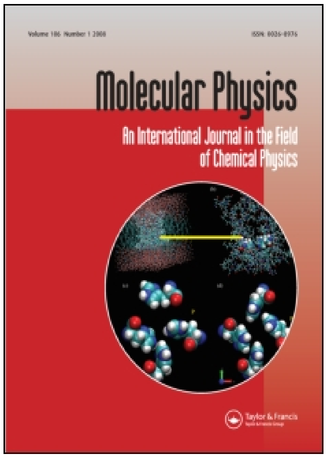

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RESEARCH ARTICLE

The effect of steepness of soft-core square-well potential model on some fluid properties

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The effect of repulsive steepness of the soft-core square well (SCSW) potential model on the second virial coefficient, critical behaviour (two- phase region and the position of critical point), and coordination number are investigated. The soft-core thermodynamic perturbation theory (TPT) presented by Weeks-Chandler-Anderson (WCA) recently developed by Ben-Amotz and Stell (BAS) has been used for the reference system, and the Barker-Henderson TPT for the perturbed system. The Barker-Henderson macroscopic compressibility approximation has been used for all order perturbation terms in which the second-order one is improved by assuming that the molecules in every two neighbouring shells are correlated upon the original assumption. By using the hard-sphere isothermal compressibility consistency for the radial distribution function (RDF), an analytical closed expression has been derived for the Helmholtz free energy function contained effective hard-sphere diameter. The accuracy of the model has been examined for the hard-core system, and an appropriate range found for the attractive width of the potential well (R), then the effect of steepness parameter on the critical quantities, coordination number, and the inversion temperature of the second virial coefficient, has been investigated qualitatively. The predicted results are in good agreement with the computer simulation data for the critical constants, and coordination number at the limit of the hard-core square-well potential model at least qualitatively, and for the attractive range $1.55 \leq R \leq 1.7$, quantitatively. It was found that the steepness of the potential model has a marginal effect on the critical behaviour, and also every thermodynamic quantity at low and medium temperatures for which the molecular penetration is negligible, but since the penetration at high temperatures is significant, the role of the steepness of potential on the inversion temperature of the second virial coefficient and coordination number is highlighted.

Keywords: equation of state; thermodynamic perturbation theory; soft-core square well potential model; steepness of potential model

1. Introduction

For a long time, the square-well (SW) potential model has been the subject of extensive investigations using deferent statistical mechanical methods, either as simulation techniques [1,2] or as a theoretical approach, since the SW fluid represents a good and simple model that includes the attractive and repulsive interactions which is able to reproduce the behaviour of simple fluids, and also it is applicable for the complex fluids such as mixtures, chain molecules, associating fluids, and polar fluids. Moreover, different values of the interaction range cover a large variety of various system models from sticky or adhesive range through medium to long range hard-sphere which it may be regarded as a new parameter for the non-conformal changes affect on fluids [3].

Among the theoretical aspects, perturbation theories have been a decisive step in calculating and understanding the thermodynamic properties of fluids. Some versions of the perturbation theories such as, the Barker–Henderson second-order and higher-order expansion [4,5] for hard-sphere, the Chang and Sandler perturbation theory [6,7] for hard-sphere-chains, and the perturbed hard chain sphere equation of state presented by Hino and Prausnitz [8] are often used for systems containing spheres.

In this work, by noting the fact that with choosing a suitable criterion for effective hard-sphere, one may use the step function approximation for the reference system, we have used the Barker–Henderson macroscopic compressibility approximation for the second-order and higher-order perturbation terms in which the second-order one is improved by assuming that the number of molecules in every two neighbouring shells are correlated upon the original assumption [9,10]. We have derived a simple close analytical expression for

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the soft-core square well (SCSW) potential model in which directly using a hard-sphere (HS) reference system rather than indirectly via a soft-repulsive reference system as used by Ben-Amotz and Stell (BAS) perturbation theory [11].

