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Reformulation of liquid perturbation theory for low temperatures

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A perturbation strategy is proposed which allows liquid perturbation methodology to be applied to extremely low temperature situations for which the available liquid integral equation theory and traditional thermodynamic perturbation theory fail. The possibility of avoiding the low temperature problem of the thermodynamic perturbation theory not only is of relevance to the investigation of complex fluids, but also may be useful for reformulation of other liquid theories to achieve higher accuracy and avoid the respective low temperature problems.

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I. INTRODUCTION

Two typical theoretical approaches for calculation of properties of liquid matter are Ornstein-Zernike (OZ) integral equation (IE) theory and thermodynamic perturbation theory (TPT) [1]. Although the OZ IE theory has been made more and more accurate in recent years [2], for extremely short-ranged potentials where the vapor-liquid transition is deeply buried inside the metastable region, the performance of the OZ IE theory is less satisfactory, and the numerical procedure may even fail to converge [3]. The TPT for a fluid state is classified into two categories. One is the formulation due to Zwanzig [4], in which the perturbation free energy is expressed as a power series in the inverse temperature $\beta = 1/kT$ (k is the Boltzmann constant and T the absolute temperature) and an n-order term is involved with distribution functions of order up to $2n$. The higher-order terms of Zwanzig's series hence progressively become more complicated and numerically inaccessible. In 1967, Barker and Henderson [5] propose a macroscopic compressibility approximation (MCA) for the second-order term of Zwanzig's formulation. Since then the first- and second-order versions of Zwanzig's formulation have been generally accepted as trustworthy liquid theories.

The present author [6] proposed a second category of the TPT in which the perturbation part is expressed as a power series in a coupling parameter ξ. In contrast to Zwanzig's formulation, the successively emerging n-order terms in Zhou's formulation involve only $(n-1)$th derivatives evaluated at $\xi=0$ of a radial distribution function for an imaginary fluid; hence Zhou could easily formulate the third- [6] and fifth-order [7] versions of his TPT by numerically acquiring the derivatives of interest. In Zwanzig's formulation the expansion parameter is β; obviously the first- and second-order versions of Zwanzig's formulation deteriorate as the temperature decreases. In Zhou's version, although the expansion parameter ξ is set to be a constant 1, the magnitude of the expansion term is still proportional to β; hence Zhou's TPT version will also worsen as the temperature decreases. In fact, for sufficiently low temperature, both perturbation expansions by Zwanzig and Zhou will not converge at all. Unfortunately, the low temperature problem is also inherent to the OZ IE theory, which also monotonically deteriorates as the temperature drops. When the temperature is below the critical temperature, the OZ IE theory even loses its physical solution in the two-phase coexistence region. This undesirable property makes the OZ IE theory very inconvenient for depicting the vapor-liquid coexistence curve. Furthermore, the OZ IE theory possibly leads to incorrect and nonmatching branches of the binodal in the vicinity of the vapor-liquid critical point. Another situation that can also occur in OZ IE theory is the determination of the boundaries of phase stability of density-dependent pair potentials [8]. For these potentials the thermodynamic critical points are not associated with diverging correlations, and thus the lack of a solution curve of the OZ IE theory is no longer necessarily a signature of a phase transition. However, the TPT can tackle these potentials in the same way exactly as it tackles density-independent pair potentials [8].

In complex fluids the effective potential between mesoscopic particles is usually very short ranged; the critical temperature is correspondingly very low, and the temperature of interest is therefore also very low. Considering the host of difficulties plaguing the OZ IE theory at low temperatures and the inability of the OZ IE theory to determine the boundaries of phase stability of density-dependent pair potentials, it would obviously be useful to transform the divergent series of the TPT at very low temperature into a convergent one or to speed up the convergence rate of the series at higher temperatures. This would not only be of striking theoretical significance but would also greatly push the theoretical investigation of problems from simple to complex fluids. The present paper illustrates a strategy for realizing this aim in Zhou's formalism, but the same strategy can be implemented in any version of the TPT.

II. THEORETICAL DESCRIPTION

The system of present interest is described by an interparticle potential $u(r)=u_{\mathrm{ref}}(r)+u_{\mathrm{per}}(r)$ with $u_{\mathrm{ref}}(r)$ a reference potential and $u_{\mathrm{per}}(r)$ the remaining perturbation part. The excess Helmholtz free energy per particle, f_{ex}, for the system of number density ρ is given in Zhou's formulation [6,7] by

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$$\beta f_{\mathrm{ex}} = \beta f_{\mathrm{ex\ ref}} + \sum_{n=1}^{\infty} \beta f_{\mathrm{per}\ n}, \tag{1a}$$

$$\beta f_{\mathrm{per}\ n} = (1/n!) 2\pi\rho \int dr\, r^2 \beta u_{\mathrm{per}}(r)\, g_{\mathrm{imag}}{}^{(n-1)}(r,\xi,\rho,T)|_{\xi=0}. \tag{1b}$$

Here $f_{\mathrm{ex\ ref}}$ is the reference fluid counterpart of f_{ex}, $g_{\mathrm{imag}}^{(n-1)}(r,\xi,\rho,T)|_{\xi=0}$ are the $(n-1)$th derivatives evaluated at $\xi=0$ of $g_{\mathrm{imag}}(r,\xi,\rho,T)$ with respect to ξ, $g_{\mathrm{imag}}(r,\xi,\rho,T)$ is the radial distribution function (RDF) of a bulk imaginary fluid with an imaginary pair potential $u(r;\xi) = u_{\mathrm{ref}}(r) + \xi u_{\mathrm{per}}(r)$. Correspondingly, $g_{\mathrm{imag}}^{0}(r,\xi,\rho,T)|_{\xi=0} = g_{\mathrm{imag}}(r,0,\rho,T)$ is the RDF at temperature T and density ρ of the reference fluid dictated by the reference potential $u_{\mathrm{ref}}(r)$.

