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Thermodynamic perturbation theory in fluid statistical mechanics

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A methodology is proposed that pushes the thermodynamic perturbation theory (TPT) from first order to higher order. The second-order correction is superior to a macroscopic compressibility (MC) approximation of Barker and Henderson. The present third-order TPT performs far better than the original first-order TPT and second-order TPT based on the MC approximation for many subfields in fluid statistical mechanics, such as predicting excess Helmholtz free energy, excess chemical potential, bulk pressure, gas-liquid coexistence, and solid-liquid equilibrium of very short-range potential fluids. A nonuniform version of the TPT is proposed; it is also shown that the nonuniform third-order TPT performs far better than the nonuniform first-order TPT in predicting density profile of fluids in critical region. The present report indicates that the TPT still can be a "universal" and accurate theoretical tool that has general applicability in fluid statistical mechanics, especially in soft-matter physics.

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I. INTRODUCTION

Liquid state theory had been developed greatly during the past 40 years, different basic concepts for determination of structure and thermodynamics had been proposed and applied successfully, some of which can be listed as integral equation theory (IET) [1], thermodynamic perturbation theory (TPT) [1,2], simulation method [3], and density functional theory (DFT) [4]. As the first quantitatively satisfactory theory of the liquid state, the TPT is extremely influential in the modern theory of fluids. The TPT can predict excess Helmholtz free energy (EHFE), a fundamental thermodynamic quantity from which any other thermodynamics can be derived out. The TPT is also extended to calculate the EHFE of a crystal, and therefore the TPT dominates in the field of solid-liquid and solid-gas transition. The TPT, by combination with the concept of weighted density, results in inhomogeneous EHFE density functional for a tail part of a nonhard-sphere potential, and therefore also contributes to the development of the classical DFT [4,5], which dominates over the theoretical investigation of inhomogeneous phenomena (including solid [6]) over the past two decades. Therefore, one can conclude that the TPT has played an important role in fluid and solid statistical mechanics. During the past decade, soft matter has drawn a lot of attention by researchers, and the focus of attention has moved to the hard sphere with a short-range attraction, ubiquitous in physical systems constituted by macroparticles [7]. Accompanying the change of interest focus, there appear signs that the TPT is becoming less and less popular. The reason for such unfavorable situation is twofold. One is that the first-order TPT is very inaccurate for short-range and/or discontinuous potentials; the second-order version of the TPT, i.e., the macroscopic compressibility (MC) approximation suggested by Barker and Henderson [8], only improves the first-order TPT very little, or is even more inaccurate than the first-order counterpart when nonuniform phenomena are under consideration. The other reason is that a self-consistent Ornstein-Zernike (OZ) integral equation theory (IET) is made more and more accurate by incorporating one or more self-consistent conditions [9]. It is shown that one version [10] of the self-consistent OZ IET can be acceptably accurate for case of potentials of an intermediate range. However, it should be pointed out that a theoretical description for extremely short-range potentials is still a challenge. Considering that the self-consistent OZ IET is unusually unwieldy for thermodynamics calculations, and its extension to inhomogeneous free energy functional is, if not impossible, at least very unstraightforward; On the contrary, the TPT is free of the disadvantages associated with the self-consistent OZ IET. Therefore, it is a pressing task to improve the accuracy of the current TPT but still retain the simplicity of calculation. Such a task would greatly push the theoretical investigation of problems from simple fluids to complex fluids, from uniform phenomena to nonuniform phenomena. The present report will report such an endeavor.

II. THEORETICAL FORMALISM

Consider a pair potential that can be written as a sum of a reference part and a perturbation part,

$$u(r) = u_{ref}(r) + u_{per}(r). \tag{1}$$

Now introduce a coupling parameter $0 \leqslant \lambda \leqslant 1$ that linearly connects the reference and full potential,

$$u(r;\lambda) = u_{ref}(r) + \lambda u_{per}(r). \tag{2}$$

The EHFE $F_{ex}(\lambda)$ of a system of N particles in a volume V interacting via the pair potential

$$u(r;\lambda)$$

at temperature T is

$$F_{ex}(\lambda) = -kT \ln\left(\int d\mathbf{r}^N e^{-\beta\Sigma_{i<j} u(r_{ij};\lambda)} \bigg/ V^N \right), \tag{3}$$

where $\beta = 1/kT$, k is Boltzmann's constant, and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. Differentiating with respect to λ and making use of definition

