeta = 1$. Hereafter, we denote nth partial derivative of any function $X(\zeta,r)$ with respect to ζ as $X^{(n)}(\zeta,r)$.

A general closure relation for the DCF $c(\zeta,r)$ provided by liquid state theory is [1,7]

$$c(\zeta,r) = \exp(-\beta u(\zeta,r) + y(\zeta,r) + B(\zeta,r)) - y(\zeta,r) - 1 \tag{4}$$

where $y(\zeta,r)$ is the indirect correlation function defined as $h(\zeta,r) - c(\zeta,r)$ and $h(\zeta,r) = g(\zeta,r) - 1$ is the total correlation function of the fictitious fluid. The bridge function $B(\zeta,r)$ is a sum of an infinite series of the "bridge diagrams" [7]. Since $g(\zeta,r)$, and hence $h(\zeta,r)$, as well as $c(\zeta,r)$ are expanded in a series in ζ, the correlation function $y(\zeta,r)$ is also a series in ζ. The nth order coefficient in its series is given by $y^{(n)}(\zeta,r) = h^{(n)}(\zeta,r) - c^{(n)}(\zeta,r)$.

In a similar manner, the bridge function $B(\zeta,r)$ also should be considered as a series in ζ. Several approximations to $B(\zeta,r)$ in terms of $y(\zeta,r)$ and certain empirical parameters are available [7]. However, to simplify the present formulation, we assume that $B(\zeta,r)$ is independent of ζ. Thus, the bridge function of the perturbed system, close to $\zeta = 0$, is assumed to be the same as that of the reference system. This approximation has been used by Zhou [5] as all the derivatives of $g(\zeta,r)$, needed in the theory, are to be computed only at $\zeta = 0$. Adequacy of this assumption, except for very short-range potentials, has also been established by Zhou by comparing its results with simulation data [6].

A. Third order theory

First of all, we elaborate the method for third order TPT wherein the series in Eqs. (2) and (3) are truncated after the first three terms. As $B(r)$ is assumed to be independent of ζ, differentiating Eq. (4) with respect to ζ we get

$$c^{(1)}(\zeta,r) = (-\beta u_{\mathrm{pert}}(r) + y^{(1)}(\zeta,r))g(\zeta,r) - y^{(1)}(\zeta,r), \tag{5}$$

where we have used the definition of the pair distribution function $g(\zeta,r)$ given by [1,7]:

$$g(\zeta,r) = \exp(-\beta u(\zeta,r) + y(\zeta,r) + B(r)). \tag{6}$$

In a similar manner the second derivative is obtained as

$$\begin{aligned} c^{(2)}(\zeta,r) = {} & (-\beta u_{\mathrm{pert}}(r) + y^{(1)}(\zeta,r))^2 g(\zeta,r) \\ & + y^{(2)}(\zeta,r)(g(\zeta,r) - 1). \end{aligned} \tag{7}$$

To get another set of relations between $c^{(n)}(\zeta,r)$ and $y^{(n)}(\zeta,r)$, we consider the Ornstein Zernike equation (OZE) in Fourier space:

$$h(\zeta,k) = \frac{c(\zeta,k)}{1 - \rho c(\zeta,k)}, \tag{8}$$

where $h(\zeta,k)$ and $c(\zeta,k)$ are the Fourier transforms of $h(\zeta,r)$ and $c(\zeta,r)$, respectively. For instance, the transform of $h(\zeta,r)$ and its inverse are defined as

$$h(\zeta,k) = 4\pi \int_0^\infty \frac{\sin(kr)}{kr} h(\zeta,r) r^2 dr, \tag{9}$$

$$h(\zeta,r) = \frac{1}{2\pi^2} \int_0^\infty \frac{\sin(kr)}{kr} h(\zeta,k) k^2 dk. \tag{10}$$

Differentiating Eq. (8) with respect to ζ we obtain

$$h^{(1)}(\zeta,k) = c^{(1)}(\zeta,k) s^2(\zeta,k), \tag{11}$$

where the structure factor $s(\zeta,k)$ is defined as

$$s(\zeta,k) = \frac{1}{1 - \rho c(\zeta,k)}. \tag{12}$$

In a similar way, the second derivative $h^{(2)}(\zeta,k)$ is obtained as

$$h^{(2)}(\zeta,k) = c^{(2)}(\zeta,k) s^2(\zeta,k) + 2\rho (c^{(1)}(\zeta,k))^2 s^3(\zeta,k). \tag{13}$$