In order to make the present coupling parameter expansion calculation clear to readers, it is necessary to introduce in detail information on the calculation of $g_{\mathrm{imag}}^{(n-1)}(r,\xi,\rho,T)|_{\xi=0}$. As in Refs. [6,7], calculation of the derivatives is completed by a finite difference technique combined with an interpolation multinomial. First, $g_{\mathrm{imag}}(r,\xi,\rho,T)$ is calculated at $\xi = \pm 2\Delta\xi$, $\pm\Delta\xi$, and 0. Here $\Delta\xi$ is a small increment ranging from 0.001 to 0.01. The OZ IE combined with a bridge function approximation for the imaginary pair potential $u(r;\xi)$ is solved numerically with a rapid and stable algorithm due to Labik, Malijevsky, and Vonka [9]. The $g_{\mathrm{imag}}(r,\xi,\rho,T)$ obtained at discrete values of r and ξ is employed to calculate $g_{\mathrm{imag}}^{(n-1)}(r,\xi,\rho,T)|_{\xi=0}$ with $n=2,3$ at the same discrete values of r. In Refs. [6,7], the hard sphere potential is chosen as the reference potential, and a hard sphere bridge function approximation due to Malijevsky and Labik [10] (ML) is employed for the imaginary fluid dictated by $u(r;\xi)$ with $\xi = \pm 2\Delta\xi, \pm\Delta\xi$ as well as by $u(r;\xi)$ with $\xi=0$. The reason that one is allowed to employ the ML hard sphere bridge function for the imaginary fluid dictated by $u(r;\xi)$ with $\xi = \pm 2\Delta\xi, \pm\Delta\xi$ is that the ξ involved is very small, so $u(r;\xi)$ is actually very near to the chosen reference potential, i.e., the hard sphere potential in the context of Refs. [6,7]. If other reference potentials different from the hard sphere potential are employed, then one has to formulate a new bridge function approximation for use. Because of the very small value of ξ, the critical temperature $T_{\mathrm{imag}\ c}$ of the imaginary fluid dictated by $u(r;\xi)$ is actually extremely low. As a result, the temperature of interest T is actually always higher than $T_{\mathrm{imag}\ c}$. In consequence, one does not worry about running into the vapor-liquid two-phase region of the imaginary fluid when the OZ IE theory is solved.

Obviously, the magnitude of each $\beta f_{\mathrm{per}\ n}$ term depends on the magnitude of both the reduced perturbation potential $\beta u_{\mathrm{per}}(r)$ and $g_{\mathrm{imag}}^{(n-1)}(r,\xi,\rho,T)|_{\xi=0}$. It has been shown [7] that for the hard sphere reference potential and a target hard sphere plus square well fluid the magnitudes of $g_{\mathrm{imag}}^{3}|_{\xi=0}$ and $g_{\mathrm{imag}}^{4}|_{\xi=0}$ become unusually large as the reduced temperature of interest $T^* = kT/\varepsilon$ (ε is the energy parameter) becomes progressively lower. Therefore a key factor influencing the convergence of the TPT is the magnitude of $\beta u_{\mathrm{per}}(r)$. In the current investigation based on the TPT, the hard sphere potential is exclusively chosen as $u_{\mathrm{ref}}(r)$. From the mathematical point of view $u_{\mathrm{ref}}(r)$ is not limited only to the hard sphere potential; any model or real potential can be a candidate for $u_{\mathrm{ref}}(r)$ as long as the corresponding $f_{\mathrm{ex\ ref}}$ and $g_{\mathrm{imag}}^{(n-1)}(r,\xi,\rho,T)|_{\xi=0}$ can be reliably and quickly obtained.