We have used the SCSW potential model:

$$U(r) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{n} - \left(\frac{\sigma}{r}\right)^{(n/2)}\right] & r \le r_m \\ -\varepsilon & r_m < r \le R\sigma \\ 0 & r > R\sigma \end{cases} \tag{1}$$

where $r_{\mathrm{m}} = 2^{2/n}\sigma$, ε is the well depth (minimum potential function), σ is intermolecular separation in which potential function is zero, R is the reduced well width, and n is the steepness of repulsive wall (which is reciprocal of softness, $1/n$). In the following section, we show succinctly that how one can approximately use the effective HS diameter for the repulsive part of the potential model as a reference system, like BAS perturbation theory.

2. Theory

In the Barker and Henderson approach the excess Helmholtz free energy can be expressed as,

$$\frac{\beta F^{ex}}{N} = \frac{\beta F_0^{ex}}{N} + \frac{\beta F_1}{N} + \frac{\beta F_2}{N} + \cdots \tag{2}$$

where F_0^{ex} is the excess free energy of the hard-sphere reference fluid; F_1, $F_2, \ldots$ are the first-order, second-order, and higher-order perturbation terms, respectively, and $\beta = 1/kT$ where k is Boltzmann constant.

2.1. *Reference system potential for SCSW model*

The starting point of many soft-core thermodynamic perturbation theories as WCA theory [12–14] is to decompose the potential model into the sum of repulsive, $U_0(r)$, and preturbative, $U_1(r)$, terms as,

$$U_0(r) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{n} - \left(\frac{\sigma}{r}\right)^{n/2}\right] + \varepsilon & r < r_m \\ 0 & r \ge r_m \end{cases} \tag{3a}$$

$$U_1(r) = \begin{cases} -\varepsilon & r < R\sigma \\ 0 & r \ge R\sigma. \end{cases} \tag{3b}$$

The other key point of WCA theory pertains to the method used to relate the thermodynamic properties of a soft-repulsive reference fluid to that of a hard-sphere fluid with an effective hard sphere diameter depends on both temperature and density, known as iso-compressibility criterion. Owing to the fact that density dependency of the effective hard sphere diameter has very insignificant effect, we try to use a criterion which depends only on temperature, and give an analytical expression for σ_{HS}. For these reasons, we use the Boltzmann factor criterion (BFC) [15], according to which σ_{HS} takes the value of r in such a way that

$$\beta u_0(r = \sigma_{\mathrm{HS}}) = \zeta \tag{4}$$

where ζ is a parameter which may varies from 0.5 to 1.5. By substituting Equation (3a) as the reference system in Equation (4), one may solve it to obtain the effective hard-sphere diameter, $\sigma_{\mathrm{HS}}(T)$

$$\sigma_{\mathrm{HS}}(T) = \sigma\left[\frac{2}{1+\sqrt{\zeta/\beta\varepsilon}}\right]^{2/n} = \sigma \times [\gamma(T)]. \tag{5}$$

It has been shown that σ_{HS} from BFC criterion with $\zeta = 1$ by step function approximation equals to the BH criterion [16], and also regarding the fact that collision of two particles occurs in a plane, we choose $\zeta = 1$. Note that the BFC criterion has extensively been used by Ben–Amotz–Stell as BAS perturbation theory [11]. By supposing the step function of reference system the SCSW model, Equation (1), is rewritten as

$$U(r) = \begin{cases} \infty & r \le \sigma_{\mathrm{HS}} \\ -\varepsilon & \sigma_{\mathrm{HS}} < r \le R\sigma \\ 0 & r > R\sigma \end{cases} \tag{6a}$$

and thereby the decomposed reference and perturbative terms according to Equation (14) like Equations (3a) and (3b), are

$$U_0(r) = \begin{cases} \infty & r \le \sigma_{\mathrm{HS}} \\ 0 & r > \sigma_{\mathrm{HS}} \end{cases} \tag{6b}$$

$$U_1(r) = \begin{cases} 0 & r \le \sigma_{\mathrm{HS}} \\ -\varepsilon & \sigma_{\mathrm{HS}} < r \le R\sigma \\ 0 & r > R\sigma. \end{cases} \tag{6c}$$

One may conclude from the above discussion that we can use every HS expression for F_0^{ex} with effective hard sphere diameter as a reference system.

