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Phase diagram of the hard-core Yukawa fluid within the integral equation method

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In this study, the integral equation method proposed recently by Sarkisov [J. Chem. Phys. **114**, 9496 (2001).], which has proved accurate for continuous potentials, is extended successfully to the hard sphere potential plus an attractive Yukawa tail. By comparing the results of thermodynamic properties, including the liquid-vapor phase diagram, with available simulation data, it is found that this method remains reliable for this class of models of interaction often used in colloid science.

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The hard-core Yukawa (HCY) potential type

$$u(r) = \begin{cases} \infty, & r < \sigma, \\ \varepsilon\sigma \exp[-\lambda(r-\sigma)]/r, & r \geqslant \sigma, \end{cases} \tag{1}$$

has often been used to model effective interactions between pairs of particles of size σ separated by a distance r in simple as well as complex fluids. Depending on the sign of the strength ε and the decay of the tail through parameter λ, a vast amount of physical systems can be described, which are as different as charged-stabilized colloids, colloid/polymer mixtures, dense plasma, ionic fluids [1], fullerenes [2,3], and protein liquids [3]. When ε is negative, the tail of HCY potential is attractive and fundamental issues such as phase transitions, namely, solid-fluid and fluid-fluid transitions, in colloid science can be investigated.

The prediction of microscopic and macroscopic properties as well as the phase diagrams of the attractive HCY fluids have been reported in the literature either by Monte Carlo (MC) or molecular dynamics (MD) simulation tools [4–12]. Theoretical approaches have also been performed in the framework of the statistical physics of fluids, such as the density functional theory [13] and the integral equations (IE) method. The latter, consisting in solving the Ornstein-Zernike (OZ) equation together with an approximate closure relation, is a powerful means for this purpose [14]. As a matter of fact, recently, semianalytical methods such as self-consistent OZ approximation (SCOZA) [9], generalized mean spherical approximation (GMSA) [15], modified hypernetted chain (MHNC), and hybrid mean spherical approximation (HMSA) [16] have been used for the description of structure and thermodynamics of the HCY model with various ranges of attraction.

A reliable integral equation has been proposed recently by Sarkisov [17], which reaches a good degree of thermodynamic consistency for a wide class of Lennard-Jones type potentials [18], even in the vicinity of the critical point [19]. One advantage of this IE over the above mentioned ones is that there is no adjustable parameter to be optimized in the approximate closure relation. The aim of this work is to present an extension of Sarkisov's approach to the case of potentials such as those given by Eq. (1) comprising a hard-core. By applying it to the case of attractive HCY with $\lambda = 1.8$, we show that a correct description of thermodynamic properties and the liquid-vapor phase diagram can be obtained. Our results are compared to studies that have been published using either simulation or theoretical approaches.

According to the OZ equation, for a fluid with number density ρ, the total correlation function between two particles $h(r)$ is the sum of the direct correlation function $c(r)$ and the indirect correlation function $\gamma(r)$ such as

$$h(r) = c(r) + \rho \int h(r')c(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}' = c(r) + \gamma(r). \tag{2}$$

In the integral equation method, Eq. (2) is solved together with a closure relation

$$g(r) = \exp[-\beta u(r) + \gamma(r) + B(r)], \tag{3}$$

where $\beta = 1/k_B T$ is the inverse temperature T (k_B being Boltzmann's constant) and $g(r)$ [$=h(r)+1$] is the pair-correlation function. Equation (3) depends on the so-called bridge function $B(r)$, which represents an infinite sum of elementary bridge diagrams [20]. A careful analysis by Martinov *et al.* [21] has shown that the bridge function is not a functional of the indirect correlation function solely, but it also depends on the interaction potential, via $\gamma^*(r) = \gamma(r) - \beta\rho\sigma^3 u_2(r)$, where $u_2(r)$ is the attractive part of the pair potential according to the Weeks, Chandler, and Andersen (WCA) splitting [22]. Following Sarkisov's scheme [17] as applied to the Lennard-Jones potential, $B(r)$ is written as