Equations (11) and (13) now provide $y^{(1)}(\zeta,k)$ and $y^{(2)}(\zeta,k)$. As the RDF $g(0,r)$ and the structure factor $s(0,k)$ of the reference system are known, Eqs. (5) and (7) can be evaluated at $\zeta = 0$. Thus, the closed set of four linear equations, defining the third order theory, are given by

$$c^{(1)}(0,r) = (-\beta u_{\mathrm{pert}}(r) + y^{(1)}(0,r)) g(0,r) - y^{(1)}(0,r), \tag{14}$$

$$\begin{aligned} c^{(2)}(0,r) = {} & (-\beta u_{\mathrm{pert}}(r) + y^{(1)}(0,r))^2 g(0,r) \\ & + y^{(2)}(0,r)(g(0,r) - 1), \end{aligned} \tag{15}$$

$$y^{(1)}(0,k) = c^{(1)}(0,k)(s^2(0,k) - 1), \tag{16}$$

$$y^{(2)}(0,k) = c^{(2)}(0,k)(s^2(0,k) - 1) + 2\rho(c^{(1)}(0,k))^2 s^3(0,k). \tag{17}$$

We solve this system of equations using a simple iterative method. Starting with guess solutions for $y^{(1)}(0,r)$ and $y^{(2)}(0,r)$, which are usually taken as zero, we determine $c^{(1)}(0,r)$ and $c^{(2)}(0,r)$. Then their Fourier transforms are obtained using an FFT algorithm, thereby obtaining $y^{(1)}(0,k)$ and $y^{(2)}(0,k)$. Inverse Fourier transforms of these functions provide $y^{(1)}(0,r)$ and $y^{(2)}(0,r)$ for the next iteration, and the procedure is continued until convergence is obtained. More details of the numerical procedure are discussed in the next section.

The correlation functions $c(1,r)$ and $g(1,r)$ of the actual system are obtained from Eqs. (2) and (3), respectively, by putting $\zeta = 1$. The CPE for Helmholtz free energy density $f(\rho)$ of a homogeneous fluid is given by [1]

$$f(\rho) = f_{\text{ref}}(\rho) + \frac{\rho^2}{2}\int_0^1 d\zeta \int d\vec{r}\; u_{\text{pert}}(r) g(\zeta,r), \tag{18}$$

where $f_{\text{ref}}(\rho)$ is the free energy density of the reference system. Substituting Eq. (3) in Eq. (18) and integrating over ζ, we get

$$f(\rho) = f_{\text{ref}}(\rho) + \frac{\rho^2}{2}\int d\vec{r}\; u_{\text{pert}}(r) \times \left(g_0(r) + \frac{1}{2!}\, g^{(1)}(0,r) + \frac{1}{3!}\, g^{(2)}(0,r) \right). \tag{19}$$

Here we have used the shortened notation for the derivatives $(\partial^n g(r)/\partial \zeta^n)_{\zeta=0}$, which is readily obtained as $y^{(n)}(0,r) + c^{(n)}(0,r)$. Thus, the method provides the DCF, RDF as well as the free energy density.

B. General order theory

The method outlined above can be generalized to any arbitrary order. Writing $g(\zeta,r)$ in the short form

$$g(\zeta,r) = \exp(f(\zeta,r)), \tag{20}$$

$$f(\zeta,r) = -\beta(u_{\text{ref}}(r) + \zeta u_{\text{pert}}(r)) + y(\zeta,r) + B(r), \tag{21}$$

the general expression for its nth order derivative is found to be

$$g^{(n)}(\zeta,r) = \sum_{m=0}^{(n-1)} \left[C_m^{(n-1)}\right] f^{(n-m)}(\zeta,r)\, g^{(m)}(\zeta,r), \quad n \geqslant 1, \tag{22}$$

where $[C_m^{(n-1)}]$ is the binomial coefficient. The derivatives $f^{(n)}(\zeta,r)$ are given by

$$f^{(n)}(\zeta,r) = -\beta u_{\text{pert}}(r)\, \delta_{n,1} + y^{(n)}(\zeta,r), \quad n \geqslant 1, \tag{23}$$

where $\delta_{n,1}$ is the Kronecker δ. The derivatives $g^{(n)}(\zeta,r)$ can be computed using Eq. (22) in a recursive manner, using $f^{(n)}(\zeta,r)$ either from initial guess or previous iteration. Now, using Eq. (6), we rewrite the closure in Eq. (4) as

$$c(\zeta,r) = g(\zeta,r) - y(\zeta,r) - 1, \tag{24}$$

which readily provides its nth order derivative,

$$c^{(n)}(\zeta,r) = g^{(n)}(\zeta,r) - y^{(n)}(\zeta,r), \quad n \geqslant 1. \tag{25}$$