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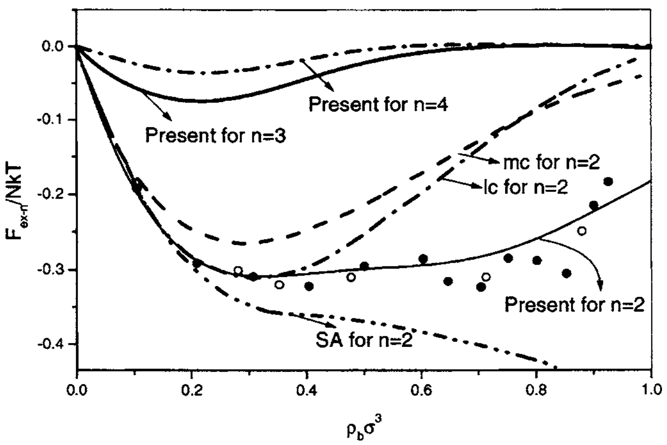

FIG. 1. $F_{ex\text{-}n}/NkT$ for the SW potential with $\zeta=1.5$ and $T^*=1$. The solid and open points give the simulation results (for $F_{ex\text{-}2}/NkT$) of Barker and Henderson [22] and Alder *et al.* [23], respectively.

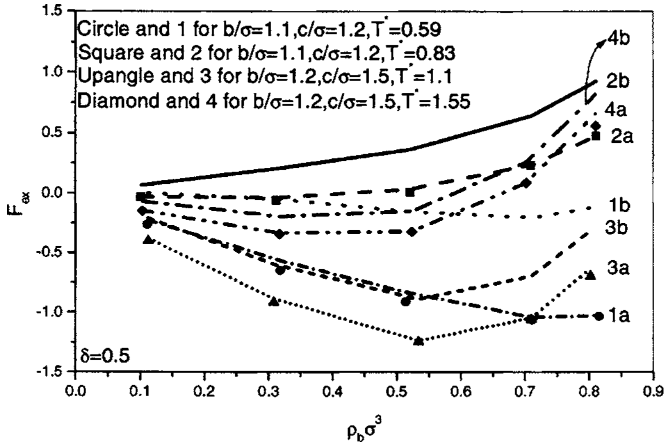

FIG. 2. The F_{ex} vs density $\rho_b\sigma^3$ for the core-softened fluid. Symbols are for the present grand canonical ensemble Monte Carlo (GCEMC) simulations, while lines are for TPT predictions. *a* stands for the present third-order TPT, while *b* the original first-order TPT.

of two-body distribution function $\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2;\lambda)$,

$$\partial F_{ex}(\lambda)/\partial\lambda = 1/2\int\int d\mathbf{r}_1 d\mathbf{r}_2 u_{per}(r_{12})\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2;\lambda). \quad (4)$$

For a uniform liquid state, Eq. (4) reduces to

$$\partial F_{ex}(\lambda)/\partial\lambda = N2\pi\rho_b\int dr r^2 u_{per}(r)g(r,\lambda,\rho_b), \quad (5)$$

where $g(r,\lambda,\rho_b)$ is the radial distribution function (rdf) of bulk fluid with pair potential

$$u(r;\lambda)$$

and bulk number density $\rho_b{=}N/V$. Correspondingly one has

$$\partial^n F_{ex}(\lambda)/\partial\lambda^n = N2\pi\rho_b\int dr r^2 u_{per}(r)\partial^{(n-1)}g(r,\lambda,\rho_b)/\partial\lambda^{(n-1)},$$
$$n \geqslant 1. \quad (6)$$

Expanding $F_{ex}(\lambda)$ around $\lambda=0$, one obtains

$$F_{ex}(\lambda) = F_{ex}(0) + \sum_{n=1}^{\infty}\lambda^n\frac{\partial^n F_{ex}(\lambda)/\partial\lambda^n|_{\lambda=0}}{n!}. \quad (7)$$

The EHFE F_{ex} for the system of N particles in a volume V interacting via the full pair potential Eq. (1), corresponds to $F_{ex}(1)$, and $F_{ex}(0)$ corresponds to the reference fluid EHFE $F_{ex\text{-}ref}$. Therefore, we have

$$F_{ex} = F_{ex\text{-}ref} + \sum_{n=1}^{\infty}\frac{1}{n!}N2\pi\rho_b\int dr r^2 u_{per}(r) \times\left|\frac{\partial^{(n-1)}g(r,\lambda,\rho_b)}{\partial\lambda^{(n-1)}}\right|_{\lambda=0}. \quad (8)$$