If one diverts one part of the attractive ingredient in $u(r)$ into $u_{\mathrm{ref}}(r)$, then the magnitude of the resultant reduced perturbation part [still denoted by $\beta u_{\mathrm{per}}(r)$] will decrease concomitantly. Correspondingly, the resultant reduced reference potential [still denoted by $\beta u_{\mathrm{ref}}(r)$ and hereafter called the nonhard sphere reference potential] will deviate from the hard sphere reference potential. A long-tested modified hypernetted chain (MHNC) approximation [11] will be applied to the nonhard sphere reference fluid, an associated effective hard sphere density will be determined by the so-called global consistency constraint in which the equality of the pressure, as calculated, respectively, from the virial and the fluctuation methods, is imposed. For the hard sphere bridge function which is needed as input to switch on the MHNC approximation, we employ the ML hard sphere bridge function [10] for the domain of $r > \sigma$ (σ is the hard sphere diameter) and a recently proposed hard sphere bridge function due to the present author [12] for the domain of $r < \sigma$. However, the hard sphere bridge function for $r < \sigma$ should be shifted by a density-dependent constant to make the hybrid hard sphere bridge function continuous at $r = \sigma$. Individual terms in this hard sphere bridge function are given by simulation data-fitting formula of different authors, i.e., of Groot, van der Erden, and Faber [13], Balance and Speedy [14], and Verlet and Weis [15]. This function is therefore denoted the GvEF-BS-VW hard sphere bridge function. Upon solution of the MHNC approximation for the nonhard sphere reference fluid dictated by $u_{\mathrm{ref}}(r)$ over the whole density domain ranging from zero density to notably high density, one can obtain $f_{\mathrm{ex\ ref}}$ by integrating the resulting equation of state. As an accompaniment of the solution of the MHNC approximation, the effective hard sphere density is obtained as a function of the bulk density for the nonhard sphere reference fluid. This information will be used to calculate $g_{\mathrm{imag}}(r,\xi,\rho,T)$ at $\xi = \pm 2\Delta\xi, \pm\Delta\xi$. Such a grafting procedure is permitted since the ξ involved is very small, so the imaginary fluid dictated by $u(r;\xi)$ is actually very near the nonhard sphere reference fluid dictated by $u_{\mathrm{ref}}(r)$. $g_{\mathrm{imag}}(r,\xi,\rho,T)$ at $\xi = \pm 2\Delta\xi, \pm\Delta\xi$ in combination with $g_{\mathrm{imag}}(r,\xi,\rho,T)$ at $\xi=0$, which is just obtained from the situation of the nonhard sphere reference fluid, is employed to calculate $g_{\mathrm{imag}}^{(n-1)}(r,\xi,\rho,T)|_{\xi=0}$ with $n=2,3$ to switch on the present TPT calculation.

Several illustrating calculations will be performed on several model potentials to confirm the validity of the above idea and numerical procedure. The calculation touches on the vapor-liquid coexistence curve, the location of the critical point, and the equation of state. The sample potentials are a hard core attractive Yukawa potential [16] $u_Y(r,z)$, a hard sphere square well potential [17] $u_{\mathrm{SW}}(r,\lambda)$, a core-softened potential [18] $u_{\mathrm{CS}}(r,b,c,\delta)$, and a Girifalco potential [19] $u_G(r)$ for C_{60} molecules. The potential details and the definition of the respective parameters can be found in Refs. [16–19] and are listed here for the sake of convenience:

$$u_Y(r,z) = \begin{cases} \infty, & r/\sigma \leq 1, \\ -\varepsilon\sigma \exp[-z(r-\sigma)/\sigma]/r, & r/\sigma > 1, \end{cases} \tag{2}$$

$$u_{\mathrm{SW}}(r,\lambda)=\begin{cases}\infty, & r/\sigma\leqslant 1,\\ -\varepsilon, & \lambda\geqslant r/\sigma>1,\\ 0, & r/\sigma>\lambda,\end{cases}\tag{3}$$

$$u_{\mathrm{CS}}(r,b,c,\delta)=\begin{cases}\infty, & r/\sigma\leqslant 1,\\ -\varepsilon\delta, & b\geqslant r/\sigma>1,\\ -\varepsilon, & c\geqslant r/\sigma>b,\\ 0, & r/\sigma>c,\end{cases}\tag{4}$$

$$u_G(r)=-\alpha_1\left(\frac{1}{s(s-1)^3}+\frac{1}{s(s+1)^3}-\frac{2}{s^4}\right)+\alpha_2\left(\frac{1}{s(s-1)^9}+\frac{1}{s(s+1)^9}-\frac{2}{s^{10}}\right).\tag{5}$$

Here z, λ, and b,c measure the range of the potentials u_Y, u_{SW}, and u_{CS}, respectively; the parameter δ in the potential u_{CS} measures the noncontinual degree of the core-softened potential tail. For the Girifalco potential $u_G(r)$, $s=r/d$, $\alpha_1=N^2A/12d^6$, and $\alpha_2=N^2B/90d^{12}$; N and d are the number of carbon atoms and the diameter, respectively, of the fullerene particles, $A=32\times10^{-60}$ erg cm^6 and $B=55.77\times10^{-105}$ erg cm^{12} are constants entering the Lennard-Jones 12-6 potential through which two carbon sites on different spherical molecules are assumed to interact. For C_{60}, $d=0.71$ nm, the node of the potential $u_G(r)$, the minimum, and its position are $r_0\cong0.959$ nm, $\varepsilon\cong0.444\times10^{-12}$ erg, and $r_{\min}=1.005$ nm, respectively.

The first three potentials have a hard sphere core whose diameter is chosen as σ, i.e., the hard sphere diameter of the present hybrid hard sphere bridge function. The Girifalco potential has only a very steep continuous core. The node of $u_G(r)$ is chosen as the hard sphere diameter σ.