The structure factor introduced in Eq. (12) is rewritten as

$$s(\zeta,k) = 1 + \rho c(\zeta,k)\, s(\zeta,k). \tag{26}$$

This equation can be differentiated using Lebniz rule to obtain

$$s^{(n)}(\zeta,k) = \rho \sum_{m=0}^{n} \left[C_m^n\right] c^{(n-m)}(\zeta,k)\, s^{(m)}(\zeta,k), \quad n \geqslant 1. \tag{27}$$

Transferring the last term in the sum to the left-hand side and using Eq. (12) we get

$$s^{(n)}(\zeta,k) = [s^{(0)}(\zeta,k)]\, \rho \sum_{m=0}^{(n-1)} \left[C_m^n\right] c^{(n-m)}(\zeta,k) \times s^{(m)}(\zeta,k), \quad n \geqslant 1. \tag{28}$$

Using the values of $c^{(m)}(\zeta,k)$ from the current iteration, Eq. (28) can be evaluated recursively. Finally, using $s(\zeta,k) = 1 + \rho h(\zeta,k)$, the derivatives of $y(\zeta,k) = h(\zeta,k) - c(\zeta,k)$ are expressed as

$$y^{(n)}(\zeta,k) = \rho^{-1}\, s^{(n)}(\zeta,k) - c^{(n)}(\zeta,k), \quad n \geqslant 1. \tag{29}$$

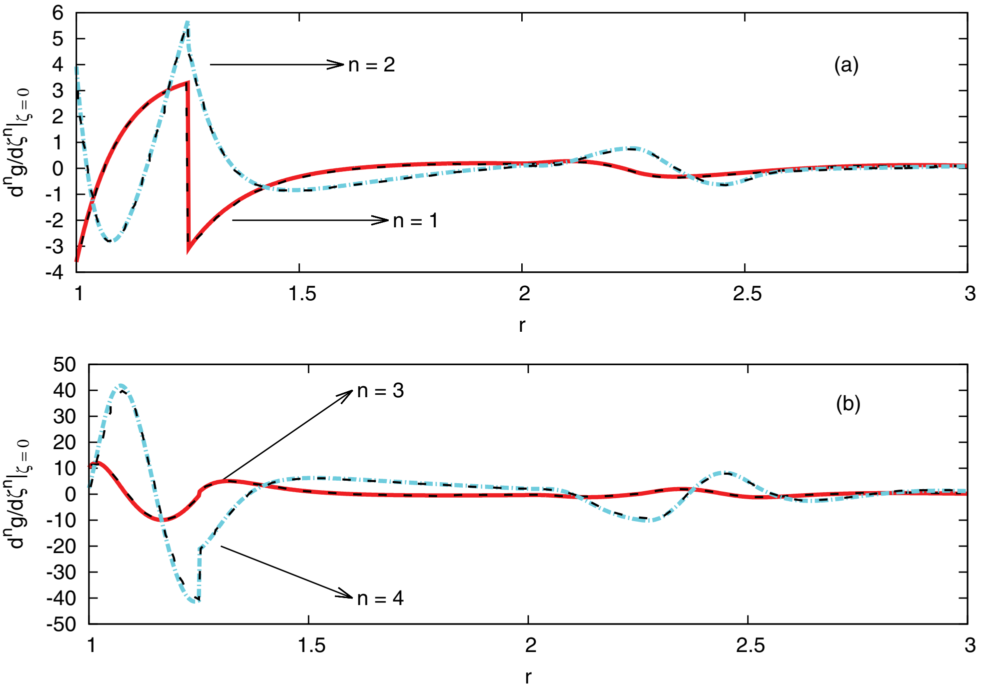
Equations (25) and (29) provide the general equations for the derivatives. These can be readily solved using the same iteration method outlined for third order theory.