Truncating the series at the first order, Eq. (8) leads to the first-order TPT due to Zwanzig [2],

$$F_{ex} = F_{ex\text{-}ref} + F_{ex\text{-}Tail} = F_{ex\text{-}ref} + N2\pi\rho_b\int dr r^2 u_{per}(r)g(r,0,\rho_b), \quad (9)$$

where $g(r,0,\rho_b)$ stands for the rdf of the reference fluid of number density ρ_b. Higher order terms are concerned with calculation of derivatives of the $g(r,\lambda,\rho_b)$ with respect to λ at $\lambda=0$. We will calculate these derivatives numerically by finite difference; this incurs calculation of $g(r,\lambda,\rho_b)$ with $\lambda=0,\pm\Delta\lambda,\pm2\Delta\lambda$, where $\Delta\lambda=0.01$ is a small increment. Due to the nonlinearity of the OZ IET, the OZ IE has to be solved numerically, in combination with a bridge function approximation, to produce $g(r,\lambda,\rho_b)$. Although a very accurate hard-sphere (i.e., $\lambda=0$ case) bridge function approximation free of adjustable parameter is well known, we do not hold a good knowledge of the approximation for non-hard-sphere cases, i.e., $\lambda\neq0$, without any adjustable parameter. Considering that $\lambda=\pm\Delta\lambda,\pm2\Delta\lambda$ with $\Delta\lambda=0.01$ is near the hard-sphere case, we approximate the bridge function for the former by the bridge function approximation for the latter. For the hard-sphere bridge function approximation, we employ the Malijevsky-Labik bridge function [11]. An algorithm by Labik *et al.* [12] for solving the OZ IE is employed.

Although we expect to improve the performance of the TPT by retaining more terms, the numerical accuracy adds a limit on the maximum number of the terms retained. The above algorithm only allows one to retain the terms up to the third order; inclusion of higher terms only induces deviation of F_{ex} as a function of density from a smooth curve, and this will induce significant error for the derivative quantities such as pressure, excess chemical potential, and determination of critical point whose calculation involves first- or even third-order differential of F_{ex} with respect to density. Therefore, we will concentrate on the third-order TPT in the present report, i.e.,

$$F_{ex} = F_{ex\text{-}ref} + F_{ex\text{-}Tail}, \quad and\ F_{ex\text{-}Tail} = \sum_{n=1}^{3}F_{ex\text{-}n}, \quad (10)$$

where

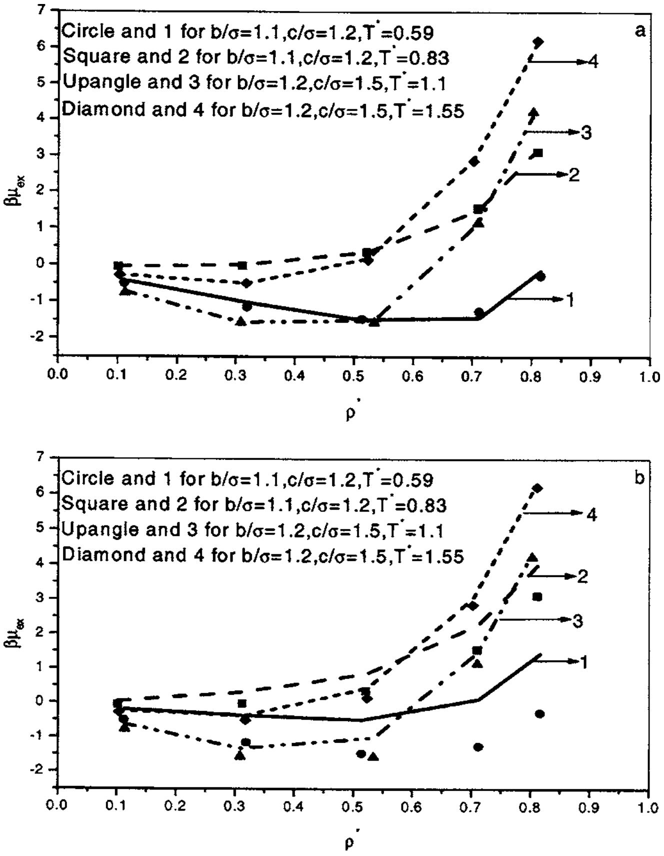

FIG. 3. The $\beta\mu_{ex}$ vs density ρ^* for the core-softened fluid of δ=0.5. Symbols are for the present grand canonical ensemble Monte Carlo (GCEMC) simulations, while lines are for the present third-order TPT (a) and the second-order MC approximation TPT (b) predictions.