$$B(r) = [1 + 2\gamma^*(r)]^{1/2} - 1 - \gamma^*(r). \tag{4}$$

When a potential containing a hard sphere part such as Eq. (1) is considered, the solutions of integral equations given by Eqs. (2) and (3) inside the core region are those of the Percus-Yevick [23] approximation whatever the bridge function used. In this case, Llano-Restrepo and Chapman [24] have shown from simulation results of the bridge function that $B(r)$ is a functional of $\gamma(r)+f(r)$, with a good degree of accuracy, where $f(r) = \exp[-\beta u(r)] - 1$ is the Mayer function. Later, Lee [25] has shown for the pure HS potential, using a Verlet-modified-type bridge function, that an efficient renormalization is $\gamma(r) + \rho\sigma^3 f(r)/2$. We extend here these ideas to

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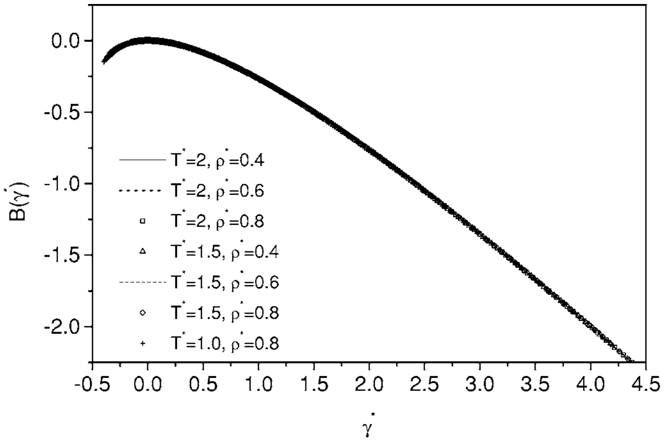

FIG. 1. Bridge function for the attractive HCY potential as a function of the renormalized indirect correlation function $\gamma^* = \gamma(r) + \rho\sigma^3 f(r)/2$ considered in this work for several temperatures and densities.

potentials given by Eq. (1), having a hard-core as well as an attractive tail, by taking

$$\gamma^*(r) = \begin{cases} \gamma(r) + \rho\sigma^3 f(\sigma)/2, & r < \sigma, \\ \gamma(r) + \rho\sigma^3 f(r)/2, & r \geqslant \sigma. \end{cases} \tag{5}$$

As pointed out by Duh and Haymet [26], the choice of the renormalization has to be guided by the unique functionality with respect to $\gamma^*(r)$. In Fig. 1, we have drawn $B[\gamma^*(r)]$ for the different thermodynamic states investigated here (see Tables I and II) using Eq. (5). It is clearly seen that the unique functionality is achieved for the scheme proposed here.

TABLE I. Compressibility factor, $Z = \beta P/\rho$ of the attractive HCY fluid with $\lambda = 1.8$. "Sar. new" and "Sar." correspond to the results obtained with Sarkisov's bridge function, respectively, using the renormalization procedure given by Eq. (5) and the standard one. The SCOZA results of Pini *et al.* [9] are included, as well as the MC and MD simulation data of Henderson *et al.* [4] and Rey *et al.* [6] for comparison. According to these authors, the uncertainty in the MD and MC data is 0.05.

k_BT/ε	$\rho\sigma^3$	MC/MD	Sar. new	Sar.	SCOZA
∞	0.4	2.52[a]	2.500	2.502	2.518
	0.6	4.22[a]	4.222	4.226	4.283
	0.8	7.65[a]	7.568	7.549	7.750
2	0.4	1.12[b]	1.121	1.098	1.120
	0.6	2.00[b]	1.965	1.899	1.977
	0.8	4.46[b]	4.310	4.191	4.433
1.5	0.4	0.67[b]	0.664	0.637	0.667
	0.5	0.81[b]	0.824	0.777	
	0.6	1.22[b]	1.203	1.133	1.22
	0.8	3.37[b]	3.178	3.066	3.333
1	0.6	−0.24[b]	−0.343	−0.379	
	0.7	0.19[b]	−0.014	−0.037	
	0.8	1.17[b]	0.804	0.825	

[a] Reference [4].
[b] Reference [6].