III. APPLICATION TO SQUARE WELL FLUIDS

We applied the theory described above to square-well (SW) fluids as ample amount of simulation data, for different SW widths, are available for comparison. RDF for ranges 1.3 and 1.5 and phase diagrams for ranges 1.25 to 2.3 are considered to test the accuracy of the present theory. First order theory is known to be highly inaccurate for these cases. Results of calculations using third, fifth, and seventh order versions of the present theory are compared with those of first order theory and simulations. Reduced units ($\epsilon/k_B = \sigma = 1$, where ϵ is the well depth and σ is hard sphere diameter) are used throughout the paper.

A. Numerical procedure

The numerical procedure used to solve the coupled set of linear equations for the derivatives $c^{(n)}(0,r)$ and $g^{(n)}(0,r)$ is as follows. It is assumed that $c^{(0)}(0,r) = c_0(r)$ and $g^{(0)}(0,r) = g_0(r)$ are known. If only $g_0(r)$ is known, $c_0(r)$ can be calculated using the OZE and a proper numerical procedure [8,9]. To compute the derivatives, say, in nth order theory, Eq. (25) in real space and Eq. (29) in Fourier space are solved employing an iterative procedure. First of all, we choose guess solutions for $y^{(m)}(0,r)$, for all m in the range $1 \leqslant m \leqslant n$, and compute $g^{(m)}(0,r)$, recursively, using Eq. (22). In practice, we take null solutions as the starting guesses. Then, $c^{(m)}(0,r)$ are obtained using Eq. (25). Next, their Fourier transforms $c^{(m)}(0,k)$ are computed using an FFT algorithm. Mesh widths in the range 0.01 to 0.001 are found to be adequate. These are employed in Eq. (28) to obtain $s^{(m)}(0,k)$ recursively. These functions, when used in Eq. (29), provide $y^{(m)}(0,k)$. Inverse Fourier transformation give $y^{(m)}(0,r)$. This completes the first iteration. However, before starting the next iteration, we employ a linear mixing of the initial and new solutions: $\alpha y^{(m)}(0,r) + (1-\alpha) y^{(m)}(0,r) \rightarrow y^{(m)}(0,r)$. They are then used in Eq. (25) for the second iteration. The procedure is repeated until the root mean square differences between successive iterates of $y^{(m)}(0,r)$, for all m, are less than a prescribed tolerance. We find that $\alpha = 0.5$ and tolerance of 10^{-8} are adequate to get accurate solutions.