2.2. *Perturbation term*

In Equation (2),

$$\frac{\beta F_1}{N} = 2\pi\rho\beta\int_0^{\infty} g_0(r)u_1(r)r^2\mathrm{d}r$$

$$\frac{\beta F_2}{N} = -\pi\rho\beta^2\left(1+2K\eta^2\right)\int_0^{\infty} u_1^2(r)kT\left(\frac{\partial\rho}{\partial p}\right)_0 g_0(r)r^2\mathrm{d}r \tag{7}$$

where $\eta = (\pi/6)\rho\sigma_{\mathrm{HS}}^3$ is the packing fraction. By assuming that the number of molecules in every two neighbour shells is correlated, Zhang [9] added factor $(1+2K\eta^2)$ to Barker–Henderson's second-order macroscopic compressibility expression in which $K \approx 1/\eta_{\mathrm{con}}^2$, $\eta_{\mathrm{con}} = 0.493$. For the higher-order perturbation terms other approximation given by Barkar and Henderson [5]

$$F_i = \frac{F_1(2F_2/F_1)^{i-1}}{i!}. \tag{8}$$

Substituting Equation (7) into Equation (8), leads to

$$\frac{\beta F^{ex}}{N} = \beta F^{ex}_{\mathrm{HS}}/N - \left(\frac{12\eta\alpha}{\gamma^3(T^*)}\right) \left[\frac{\beta\varepsilon}{\alpha} + \frac{1}{2!}\left(\frac{\beta\varepsilon}{\alpha}\right)^2 + \frac{1}{3!}\left(\frac{\beta\varepsilon}{\alpha}\right)^3 + \cdots\right] \int_{\gamma(T^*)}^{R} g_0(x)x^2\mathrm{d}x \tag{9a}$$

or

$$\frac{\beta F^{ex}}{N} = \beta F^{ex}_{\mathrm{HS}}/N - \left(\frac{12\eta\alpha}{\gamma^3(T^*)}\right) \left[\exp\left(\frac{\beta\varepsilon}{\alpha}\right) - 1\right] \int_{\gamma(T^*)}^{R} g_0(x)x^2\mathrm{d}x \tag{9b}$$

$\gamma(T^*)$ was introduced in Equation (5), and $\alpha^{-1} = (1 + 2K\eta^2)(k_T^{\mathrm{red}})_0$. Since the reference system is the effective hard sphere system in Equation (6b), the subscript 0 may be changed to HS.

By using Equation (9b), we are ready to obtain an analytical form of EOS using the effective HS Carnahan Starling [17,18] expression for reference system:

$$\frac{\beta F^{ex}_{\mathrm{HS}}}{N} = \frac{4\eta - 3\eta^2}{(1-\eta)^2} \tag{9c}$$

and reduced isothermal compressibility with the HS Carnahan Starling expression

$$\left(k_T^{\mathrm{red}}\right)_{\mathrm{HS}} = \left(\frac{\partial}{\partial\rho}(Z_{\mathrm{HS}}\rho)\right)_{\beta}^{-1} = \frac{(1-\eta)^4}{1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4} \tag{9d}$$

and, $g_0(r)$ is simply given by [19]

$$g_0(r) = \begin{cases} 0 & r < \sigma_{\mathrm{HS}} \\ g_{\mathrm{HS}}(r) & \sigma_{\mathrm{HS}} \le r \le R\sigma \\ 1 & r > R\sigma. \end{cases} \tag{10}$$

In Equation (10), we have considered a general form for the radial distribution function of the reference system and there is no need to state the complicated mathematical expression for it. In fact we have used the radial distribution function expression, which generates a consistency for the hard sphere isothermal compressibility with the approximation $g_0(r) = 1$ for $r > R\sigma$. Owing to the fact that the reference potential is very short range, we required the following approximation [19]:

$$24\eta \int_{R}^{\infty} [g_0(x) - 1]x^2\mathrm{d}x = 0 \tag{11}$$

where x is the intermolecular separation in units of the hard-core diameter σ. By using the isothermal compressibility equation

$$\left(k_T^{\mathrm{red}}\right)_{\mathrm{HS}} = kT\left(\frac{\partial\rho}{\partial p}\right)_{\mathrm{HS}} = 1 + \rho \int_0^{\infty} [g_0(r) - 1]4\pi r^2\mathrm{d}r \tag{12}$$