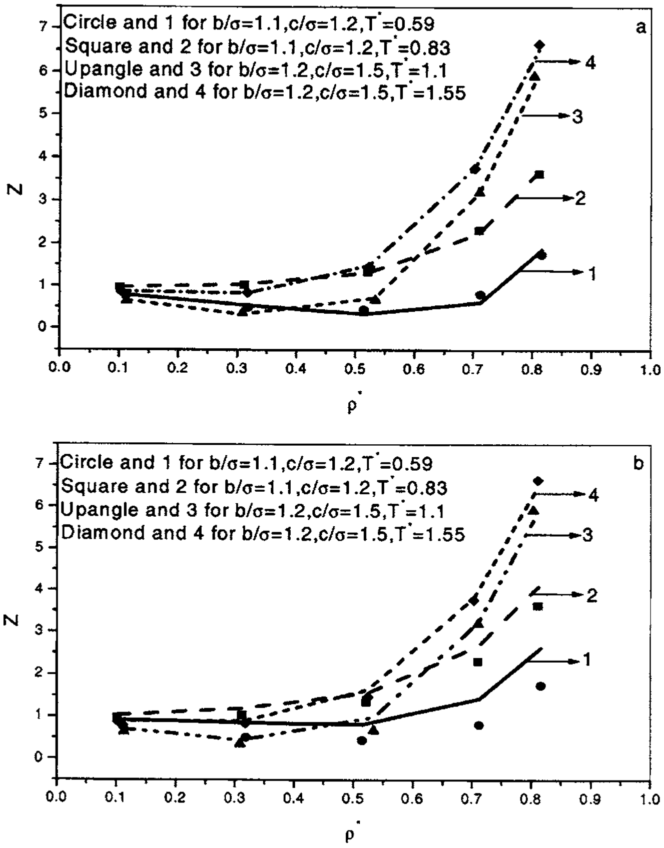

FIG. 4. The Z vs density ρ^* for the core-softened fluid of δ =0.5. Symbols are for the present grand canonical ensemble Monte Carlo (GCEMC) simulations, while lines are for the present third-order TPT (a) and the second-order MC approximation TPT (b) predictions.

$$F_{ex\text{-}n} = \frac{1}{n!}N2\pi\rho_b \int drr^2 u_{per}(r) \left.\frac{\partial^{(n-1)}g(r,\lambda,\rho_b)}{\partial\lambda^{(n-1)}}\right|_{\lambda=0}.$$

In the present report, we are limited to potentials with a hard-sphere core. Therefore, the reference fluid is the hard-sphere fluid, $F_{ex\text{-}ref}$ is calculated by a well-known Carnhan-Starling equation of state (CS EOS) [13].

In Fig. 1, the present calculation and those from several previous approximations for the $F_{ex\text{-}2}$ of a square well potential fluid denoted by Eq. (11) are presented as a function of density; the present calculations for the $F_{ex\text{-}3}$ and $F_{ex\text{-}4}$ are also presented. In Fig. 1, MC, LC, SA are, respectively, abbreviations for macroscopic compressibility, local compressibility, and superposition approximation.

$$\begin{aligned} u(r) &= \propto \quad && r/\sigma \leqslant 1, \\ &-\varepsilon && 1 < r/\sigma < \zeta, \\ &0 && r/\sigma \geqslant \zeta, \end{aligned} \tag{11}$$

where ε, ζ are, respectively, the energy parameter and the potential range parameter. Throughout the text, a reduced temperature is denoted as $T^*=kT/\varepsilon$. The present improvements over the previous approximations are tremendous, especially for cases of intermediate and high densities; it is shown that the third-order correction $F_{ex\text{-}3}$ is still evident around the critical density, and its inclusion is therefore necessary. The absolute value of $F_{ex\text{-}4}$ is very small compared with the sum of the previous terms. The F_{ex} from the third-order TPT and the original first-order TPT are presented for a very short-range core-softened fluid in Fig. 2,