SW range = 1.25, T = 1.0, density = 0.75

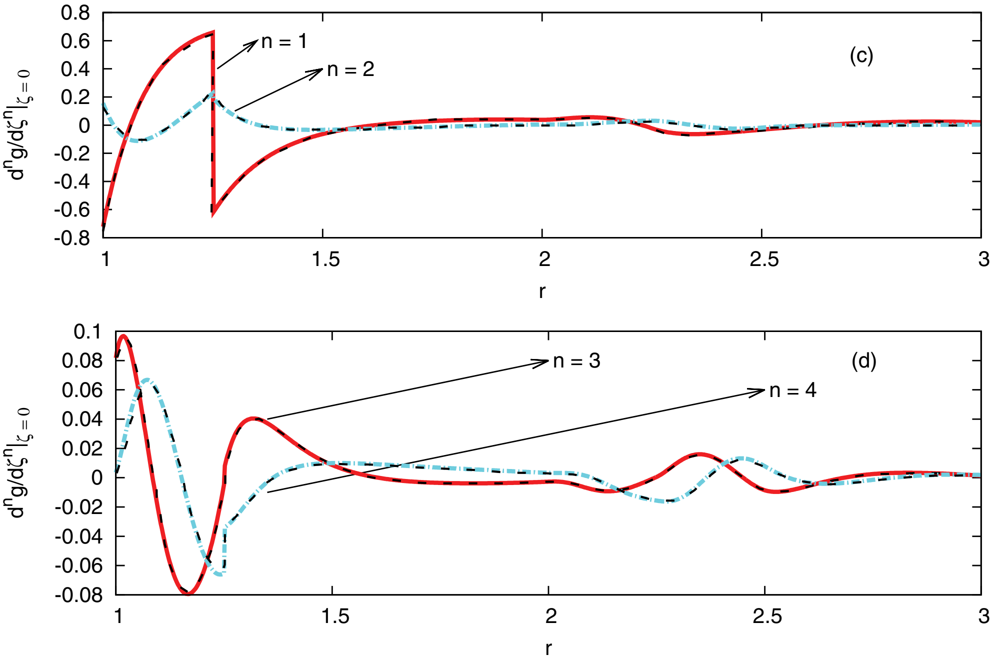


FIG. 1. (Color online) Panels (a) and (b) are derivatives of $g(r)$ up to fourth order for SW fluid of range 1.25 at reduced temperature $T = 0.2$ and reduced density $\rho = 0.75$, respectively. Panels (c) and (d) are derivatives of $g(r)$ up to fourth order for SW fluid of range 1.25 at reduced temperature $T = 1.0$ and reduced density $\rho = 0.75$, respectively. Solid line and dash-dotted lines, present theory; dashed lines, Zhou's results [6].

B. Structural properties

For application to SW fluids, the hard sphere (HS) fluid is the natural reference system. Even though any bridge function can be used in Eq. (4) to determine the properties of the HS system, we have used $B(r)$ provided by Malijevsky and Labik [10], as used by Zhou [6]. The OZE is then solved for the HS system using the standard iterative method [11]. With the properties HS so determined, the derivatives up to fourth order [$g^{(n)}(0,r)$, $n = 1,4$] from the present theory can be directly compared with those of Zhou. Figure 1 shows this comparison and we find that the derivatives obtained from the present method and the finite difference method used by Zhou match with negligible deviations. However, our numerical scheme is much simpler and even higher order derivatives can be easily calculated without resorting to any smoothing procedures. RDF of SW fluids obtained using fifth order and

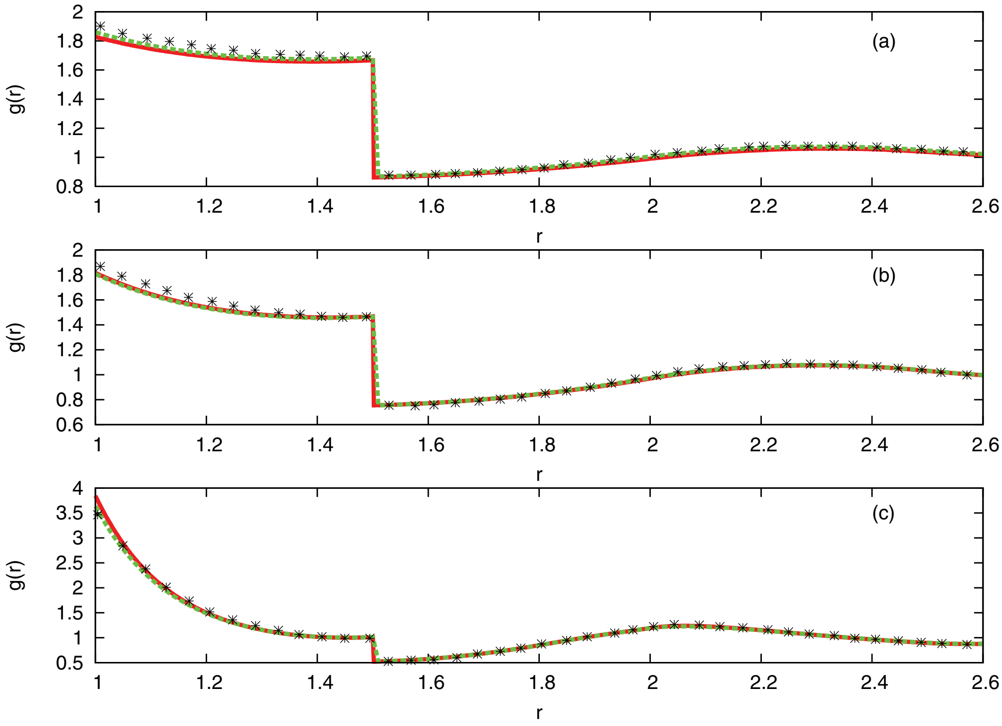


FIG. 2. (Color online) $g(r)$ for SW fluid of range 1.5 at reduced temperature $T = 1.5$. Panels (a), (b), and (c) are for reduced density $\rho = 0.2$, 0.4, and 0.8, respectively. Soild lines, fifth order TPT; dashed lines, seventh order TPT; stars, simulation results [15].