Now, the remaining question is the separation of the potential into the reference part and the perturbational part. As all of the basic inputs for the present perturbation stategy are calculated by the OZ IE approach, it is helpful to retrace the relationship between the prediction accuracy of the OZ IE approach and the location in the phase diagram of the state point under consideration. For the supercritical state, it is well known that the greater the distance from the critical temperature T_c to the T of interest, the more accurate is the OZ IE approach. For the subcritical state there exists a vapor-liquid two-phase region where the OZ IE approach is not physically and/or mathematically solvable at all; the solvable region of the OZ IE approach is confined to the vapor and liquid phase sides. As for the relationship between T_c and the potential parameters, it is known that (1) the longer the attractive range, the higher is T_c; (2) the higher the energy parameter ε, the higher is T_c. As a result, the principle for choice of the proper $u_{\mathrm{ref}}(r)$ should be that the attractive range or the energy parameter of $u_{\mathrm{ref}}(r)$ should be shorter or smaller than those of the $u(r)$, or any combination of those two ways, such that the critical temperature $T_{\mathrm{ref}\ c}$ of the nonhard sphere reference fluid is sufficiently lower than the temperature of interest. This helps to obtain $f_{\mathrm{ex\ ref}}$ accurately for the nonhard sphere reference fluid within the whole density range by the OZ IE approach, and also $g_{\mathrm{imag}}(r,\xi,\rho,T)$ for the imaginary fluid. Thus one has to strike a balance between a low magnitude of $\beta u_{\mathrm{per}}(r)$ and a low $T_{\mathrm{ref}\ c}$ of the corresponding nonhard sphere reference fluid. Generally speaking, the basic and main ingredient of $u_{\mathrm{ref}}(r)$ should be repulsive. As a result, for the first three potentials above, the purely repulsive hard sphere core should be completely included into $u_{\mathrm{ref}}(r)$. For the Girifalco potential, the part with r smaller than the node r_0 should be completely classified into $u_{\mathrm{ref}}(r)$; this is why the node r_0 is chosen as the hard sphere diameter σ of the present hybrid hard sphere bridge function. As for the part with r larger than σ, a reasonable assignment proportion is that $1/2.5$ times the part is included into $u_{\mathrm{ref}}(r)$ and the remaining part into $u_{\mathrm{per}}(r)$. The assignment proportion $1/2.5$ is our quantitative criterion for the specific partition of the full interparticle interaction; the criterion is obtained by trial and error with the help of the principle for choice of the proper $u_{\mathrm{ref}}(r)$ just discussed. The rationality of this criterion will be demonstrated next for the cited sample potentials, and we will explain its "universality" for different potential functions. It is well known that, for most fluids, the ratio of the critical temperature T_c to the triple point temperature T_t generally lies between 2 and 5 [1]. The lower temperature limit of interest is usually a little below T_t. Moreover, the accuracy of the OZ IE approach depends on the relative deviation of the temperature of interest from the critical temperature. As a result of the above facts, a gerneral $1/2.5$ criterion suffices for the needs of the present perturbation strategy. One also does not worry about whether this approach can be used in a predictive manner if an assessment provided by computer simulation is unavailable, as the $1/2.5$ criterion always suffices for different potential functions as will be shown later. It should be pointed out that, if other factors deviating from the $1/2.5$ criterion are employed, the resulting results will display small scattering around the results due to $1/2.5$ criterion; this is actually inevitable. This undesirable character originates in the following facts. One is that the OZ IE approach possibly has different precision for different potential functions tackled; the other is that different assignment proportions actually change the contribution assigned to each expansion term, so that if the order byond which the coupling parameter expansion is truncated is fixed, the final outcome is of course different. Luckily the final outcome will not noticeably worsen if the assignment proportion does not deviate from the $1/2.5$ criterion too greatly. A remarkable deviation from the $1/2.5$ criterion only leads to two kinds of consequence. One is that the convergence rate will not speed up if the proportionality factor of $1/2.5$ is replaced by a too small value; obviously, if the substitution value is zero, then the original TPT perturbation strategy is restored. The other is that the final outcome will seriously worsen or the numerical code will break down completely if the proportionality factor of $1/2.5$ is replaced by a too large value. A proportionality factor larger than $1/2.5$ means that many of the attractive ingredients are absorbed into the reference fluid; this possibly leads to an increase of the critical temperature of the reference fluid. When the reference fluid critical temperature exceeds the temperature of interest, the breaking down of the numerical code mentioned above will occur; if the reference fluid critical temperature is raised but

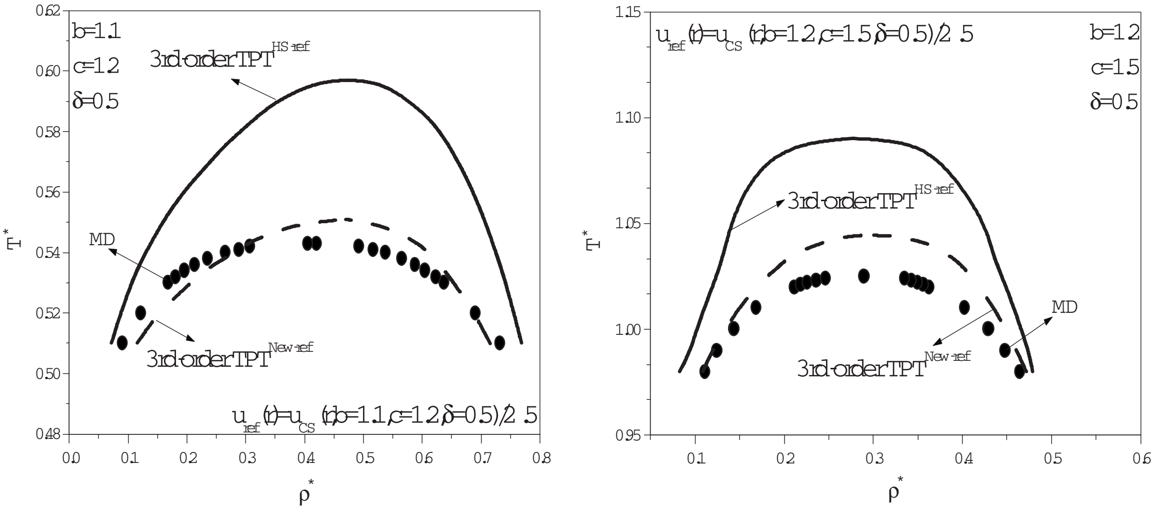

FIG. 1. Vapor-liquid coexistence curves of the core-softened fluid at two parameter combinations. The molecular dynamics (MD) results are from Ref. [18].

is still below the temperature of interest, then the final results also will worsen as the input information supplied by solving the OZ IE theory becomes more and more inaccurate.