$$\begin{aligned} u(r) &= \infty, \quad && r < \sigma, \\ &-\delta\varepsilon; && \sigma < r < b, \\ &-\varepsilon, && b < r < c, \\ &0, && r > c, \end{aligned} \tag{12}$$

where δ is less than 1 or even less than zero to make the $u(r)$ a core-softened potential. It is shown that the original first-order TPT is only qualitative, but the third-order TPT is very accurate for this most fundamental quantity. In the present Fig. 2 and following Figs. 3 and 4, and 7, the simulation data are obtained by grand canonical ensemble Monte Carlo (GCEMC) simulations carried out at constant chemical potential, volume, and temperature. The general features of the GCEMC method are described elsewhere [3]. Further, some

TABLE I. Thermodynamic properties of the core-softened fluid from the present GCEMC simulation, the present second-order TPT, and the present third-order TPT.

$\rho_b\sigma^3$	Second-order TPT			Third-order TPT		
			$b/\sigma=1.1, c/\sigma=1.2, T^*=0.59$			
	Z	$\beta\mu_{ex}$	βF_{ex}	Z	$\beta\mu_{ex}$	βF_{ex}
0.11196	0.84095 (0.75315)	−0.31477 (0.51036)	−0.15572 (−0.2635)	0.78961	−0.4336	−0.22319
0.31917	0.55543 (0.49286)	−0.89348 (−1.15797)	−0.44891 (−0.65083)	0.53329	−1.03275	−0.56837
0.51482	0.32856 (0.43914)	−1.38612 (−1.47407)	−0.71468 (−0.91321)	0.33889	−1.49381	−0.83154
0.71230	0.64087 (0.80463)	−1.27923 (−1.26074)	−0.92011 (−1.06537)	0.60675	−1.43348	−1.04246
0.81613	1.89524 (1.73936)	− 5.7010E 3 (−0.29681)	−0.90095 (−1.03617)	1.86696	−0.15876	−1.02513
			$b/\sigma=1.1, c/\sigma=1.2, T^*=0.83$			
0.10163	0.99647 (0.97125)	−8.4211E 3 (−0.06358)	−4.8923E−3 (−0.03483)	0.97887	−0.04851	−0.02737
0.31202	1.05039 (1.02322)	5.5927E 2 (−0.03532)	5.5391E−3 (−0.05854)	1.04161	0.00527	−0.03734
0.52156	1.31029 (1.3405)	0.38839 (0.35094)	7.8094E−2 (0.01043)	1.31385	0.3496	0.03624
0.70988	2.25964 (2.31204)	1.53873 (1.52465)	0.27909 (0.23062)	2.24663	1.4826	0.23444
0.81133	3.71103 (3.63619)	3.24113 (3.10908)	0.53010 (0.47289)	3.70444	3.18974	0.4737
			$b/\sigma=1.2, c/\sigma=1.5, T^*=1.1$			
0.11273	0.67617 (0.63385)	−0.67220 (−0.76726)	−0.34837 (−0.4011)	0.65747	−0.72443	−0.38188
0.3085	0.29384 (0.35335)	−1.55810 (−1.56398)	−0.85193 (−0.91733)	0.32293	−1.56452	−0.88585
0.53424	0.69413 (0.67315)	−1.52662 (−1.57309)	−1.22075 (−1.24624)	0.72968	−1.50624	−1.23569
0.71003	3.15975 (3.20225)	1.12151 (1.14245)	−1.03824 (−1.0598)	3.19557	1.1531	−1.04809
0.80243	5.72760 (5.92017)	4.09699 (4.22011)	−0.63061 (−0.70006)	5.744	4.11248	−0.63152
			$b/\sigma=1.2, c/\sigma=1.5, T^*=1.55$			
0.10336	0.87946 (0.86796)	−0.25427 (−0.2805)	−0.13373 (−0.14846)	0.87271	−0.27241	−0.14512
0.31746	0.82192 (0.83942)	0.50113 (− 0.50259)	−0.32306 (−0.34202)	0.83294	−0.5025	−0.33426
0.52381	1.48157 (1.46935)	0.16780 (0.14663)	−0.31377 (−0.32272)	1.49462	0.17517	−0.31918
0.70222	3.76789 (3.76759)	2.85843 (2.85351)	9.0542E−2 (0.08592)	3.78088	2.86976	0.08762
0.81008	6.51019 (6.65066)	6.17245 (6.21062)	0.66226 (0.55996)	6.51404	6.176	0.66111

details peculiar to this study are discussed in one of our previous work [14].