TABLE II. Inverse isothermal compressibility of the attractive HCY fluid with $\lambda = 1.8$. "Sar. new" and "Sar." correspond to the results of Sarkisov's bridge function, respectively, using the renormalization procedure given by Eq. (5) and the standard one. The SCOZA results and MC data of Pini *et al.* [9] are included for comparison. Numbers in parentheses give the error in the last figure.

k_BT/ε	$\rho\sigma^3$	MC	Sar. new	Sar.	SCOZA
∞	0.4	0.1958(2)	0.1998	0.1997	0.19744
	0.6	0.0848(5)	0.0891	0.0891	0.08721
2	0.4	0.4992(8)	0.5029	0.5255	0.50439
	0.6	0.1594(5)	0.1632	0.1693	0.15976
1.5	0.4	0.968(3)	1.0092	1.1173	1.01500
	0.6	0.2217(5)	0.2299	0.2341	0.22147

We apply this IE scheme to the attractive HCY with $\lambda = 1.8$. In order to emphasize the improvements that can be obtained by using Eq. (5) in the bridge function (4) of HCY fluids instead of Sarkisov's original scheme, the calculation of thermodynamic properties and the liquid-vapor phase diagram have been done in both cases. Using the algorithm of Labik *et al.* [27], we determine numerically the pair-correlation function and its thermodynamic derivatives from which the thermodynamic quantities of interest can be calculated easily. The derivatives of $g(r)$ have been performed in an exact manner using the tangent linear method [28] that we have developed within the IE theory [29]. The correlation functions are calculated with a numerical error less than 1%. From a technical point of view, the correlation functions are sampled on a grid of 8192 points with a mesh of 0.005σ, which implies a spatial extension $R_{\max} = 40.96\sigma$, sufficient for an accurate numerical integration and fast Fourier transform.

The compressibility factor Z is determined from the virial equation of state such as

$$Z = \frac{\beta P}{\rho} = 1 + \frac{2\pi}{3}\rho\sigma^3 g(\sigma^+) - \frac{2\pi\rho\beta}{3}\int_\sigma^{R_{\max}} r\frac{du(r)}{dr} g(r) r^2 dr, \tag{6}$$

where P is the pressure. From the latter, the inverse isothermal compressibility is derived:

$$\frac{\beta}{\rho\chi_T} = \beta\left(\frac{\partial P}{\partial \rho}\right)_T = 1 + \frac{4\pi}{3}\rho\sigma^3\left(g(\sigma^+) + \frac{\rho\sigma^3}{2}\frac{\partial g(\sigma^+)}{\partial\rho}\right) - \frac{4\pi\rho^2}{3}\int_\sigma^{R_{\max}} r\frac{du(r)}{dr}\left\{g(r) + \frac{\rho}{2}\frac{\partial g(r)}{\partial \rho}\right\} r^2 dr. \tag{7}$$

Finally, the excess chemical potential is calculated using the form proposed by Kyseliov and Martynov [30]

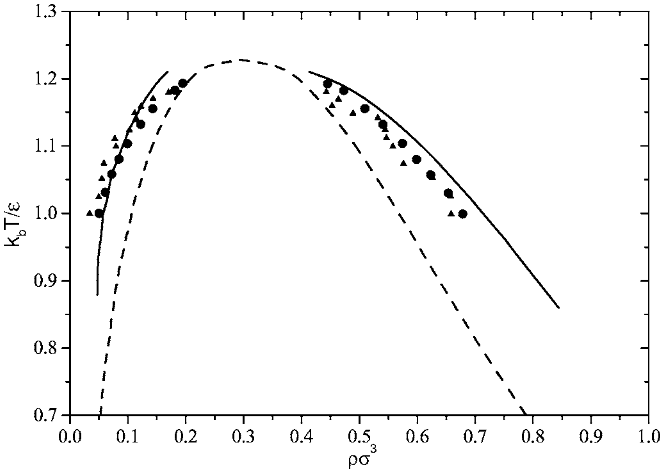

FIG. 2. Liquid-vapor phase diagram of the attractive HCY potential as obtained with Sarkisov's bridge function using the renormalization procedure given by Eq. (5). Solid and dashed lines correspond to the binodal and spinodal, respectively. The triangles and circles are the simulation data of Smit and Frenkel [5] and Pini *et al.* [9], respectively.