we obtain the following result:

$$\left(k_T^{\mathrm{red}}\right)_{\mathrm{HS}} = 1 + \left(\frac{24\eta}{\gamma(T^*)^3}\right)\left\{\int_0^{\gamma(T^*)} [g_0(x) - 1]x^2dx + \int_{\gamma(T^*)}^{R} [g_0(x) - 1]x^2\mathrm{d}x + \int_{R}^{\infty} [g_0(x) - 1]x^2\mathrm{d}x\right\}. \tag{13a}$$

Using Equation (10),

$$\left(k_T^{\mathrm{red}}\right)_{\mathrm{HS}} = 1 + \left(\frac{24\eta}{\gamma(T^*)^3}\right)\int_{\gamma(T^*)}^{R} g_{\mathrm{HS}}(x)x^2\mathrm{d}x - \frac{8R^3\eta}{\gamma(T^*)^3} \tag{13b}$$

$$\left(\frac{24\eta}{\gamma(T^*)^3}\right)\int_{\gamma(T^*)}^{R} g_{\mathrm{HS}}(x)x^2\mathrm{d}x = \left(\left(k_T^{\mathrm{red}}\right)_{\mathrm{HS}} - 1 + \frac{8R^3\eta}{\gamma(T^*)^3}\right) \tag{13c}$$

where the left side of the Equation (13c) may be regarded as the coordination number of the hard-sphere system, $N_{\mathrm{C}}^{\mathrm{HS}}$. By substitution of Equation (13c) into Equation (9b), the final closed form Helmholtz free energy expression is

$$\frac{\beta F^{ex}}{N} = \beta F^{ex}_{\mathrm{HS}}/N - \left(\frac{\alpha}{2}\right)N_{\mathrm{C}}^{\mathrm{HS}}\left[\exp\left(\frac{\beta\varepsilon}{\alpha}\right) - 1\right] \tag{14a}$$

or, equivalently,

$$\frac{\beta F^{ex}}{N} = \beta F^{ex}_{\mathrm{HS}}/N - \left(\frac{\alpha}{2}\right)\left[\exp\left(\frac{\beta\varepsilon}{\alpha}\right) - 1\right] \left(\left(k_T^{\mathrm{red}}\right)_{\mathrm{HS}} - 1 + 8R^3\eta/\gamma(T^*)^3\right). \tag{14b}$$

Equation (14a) is a good approximation of the Helmholtz free energy for a SCSW potential and it has the advantage of being analytical.

Owing to the fact that, when steepness approaches to infinity in accordance with Equation (5) $\gamma(T^*) \rightarrow 1$, and thereby the soft-core potential model used in this work, approaches to common hard-core potential model, and noting the fact that there is much Monte Carlo SW simulation data, first of all we

Table 1. Critical parameters for different values of R obtained from Monte Carlo (MC), molecular dynamics (MD), this work, second-order perturbation theory (PT), and self-consistence Ornstein–Zernike approximation (SCOZA).

R		$T^*_C = kT_C/\varepsilon$	$P_C\sigma^3/\varepsilon$	$\rho_C\sigma^3$	Z_C
1.25	MC	0.764 ± 0.004	0.081 ± 0.015	0.370 ± 0.023	0.29 ± 0.07
	MD	0.78			
	PT	0.913	0.133	0.34	0.43
	This work	0.656	0.058	0.259	0.339
	SCOZA	0.761	0.073	0.343	0.280
1.375	MC	0.974 ± 0.01	0.105 ± 0.023	0.355 ± 0.045	0.30 ± 0.11
	MD	1.01			
	PT	1.11	0.148	0.34	0.39
	This work	0.897	0.079	0.257	0.341
	SCOZA	0.978	0.079	0.291	0.278
1.5	MC	1.219 ± 0.008	0.108 ± 0.016	0.299 ± 0.023	0.30 ± 0.07
	MD	1.27			
	PT	1.35	0.153	0.31	0.36
	This work	1.188	0.104	0.255	0.344
	SCOZA	1.21	0.092	0.272	0.280
1.75	MC	1.811 ± 0.013	0.179 ± 0.02	0.284 ± 0.009	0.35 ± 0.05
	MD	1.79			
	PT	2.04	0.196	0.25	0.38
	This work	1.934	0.170	0.253	0.349
	SCOZA	1.809	0.128	0.249	0.284
2	MC	2.765 ± 0.023	0.197 ± 0.026	0.225 ± 0.018	0.32 ± 0.07
	PT	2.88	0.255	0.24	0.37
	This work	2.93	0.259	0.251	0.352
	SCOZA	2.699	0.201	0.252	0.296