In Figs. 3 and 4 the excess chemical potential μ_{ex} and compressibility factor Z ($=\beta P/\rho_b$, where P is pressure) for the core-softened fluid denoted by Eq. (12) are presented. Instead of the original first-order TPT results as done in Fig. 2, the well-known second-order MC approximation TPT results are presented together with the present third-order TPT results for a comparison. For this noncontinuous and short-range potential, the second-order MCA TPT quickly becomes unacceptably inaccurate, while the present third-order

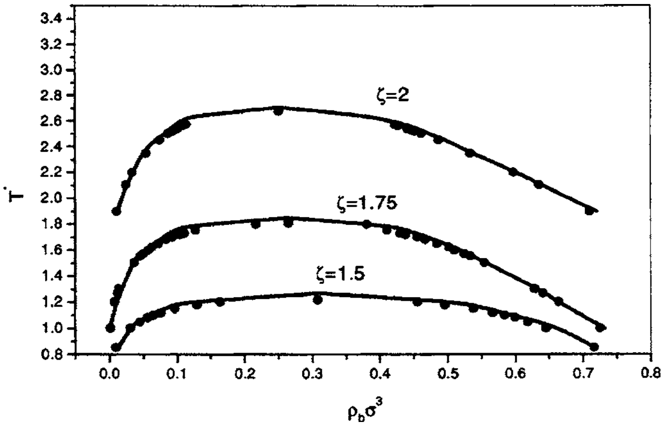

FIG. 5. Gas-liquid coexistence curve for the SW fluid for three ranges. Symbols are for the MC simulation results [19], while lines are for the present third-order TPT.

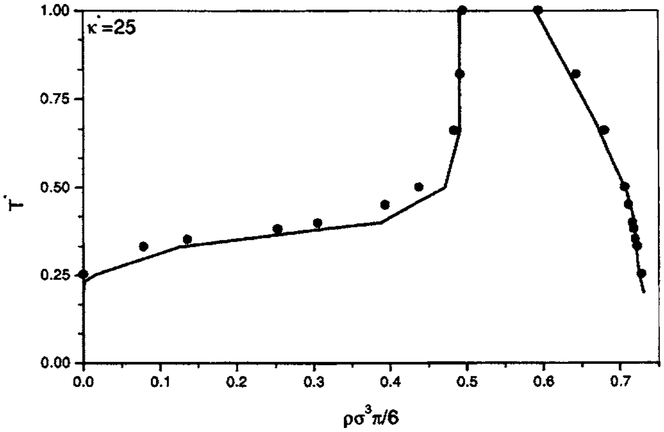

FIG. 6. Solid-liquid transition for the HCAY fluid with $\kappa^*=25$. Symbols give the simulation results [24], while lines are for the present third-order TPT.

TPT still does the job quite well. The second-order MC approximation TPT is given by [8],

$$F_{ex} = F_{ex\text{-}ref} + F_{ex\text{-}Tail}$$
$$= F_{ex\text{-}ref} + N2\pi\rho_b \int drr^2 u_{per}(r) g(r,0,\rho_b)$$
$$- N\beta^2\pi\rho_b \int drr^2 {u_{per}}^2(r) g(r,0,\rho_b) \frac{1}{\beta}\left(\frac{\partial \rho_b}{\partial P}\right)_{ref}, \tag{13}$$

where compressibility of the reference hard-sphere fluid is calculated by the CS EOS [13].

Figure 1 shows that the major contribution comes from the second order; is there any compensation of the errors between second- and third-order contributions? To answer the problem, I give a comprehensive comparison between the second- and third-order versions of the present TPT in Table I. From Table I, one can conclude that the third-order version is always more accurate than the second version for prediction of the F_{ex}, and there is not any compensation of the errors between second- and third-order contributions. However, for predictions of Z and $\beta\mu_{ex}$, the third-order version is not always more accurate than the second-order version, but is more accurate than the second-order version in most cases. We believe that this unusual phenomena is not associated with the compensation of errors but associated with the errors due to taking numerical derivatives to obtain the Z and $\beta\mu_{ex}$ from the F_{ex}. Taking into account the fact that the computational task is almost equal for both the third-order and second-order versions, we suggest the third-order version should be employed in future applications.