A comparison between different theoretical approaches and computer simulation is presented for the coexistence curves of the core-softened fluid in Fig. 1, the attractive Yukawa fluid in Fig. 2, the square well fluid in Fig. 3, and the Girifalco fluid in Fig. 4; and the critical parameters of the attractive Yukawa and square well fluids, respectively, are given in Tables I and II. Throughout the present paper, the reduced bulk density ρ^* is defined as $\rho\sigma^3$. In Fig. 4 the corresponding pressure P and chemical potential μ are also presented. We have used the superscripts HS-ref and new-ref to denote the TPT results based on the hard sphere and nonhard sphere potential as $u_{\text{ref}}(r)$, respectively. The corresponding nonhard sphere reference potentials are shown in the figures or captions of the figures. One conclusion emerging from the comparison is that for the intermediate potential range the present third-order TPT$^{\text{new-ref}}$ is on average more accurate than the self-consistent Ornstein-Zernike (SCOZA), heirarchical reference theory (HRT), MHNC approximation, third-order TPT$^{\text{HS-ref}}$, and even fifth-order TPT$^{\text{HS-ref}}$, etc. (the third-order TPT$^{\text{HS-ref}}$ is always more accurate than the traditional second-order MCA TPT [6]). What is particularly inspiring is that the TPT based on the nonhard sphere perturbation strategy achieves, even at third order, gives quantitatively very accurate predictions for the critical point location of extremely short-ranged Yukawa and square well potentials for which the HRT is numerically inaccessible and the SCOZA is only qualitatively or also numerically inaccessible. It should be pointed out that the traditional second-order MCA TPT completely fails to predict even the exis-

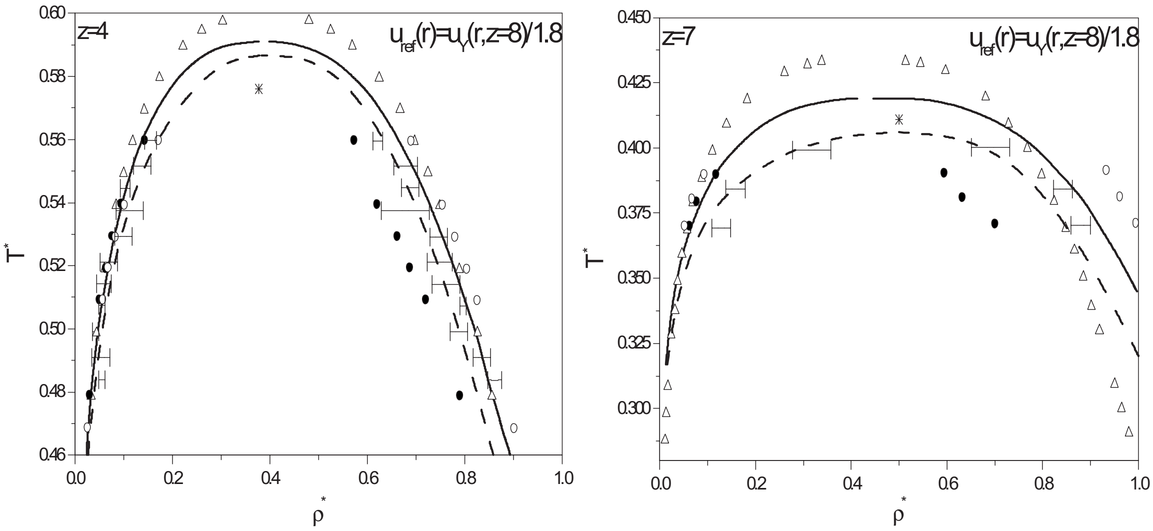

FIG. 2. Vapor-liquid coexistence curves of the attractive Yukawa fluid at two values of the inverse range parameter z. Solid lines are for results from SCOZA; triangles, HRT; full circles, generalized mean spherical approximation (GMSA); open circles, MHNC; dashed lines the present third-order TPT$^{\text{new-ref}}$; horizontal bars, Gibbs-ensemble MC results of Ref. [20]. All of the OZ IE results are reproduced from Ref. [16].

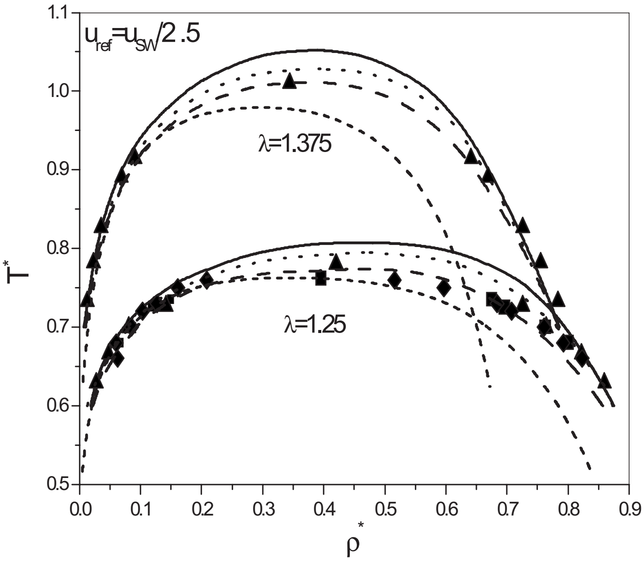

FIG. 3. Vapor-liquid coexistence for square well fluid. Points are the simulation data from Refs. [21–23], respectively, for squares, triangles, and diamonds. Solid lines are the results from the third-order TPT$^{\text{HS-ref}}$, dotted lines the fifth-order TPT$^{\text{HS-ref}}$, short-dashed lines the SCOZA reproduced from [17], and dashed lines the present 3rd-order TPT$^{\text{new-ref}}$.