seventh order version of present theory are plotted in Figs. 2, 3, and 4. For the case of range 1.5 (see Fig. 2), $g(r)$ obtained using our theory is in excellent agreement with simulation results except for a very small deviation in the SW region for $\rho = 0.2$. Similar convergence of TPT series are found for range 1.3 (see Fig. 3), even though important differences with simulation data are noticeable at $\rho = 0.4$ also. In Fig. 4 we show $g(r)$ obtained using third, fifth, and seventh order versions of the theory for SW fluid of range 1.25 at temperature $T = 0.56$ and density $\rho = 0.2$ and for SW fluid of range 1.2

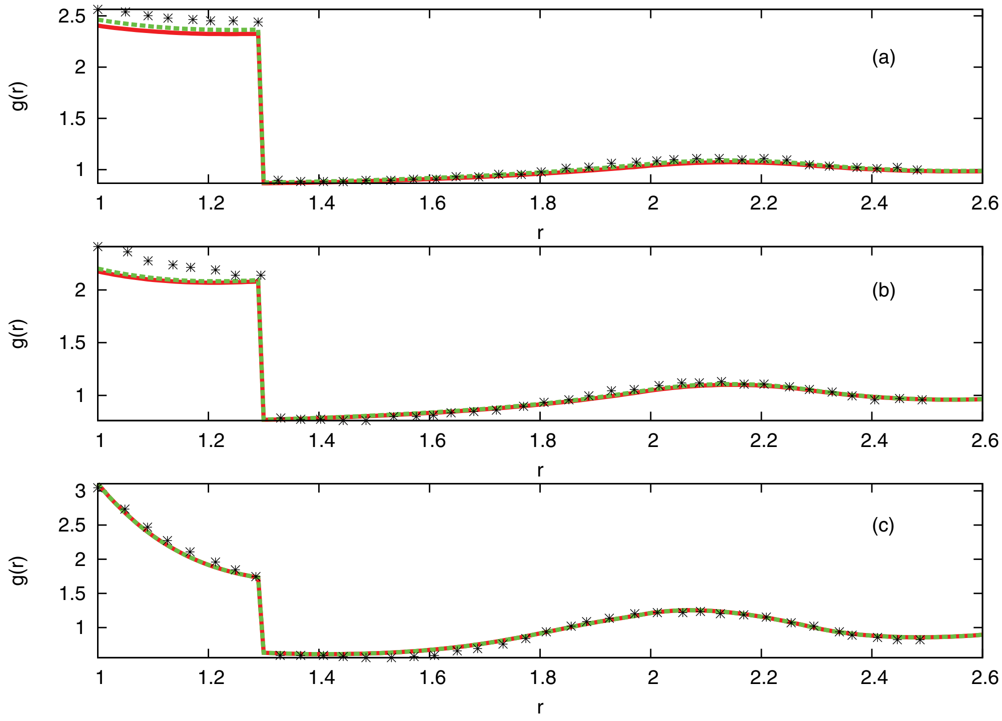


FIG. 3. (Color online) $g(r)$ for SW fluid of range 1.3 at reduced temperature $T = 1.0$. Panels (a), (b), and (c) are for reduced density $\rho = 0.2$, 0.4, and 0.8, respectively. Soild lines, fifth order TPT; dashed lines, seventh order TPT; stars, simulation results [15].

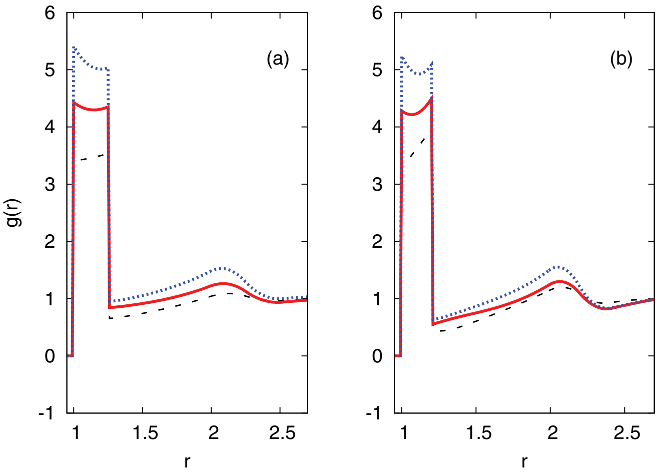


FIG. 4. (Color online) (a) $g(r)$ for SW fluid of range 1.25 at temperature $T = 0.56$ and density $\rho = 0.2$ in reduced units. (b) $g(r)$ for SW fluid of range 1.2 at temperature $T = 0.45$ and density $\rho = 0.4$ in reduced units. Dashed lines, third order TPT; soild lines, fifth order TPT; dotted lines, seventh order TPT.