Figure 5 presents the predicted gas-liquid coexistence curve for the SW fluid with several ranges, and shows that our third-order TPT also performs quite well for this global quantity except that a little deviation is observed very near the critical region. To indicate the applicability to very short-range potential fluids, a popular topic in soft-matter physics, we report the solid-liquid transition for a hard-core attractive Yukawa (HCAY) fluid of a very short range,

$$u(r) = \propto, \quad r/\sigma < 1; \quad -\varepsilon\sigma \exp[-\kappa^*(r-\sigma)/\sigma]/r,$$
$$r/\sigma > 1.$$

We employ the third-order TPT for the fluid phase F_{ex}, whereas we employ the solid phase version [15] of the first-order TPT for the solid phase F_{ex}. For the solid phase, the particles are fixed at crystal grid, $g(r,\lambda,\rho_b)$ only displays very little and negligible change due to changing of λ. Therefore,

$$\partial^{(n-1)} g(r,\lambda,\rho_b)/\partial\lambda^{(n-1)}|_{\lambda=0}$$

with $n>1$ are very near zero, and the first-order version of the TPT is sufficiently accurate for solid phase. The present Fig. 6 and Fig. 4 in Ref. [15] show that the present third-order TPT is superior to a fifth-order inverse temperature expansion approximation [16] based on a mean spherical approximation (MSA). The fifth-order inverse temperature expansion approximation is, however, limited to the HCAY fluids because of an employment of the analytical MSA.

We extend the TPT to a nonuniform case. The reference part $F_{ex\text{-}ref}([\rho])$ can be treated by any existing hard-sphere density functional approximations; in this report, the adjustable parameter free version of the Lagrangian theorem-based density functional approximation [17] is employed for the $F_{ex\text{-}ref}([\rho])$. Whereas the tail part is treated by the weighted density concept [4–6],

$$F_{ex\text{-}Tail}([\rho]) = \int d\mathbf{r}\rho(\mathbf{r}) f_{ex\text{-}Tail}[\tilde{\rho}(\mathbf{r})],$$

where $f_{ex\text{-Tail}}=F_{ex\text{-Tail}}/N$, the weighted density is defined by following the decoupled simple weighted density approximation [18],

$$\tilde{\rho}(\mathbf{r}) = \int d\mathbf{r}'(\rho\mathbf{r}') w(|\mathbf{r}-\mathbf{r}'|;\rho_b),$$

a renormalized tail part of the MSA second-order direct correlation function is chosen as the weighting function, i.e.,

$$w(r;\rho_b) = -u_{per}(r) \Big/ \int d\mathbf{r}[-u_{per}(r)].$$

It should be pointed out that in the present report, the reference systems is the hard sphere system, therefore $u_{per}(r)=0$ for $r<\sigma$, and $u_{per}(r)=u(r)$ for $r>\sigma$. Then, the nonuniform $F_{ex}([\rho])$ is a sum of $F_{ex\text{-ref}}([\rho])$ and $F_{ex\text{-Tail}}([\rho])$. With the $F_{ex}([\rho])$ as input, one can treat many inhomogeneous phenomena in the framework of DFT [4]. To give a stringent comparison between the third-order and first-order TPT in a case of nonuniformity, we present the density profile of the SW fluid in coexistence with a bulk SW fluid very near the critical point (for the $\zeta=1.5$, the critical density and critical temperature [19] are $\rho_b\sigma^3=0.3079$ and $T^*=1.2172$, respectively) in Fig. 5, which clearly displays the superiority of the third-order TPT over the original first-order TPT. The external potential $\varphi_{ext}(\mathbf{r})$ responsible for the density profile is due to a hard spherical cavity of effective radius 3σ, i.e.,

$$\begin{aligned}\varphi_{ext}(\mathbf{r}) &= \propto \quad r/\sigma > 3\\ &=0 \quad r/\sigma < 3.\end{aligned} \tag{14}$$