tence of the critical point of the latter potential. Except for the situation in Fig. 2, the nonhard sphere reference potentials for the four sample potentials are specified based on the above 1/2.5 criterion; the displayed superiority of the present predictive ability over other existing liquid state theories fully indicates the universality, rationality, and serviceability of the 1/2.5 criterion. To indicate that the 1/2.5 criterion is not the only one, the Fig. 2 case employs other partition methods. It is shown that the particular partition method that originates from the "any combinations of the two ways" suggested above also leads to very satisfactory predictions. However, we still suggest the 1/2.5 criterion to be employed for general cases as the 1/2.5 criterion's universality has reasonable foundation, as explained above.

TABLE I. Comparison of the critical temperatures and densities for attractive Yukawa fluid of two inverse range parameter values among two versions [3(b)] of the SCOZA, third-order TPT$^{\text{new-ref}}$, and fifth-TPT$^{\text{new-ref}}$ with $u_{\text{ref}}=u_Y/2.5$.

z	T_c^*	ρ_c^*	Method
25	0.2353		MC (Ref. [26])
	0.18706	0.307	SCOZA ($z_2=z$)
	0.15829	0.170	SCOZA ($z_2=165.8$)
	0.23802	0.42113	Third-order TPT$^{\text{new-ref}}$
	0.2287	0.3105	Fifth-order TPT$^{\text{new-ref}}$
100	0.1538		MC (Ref. [26])
	0.06059	0.07	SCOZA, $z_2=z$
	0.17427	0.47126	Third-order TPT$^{\text{new-ref}}$
	0.1599	0.28452	Fifth-order TPT$^{\text{new-ref}}$

From Table I one concludes that the fifth-order version of the present nonhard sphere perturbation strategy does not always overmatch the third-order version. It is well known that the critical densities of the hard core attractive Yukawa (HCAY) fluid rise along with increase of the z value; the critical density for $z=7$ is known to be 0.50 [20]. As a result, the critical densities with $z=25$ and 100 certainly exceed 0.50. Therefore, the fifth-order version always underestimates the critical densities far more seriously than the third-order version does. As for the critical temperature, between the two situations listed in Table I, one is more favorable to the third-order and the other to the fifth-order version. Therefore, the third-order version is actually superior on average to the fifth-order version. Unlike the original TPT, which employs the hard sphere potential as reference potential and as a result the analytical ML hard sphere bridge function [10] for

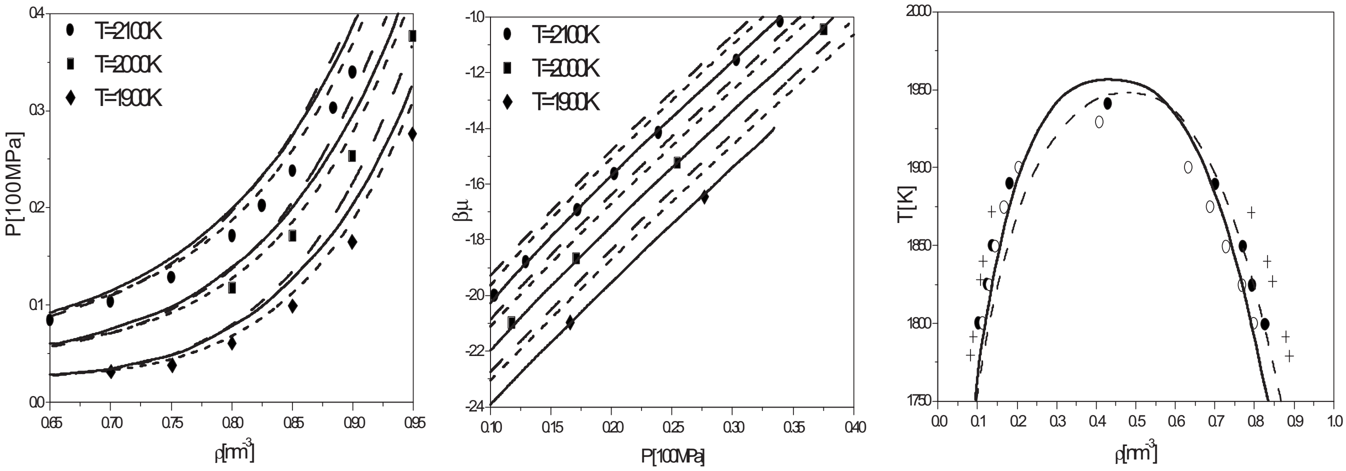

FIG. 4. Girifalco fluid thermodynamic properties. In panels for P and $\beta\mu$, the dashed and solid lines are respectively for SCOZA and MHNC results, the short-dashed lines the present third-order TPT$^{\text{new-ref}}$, and the symbols the MC results [24]. All curves are displayed from top to bottom in order of decreasing temperature. In panel for vapor-liquid coexistence, open circles are for the MHNC results, solid line the SCOZA, full circles the MC results [25], pluses the MHNC under a local consistency constraint, dashed line the present third-order TPT$^{\text{new-ref}}$. All of the OZ IE results are reproduced from Ref. [19]. $u_{\text{ref}}(r)=u_G(r)$ for $r<\sigma$ and $u_{\text{ref}}(r)=u_G(r)/2.5$ for $r>\sigma$.