at temperature $T = 0.45$ and density $\rho = 0.4$. These cases clearly show that the convergence of the series is slow for short-ranged potentials at very low temperatures and densities. Thus, for extremely short-ranged potentials, contribution from terms higher than sixth order in Taylor series expansion of $g(r)$ become very much important. In Fig. 5, $c(r)$ obtained using the seventh order version of our theory is compared with the simulation results of [12] for two cases: SW fluid of range 1.25 at $T = 2.0$, $\rho = 0.75$ and SW fluid of range 1.2 at $T = 2.0$, $\rho = 0.75$. The agreement with experiment is good in the former case, whereas slight deviation is found in the latter case. Comparison for smaller widths was not possible because of lack of simulation data for $c(r)$.

We also observed that the present approach does not have any numerical convergence problems either in the two-phase region or close to the critical region, whereas the IETs generally fail to have a solution in the two phase region and the numerical algorithms have slow convergence in the critical region. This is an interesting feature of the present theory and requires detailed investigation with different bridge functions and interatomic potentials. Further, the DCF $c(r) = c(1,r)$ obtained using the present method can find applications in density functional theories of inhomogeneous fluids. For example, in the square-gradient functional for inhomogeneous systems, the coefficient of the gradient term, called influence parameter, depends explicitly on $c(r)$ of the homogeneous system. As the IETs do not have solutions in the binodal region, interpolation techniques are required to obtain the influence parameter [13]. The DCF $c(1,r)$ of the actual system obtained from our method can be directly used to obtain the influence parameter. Finally, the present theory has the advantage of accommodating any bridge function for computing the derivatives, though we have used only the simple HS version for this paper.

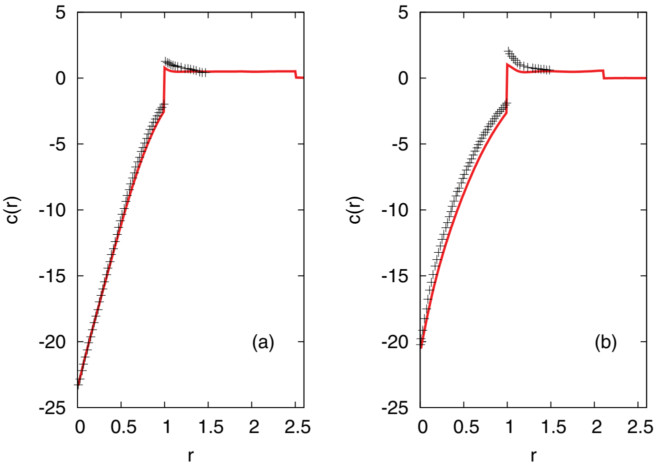


FIG. 5. (Color online) (a) $c(r)$ for SW fluid of range 2.5, temperature $T = 2.0$, density $\rho = 0.75$ in reduced units. (b) $c(r)$ for SW fluid of range 2.1, temperature $T = 2.0$, density $\rho = 0.75$ in reduced units. Solid lines, seventh order TPT results; pluses, simulations [12].

C. Liquid-vapor phase diagrams

We compare the liquid-vapor phase diagrams (LVPDs) for SW fluids of ranges 1.25, 1.375, 1.5, and 2.3 using first order,