III. DISCUSSION AND CONCLUSION

The

$$\left.\frac{\partial^{(n)} g(r,\lambda,\rho_b)}{\partial \lambda^{(n)}}\right|_{\lambda=0}$$

is a crucial quantity for numerical implementation of the present third-order TPT. Although there is a semianalytical expression for $g(r,0,\rho_b)$ [25], in order to keep self-consistency of the calculation of

$$\left.\frac{\partial^{(n)} g(r,\lambda,\rho_b)}{\partial \lambda^{(n)}}\right|_{\lambda=0}$$

by finite difference method, the $g(r,\lambda,\rho_b)$ with $\lambda=0,\pm\Delta\lambda,\pm 2\Delta\lambda$ should be calculated in a unified way with the help of the approximate OZ IET as detailed in the text. In fact, if one calculates the $g(r,\lambda,\rho_b)$ with $\lambda=\pm\Delta\lambda,\pm 2\Delta\lambda$ by the approximate OZ IET, but the semianalytical expression for $g(r,0,\rho_b)$ [25] is used, the resultant

$$\left.\frac{\partial^{(n)} g(r,\lambda,\rho_b)}{\partial \lambda^{(n)}}\right|_{\lambda=0}$$

is unusually oscillatory as a function of r even for $n=1$, and the associated F_{ex} is also unusually oscillatory as a function of ρ_b, an erroneous result which, after differentiation with respect to ρ_b, only results in mistaken Z and μ_{ex}. In fact, even if the $g(r,\lambda,\rho_b)$ with $\lambda=0,\pm\Delta\lambda,\pm 2\Delta\lambda$ is calculated in a unified way, i.e., by the approximate OZ IET as done in the present report, the present finite difference method for the

$$\left.\frac{\partial^{(n)} g(r,\lambda,\rho_b)}{\partial \lambda^{(n)}}\right|_{\lambda=0}$$

only allows one to retain the terms up to the third order. Another approximation associated with the calculation of the

$$\left.\frac{\partial^{(n)} g(r,\lambda,\rho_b)}{\partial \lambda^{(n)}}\right|_{\lambda=0}$$

is employing the Malijevsky-Labik bridge function of the hard sphere (i.e.,$\lambda=0$) for a case of nonhard sphere (i.e.,$\lambda\neq 0$). In general, the associated error is not obvious since the finite difference method is only associated with very small λ. However, the associated error will increase as the temperature decreases since lowering of temperature is equal to a rising of λ. Therefore, the present third-order TPT performs excellently for a case of not very low temperature, but the performance somewhat deteriorates when the temperature decreases, as displayed in Figs. 2–4 and 7.

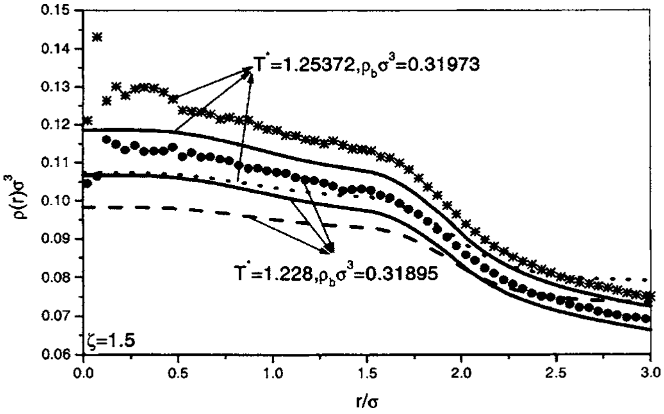

FIG. 7. Density profile of the SW fluid in coexistence with the bulk fluid near the critical point. Symbols are for the present GCEMC simulations, while solid lines are for present third-order TPT predictions; dashed or dotted lines are for the original first-order TPT predictions.

To conclude, we propose a methodology for extending the TPT to higher orders, the methodology is completely numerical, and therefore applicable to fluids of any potentials. The present third-order TPT performs very well in predicting thermodynamic and structure properties of both uniform and nonuniform cases, especially the excellent performance sustained for the two extreme cases, i.e., the extremely short-range potential and the critical region. Other applications include simplifying the numerical solution of the self-consistent OZ IET [9,10] and hierarchical reference theory [20] by externally supplying accurate free energy or other thermodynamic quantities as input, and also include supplying accurate input into a renormalization group approach [21] for fluids of extremely short range. Therefore the present-third order TPT will be of general interest for the fluid statistical mechanics, especially in the fields of soft-matter physics where simple and accurate theoretical description is still lacking. Work along these lines will be reported in succeeding publications.

ACKNOWLEDGMENTS

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