TABLE II. Critical point parameters for the square well fluid for width λ, resulting from simulations [27] (first line) and third-order $\text{TPT}^{\text{new-ref}}$ (second line) with $u_{\text{ref}}=u_{\text{SW}}/2.5$.

λ	T_c^*	ρ_c^*
0.005	0.2007	0.542
	0.21387	0.55672
0.01	0.2328	0.540
	0.24021	0.49533
0.02	0.2769	0.538
	0.27646	0.44523
0.03	0.3106	0.530
	0.30467	0.42656
0.04	0.3398	0.522
	0.32981	0.41545
0.05	0.3658	0.513
	0.35262	0.40012

supplying RDF information to be used in calculation of $g_{\text{imag}}^{(n-1)}(r,\xi,\rho,T)|_{\xi=0}$, the present TPT employs a nonhard sphere potential as the reference potential and, consequently, the bridge function for the nonhard sphere reference potential has to be determined by a thermodynamically consistent condition in the framework of the MHNC approximation. The unavoidable and small error introduced for the effective hard sphere densities may lead to small and irregular errors in the RDF information. After a numerical differential procedure, these errors will inevitably be propagated into $g_{\text{imag}}^{(n-1)}(r,\xi,\rho,T)|_{\xi=0}$. Furthermore, the propagation of the error will be strengthened enormously along with increase of the differential order. As a result, the excess Helmholtz free energy from the fifth-order version may be vested with more instability than that from the third-order version. In fact, we have observed numerical instability associated with the fifth-order version at very low temperatures; thus high order numerical differentiation on the excess Helmholtz free energy leads to results which vibrate irregularly to a small extent as a function of the bulk density. Consequently, from the view point of numerical stability, the third-order version is also suggested for general use instead of the fifth-order version. Although the second-order version is numerically stable enough, this is no advantage over the third-order version as the third-order truncation is certainly more reliable than the second-order truncation.

It is possibly helpful to give a brief discussion about the computing time needed by taking the original and the present third-order versions as examples. For the original third-order version, the computing time for a state point is mainly invested in solving the OZ IE theory free of adjustable parameter five times, calculating $g_{\text{imag}}^{(n-1)}(r,\xi,\rho,T)|_{\xi=0}$ with $n=2,3$, and calculating the integrals for each expansion term. If one calculates f_{ex} over a reduced density domain ranging from 0.005 to 1.005 with a uniform density increment of 0.02, it is shown that the original third-order version will take 47 s on a personal computer. Compared with the original third-order version, the additional computation time of the present third-order version is invested in solving the MHNC approximation. If one uses the gold search method to locate the solution of the MHNC approximation, this corresponds to solving the OZ IE theory free of adjustable parameters 15 times. As a result, the computing time for the present third-order version is four times smaller than that of the original third-order version. To calculate the phase behavior, one needs f_{ex} over a wide temperature and density range. Calculation over the density domain is described above; for the temperature range, it is helpful to give a brief discussion. Assuming one needs to calculate for a temperature domain ranging from $T^*=0.3$ to 100, it is not necessary to use a uniform temperature increment. At the temperature lower limit, the temperature increment has to be sufficiently small, such as 0.005; but at the temperature upper limit, the temperature increment can be relaxed to be as large as 5 or even 10. In the intermediate region, the temperature increment can be varied between 0.005 and 5. In summary, one does not need to worry about the possibility that the present numerical implementation of the coupling parameter expansion causes one to face an excessive numerical effort.

III. CONCLUSION

The TPT goes back to van der Waals [28]; it is based on the idea that the molecular structure of dense fluids and solids is essentially determined by a short-ranged repulsive ingredient of the underlying potential, and that a smoothly varying long-ranged attractive ingredient can be considered as a perturbation to the former. The present paper points out that, even when the reference systems are somewhat encroached on by some attractive ingredient, the perturbation picture is still valid. Considering that the perturbation strategy underlies a large category of liquid theories including OZ IE theory [1] and classical density functional theory [29] as well as the TPT [1], the present success in the framework of fluid TPT promises emergence of a different research direction for reformulation of liquid theories to achieve higher accuracy and overcome the low temperature problem. Specifically speaking, the present TPT based on the strategy of perturbation around a nonhard sphere reference system not only provides a way out of the low temperature problem of traditional TPT, and compares favorably with the most accurate OZ IE theories, but also allows a unified treatment of different potential functions whether the repulsive part of the potential functions is a discontinuous hard sphere repulsion or a very steep continuous repulsion. In particular, the third- and fifth-order $\text{TPT}^{\text{new-ref}}$ are presently the only reliable theoretical approaches for the extremely short-ranged potentials popular in complex fluids.

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APPENDIX

Is Zhou's coupling parameter expansion actually equal to Zwanzig's high temperature series expansion (HTSE)?