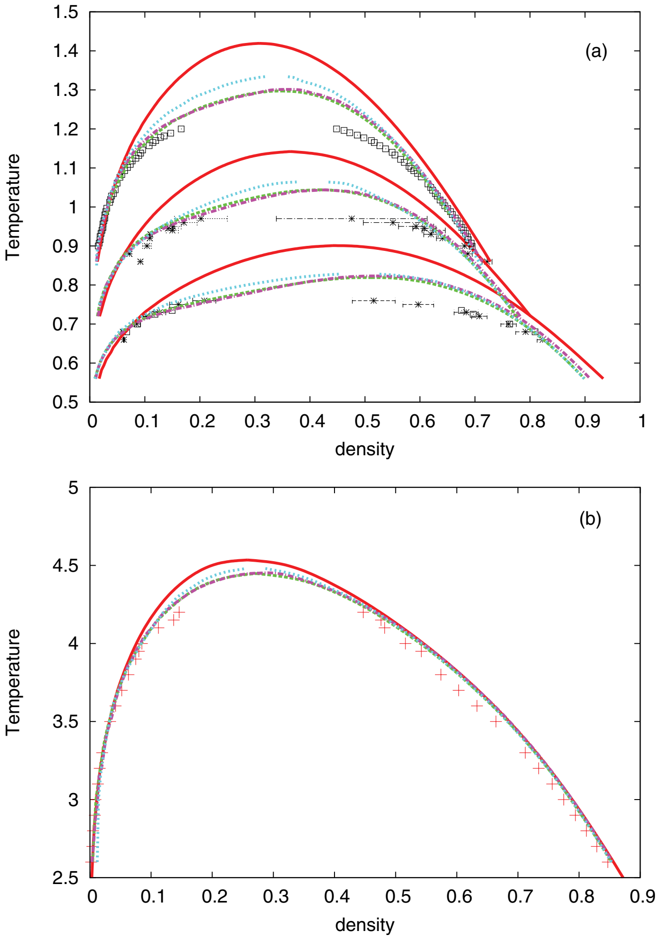


FIG. 6. (Color online) (a) Liquid-vapor coexistence curves in reduced temperature and density of SW fluids of widths 1.5, 1.375, and 1.25 in reduced units (from top to bottom). (b) Liquid-vapor coexistence curve in reduced temperature and density of SW fluid of width 2.3 in reduced units. Solid lines, first order TPT; dotted lines, third order TPT; dashed lines, fifth order TPT; dash-dotted lines, seventh order TPT; stars, squares, pluses, simulation results [16–19].

third order, fifth order, and seventh order versions of the present TPT. These are shown in Fig. 6 together with simulation data for the different ranges. It is clear that there is an enormous improvement in the results over first order TPT, which is quite apparent for smaller ranges, i.e., 1.5 and smaller. For range 2.3, the difference between fifth order and seventh order TPT is small even in the critical region and we can conclude that the perturbation series of Helmholtz free energy has practically converged. However, they differ from the first order TPT and simulation data in the critical region. Similar results are noted even for the cases of range 1.5 even though the error in first order TPT is much larger. For ranges 1.375 and 1.25, the differences between the fifth and seventh order TPT are quite small, but noticeable in certain parts of the phase plane. Thus, for the cases presented, convergence of the perturbation series of Helmholtz free energy is satisfactory and faster than that of the series of $g(r)$, which is expected. However, there is still significant deviation from the simulation results for the three cases, i.e., for SW fluids of ranges 1.25, 1.375, and 1.5. We also note that neglecting the ζ dependence of bridge function $B(\zeta,r)$ has brought in some asymmetry in the phase diagram and slight shift of the critical point towards the liquid side. Now that the perturbation series has converged, we can clearly conclude that the deviation is caused because of two reasons: First is the bridge function used in the calculation and second is long-range fluctuations. Improving the results using a better bridge function is within the scope of the theory, whereas methods of renormalization group theory need to be used to bring in better agreement in the critical region [14]. Work to include this feature and exact treatment of non-HS potentials, which is quite straightforward within our formalism, is in progress.

IV. CONCLUSIONS

In this paper we have presented an approach to the CPE in liquid state theory of simple fluids. The method combines ideas of TPT and integral equation theories. This hybrid scheme avoids the problems of IETs in the two phase region. A simple way to calculate the terms in the perturbation series expansion to any arbitrary order is illustrated. Apart from the Helmholtz free energy, the present approach also gives the RDF $g(r)$ and DCF $c(r)$ of the actual perturbed system. We have obtained thermodynamic and structural properties of the SW fluids of various ranges using up to seventh order version of our theory. We have seen that the Helmholtz free energy series has practically converged by seventh order. However, the convergence of $g(r)$ and $c(r)$ series are slower at low temperatures and low densities for narrow SWs. The results let us conclude that the accuracy of the theory is limited only by the bridge function used as the perturbation series can be calculated to any order easily until the convergence is reached. However, for very narrow potentials there is scope for further improvements in the theory by accelerating the convergence of the series.

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