$$\beta\mu^{\mathrm{ex}} = 4\pi\rho\int_0^{R_{\max}}\left[\gamma(r)+B(r)-h(r)+\frac{1}{2}h(r)\left\{\gamma(r)+\frac{4}{3}B(r)\right\}\right]r^2dr. \qquad (8)$$

A mapping of the thermodynamic space in the (T,ρ) plane has been performed using an adaptative technique as described in Ref. [18]. To this end, a two-dimensional grid with an initial temperature step $\Delta T=0.01k_B/\varepsilon$ and a density step $\Delta\rho=0.01\sigma^{-3}$ has been used. We have also considered separately from the mapping the case when β tends to zero, i.e., T tends to infinity, such that the HS potential is recovered.

In Table I, we have gathered the results for the compressibility factor Z given by Eq. (6) for several isotherms and also for the HS limiting case. These are compared to MD data [6] for finite temperatures and to the MC ones of Henderson *et al.* [4] for $T\to\infty$. The very accurate results obtained by Pini *et al.* [9] with SCOZA are also reported for comparison. The results obtained from the extended Sarkisov's IE method proposed in this work are in very good agreement with simulation data, and are improved over those from Sarkisov's original scheme. The fact that the thermodynamic quantities are well described over a wide range of states gives a physical justification of the present renormalization scheme, which meets the unique functionality. Finally, it is seen that an accuracy comparable to SCOZA is generally achieved. These observations also hold for the isothermal compressibility given in Table II.

In Fig. 2, the liquid-vapor coexistence curves are drawn for the extended IE method. For each isotherm of the mapping, the densities of the coexisting liquid and vapor have been obtained by requiring the equality of the pressures [Eq. (6)] as well as of the chemical potentials $\mu(=\mu^{\mathrm{ex}}+k_{\mathrm{B}}T\ln\rho)$ [Eq. (8)] in both phases. These IE results of the binodal line are compared to the MC data of Pini *et al.* [9], and also to those of Smit and Frenkel [5]. It is seen that the IE method of this work is reliable, though the densities of the vapor branch are slightly overestimated in the vicinity of the critical isotherm, while those of the liquid branch are overestimated at lower temperatures. Let us now infer the critical point from the position of the maximum of the spinodal line shown in Fig. 2. The spinodal line is constructed from the points where the isothermal compressibility [Eq. (7)] vanishes (see Ref. [18] for a more detailed description). We have found $T_c=1.228\pm0.002$ and $\rho_c^*=0.295\pm0.005$, which are close to the simulation results of Smit and Frenkel [5], Lomba and Almarza [7], and Pini *et al.* [9] who have found ($T_c^*=1.192$, $\rho_c^*=0.294$), ($T_c^*=1.178$, $\rho_c^*=0.313$), and ($T_c^*=1.212$, $\rho_c^*=0.312$), respectively. The approach presented here is comparable in accuracy with the SCOZA and are slightly better than the results of the MHNC and HMSA integral equations [16] for which ($T_c^*=1.21$, $\rho_c^*=0.28$) and ($T_c^*=1.25$, $\rho_c^*=0.36$) are found, respectively. Using the standard scheme of Sarkisov, the results are not as good as with the method proposed here. For the critical point, we have found $T_c^*=1.252$ and $\rho_c^*=0.31$.

In summary, we have performed calculations of the thermodynamic properties for the hard-core Yukawa potential in the framework of the integral equation theory, using the bridge function of Sarkisov [17]. By improving the renormalization procedure of the indirect correlation function initially developed for continuous potentials, we have shown that accurate results are obtained for a wide range of thermodynamic states in the case of potentials comprised of a hard-core. Compared to Monte Carlo and molecular dynamics simulations data, the liquid-vapor coexistence curves are correctly described including the location of the critical point. A wide class of complex fluids can now be tackled within the integral equation scheme considered in this work, for instance, using the HCY with different values of λ (for the purpose of studying the end critical point [8]), hard-core double Yukawa and square-well potentials. All these potentials containing a hard-core are often used for the description of the interactions in real colloidal systems [31–33]. Since the hard-core seems to be satisfactorily considered, the influence of the range of the interactions can now be investigated. Works along these lines are under progress.

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