According to the present terminology, the HTSE due to Zwanzig [4] is written as

$$F_{\text{ex Zwanzig}} = F_{\text{ex ref}} + \sum_{n=1}^{\propto} \frac{\omega_n}{n!}(-\beta)^{n-1}. \tag{A1}$$

Here the subscript "Zwanzig" of F_{ex} stands for the result due to Zwanzig, $F_{\text{ex}}=Nf_{\text{ex}}$ and $F_{\text{ex ref}}=Nf_{\text{ex ref}}$ are the whole excess Helmholtz free energy of the actual system and the reference system, and N is the number of particles in volume V occupied by the system under consideration. As implied in the text, both the actual and reference systems have the same number of particles but different interparticle potentials. The general formula for ω_n is derived [4] as follows:

$$\omega_j = j! \sum_{\substack{n_s \\ \Sigma s n_s = j}} (-1)^{\Sigma n_s - 1}\left(\sum n_s - 1\right)! \prod_{s=1}^{\propto} \frac{1}{n_s!}\left(\frac{\langle \alpha^s \rangle_0}{s!}\right)^{n_s}. \tag{A2}$$

The first four cases are, respectively,

$$\omega_1 = \langle \alpha \rangle_0,$$

$$\omega_2 = \langle \alpha^2 \rangle_0 - \langle \alpha \rangle_0^2,$$

$$\omega_3 = \langle \alpha^3 \rangle_0 - 3\langle \alpha^2 \rangle_0 \langle \alpha \rangle_0 + 2\langle \alpha \rangle_0^3,$$

$$\omega_4 = \langle \alpha^4 \rangle_0 - 4\langle \alpha^3 \rangle_0 \langle \alpha \rangle_0 - 3\langle \alpha^2 \rangle_0^2 + 12\langle \alpha^2 \rangle_0 \langle \alpha \rangle_0^2 - 6\langle \alpha \rangle_0^4. \tag{A3}$$

Here $\alpha=\Sigma_{i<j}u_{\text{per}}(r_{ij})$, $\langle \cdots \rangle_0$ stands for the average of the physical quantity $\cdots$ performed over the unperturbed ensemble.

It is easily shown [4] that ω_1 can be expressed as

$$\omega_1 = 2N\pi\rho \int r^2 u_{\text{per}}(r) g_{\text{ref}}(r) dr. \tag{A4}$$

Here $g_{\text{ref}}(r)$ is the RDF of the reference fluid.

The present coupling parameter expansion denoted by Eq. (1) can be reformulated to have a form similar to the HTSE as follows:

$$F_{\text{ex Zhou}} = F_{\text{ex ref}} + \sum_{n=1}^{\propto} \frac{\gamma_n}{n!}(-\beta)^{n-1}, \tag{A5a}$$

$$\gamma_n = \frac{1}{(-\beta)^{n-1}} 2N\pi\rho \int dr\, r^2 u_{\text{per}}(r)\, g_{\text{imag}}^{(n-1)}(r,\xi,\rho,T)\big|_{\xi=0}. \tag{A5b}$$

Corrspondingly, the subscript "Zhou" of F_{ex} stands for the result due to Zhou [6,7]. So far all of the above derivation and the corresponding Eqs. (A1)–(A5) are exact; no approximation has been introduced. Furthermore, one only has to know whether the present γ_n is exactly equal to Zwanzig's ω_n in order to judge whether the two sets of expansions are actually equal.

To help to disclose the distinction between the coupling parameter expansion and the HTSE, one may as well consider the situation of the hard sphere reference potential. Obviously the two kinds of expansion have identical zeroth terms. Next, let us first inspect γ_1 and ω_1. Equation (A5b) shows that $\gamma_1=2N\pi\rho\int dr\, r^2 u_{\text{per}}(r) g_{\text{imag}}(r,0,\rho,T)$. Considering that $u(r;0)=u_{\text{ref}}(r)$, therefore $g_{\text{imag}}(r,0,\rho,T)=g_{\text{ref}}(r)$. As a result, one concludes that $\gamma_1=\omega_1$. Second, we consider γ_n and ω_n with $n \geqslant 2$. Equation (A2) shows that ω_n with $n \geqslant 1$ is concerned only with the reference fluid ensemble average of α^s. Now the reference fluid is the hard sphere fluid, which is independent of temperature, and $\alpha=\Sigma_{i<j}u_{\text{per}}(r_{ij})$ is also independent of temperature. Hence one concludes that ω_n with $n \geqslant 1$ is also independent of the temperature. In fact, Eq. (A4) makes clear the temperature independence of ω_1. It is known that the famous MCA approximation [5] for ω_2 also shows temperature independence. On the contrary, one knows that $g_{\text{imag}}(r,\xi,\rho,T)$ with $\xi \neq 0$ depends on the temperature. As a result, $g_{\text{imag}}^{(n-1)}(r,\xi,\rho,T)|_{\xi=0}$ with $n \geqslant 2$ also depends on the temperature, which can easily be detected from the calculation proedure detailed in the text. In fact, the sample calculation displayed in Ref. [7] also discloses the temperature dependence. The temperature dependence of $g_{\text{imag}}^{(n-1)}(r,\xi,\rho,T)|_{\xi=0}$ with $n \geqslant 2$ is evidently nonlinear; hence the integral appearing in Eq. (A5b) is also nonlinear. As a result, the temperature dependence of the integral is not eliminated by simply being divided by a factor $(-\beta)^{n-1}$. To conclude, the inequality $\omega_n \neq \gamma_n$ with $n \geqslant 2$ is proven, and thus the present coupling parameter expansion is not equivalent to the HTSE.

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