PT: [21], MC: [2], MD: [22], SCOZA: [23].

examine the accuracy of the model for the hard core system, when $n \to \infty$, and obtain appropriate values for the attractive range (R). We then (qualitatively) investigate the effect of the steepness parameter on the critical quantities, coordination number, and the inversion temperature of the second virial coefficient.

3. Accuracy of the new potential model in predicting hard-core sw fluid properties

One way to test the theoretical approach used in this work is to analyse the compressibility factor, vapour–liquid phase diagram, internal energy, and also critical constants predicted by our framework and compare them with available simulation data [2,20–22] and other theoretical approaches [23]. In this analysis we have considered intermediate values of attraction range, $1.25 \le R \le 2$ for which a large number of data are reported in literature both by simulation and theory.

3.1. *Critical point and coexistence curve*

The values of critical constants estimated from simulation are summarized in Table 1, and a comparison is made with the corresponding results obtained from some theoretical approaches such as the second-order thermodynamic perturbation theory (PT) [21], self-consistent Ornstein–Zernike approximation (SCOZA) [23] based on a generalized mean-spherical approximation (MSA), and this work. As may be seen from Table 1, our model like two other theoretical ones predicts very well the behaviour of $T^*_C(R)$, $P^*_C(R)$ and $\rho^*_C(R)$. When the attractive range of the potential model increases, the critical temperature and pressure rise. The SCOZA is the best theoretical model for predicting the critical temperatures of the SW potential model which it may be used to propose an analytical expression for the reduced critical temperature and pressure [23]. All versions of perturbation theories overestimate the critical temperature and pressure for all values of R, whereas our approach underestimates for small values of R and overestimates for the large values of R, but it gives reasonable values within $1.55 \le R \le 1.7$. The qualitative behaviour of the reduced critical density as a function of R, for all three theoretical approaches is reasonable, although a clear dispersion of the simulation data predicted by several authors can been seen in literatures, which makes a comparison with the theories rather difficult.

3.2. Coordination number behaviour

The coordination number (CN) is defined as the average number of particles within the potential well which is a valuable quantity for SW model, since a thermodynamic equation of state (EOS) may be developed by using the CN [24], and also the generalized van der Waals theory [25] may be based on the CN theory. These groups of theories are generally simple, both conceptually and operationally. For the SCSW potential model, the CN may be written as

$$N_C = \left(\frac{24\eta}{\gamma^3(T^*)}\right)\int_{\gamma(T^*)}^{R} g^{\mathrm{SW}}(x)x^2\mathrm{d}x. \tag{15}$$

As may be seen, the CN depends on the molecular potential function via the pair distribution function. To determine the CN for the HSSW fluid, a number of theoretical models have been developed [26,27], from which [27]

$$N_C = \frac{\rho^*_{\max} N_C^{\mathrm{HS}} e^{1/T^*}}{\rho^*_{\max} + \rho^*(e^{1/T^*} - 1)} \tag{16}$$

where N_C^{HS} is the CN for hard-sphere fluids, $\rho^* = \rho\sigma_{\mathrm{HS}}^3$, and $\rho^*_{\max}$ is the maximum reduced density assumed to be unit by Heyes [26], but it yields correct low densities behaviour of the CN and departs markedly from simulation data at high densities. Largo and Soana [27] modified $\rho^*_{\max}$ as

$$\rho^*_{\max} = \rho^* + \frac{1}{R^3}\left(\sqrt{2} - \rho^*\right). \tag{17}$$

We may use Equation (13c) as the CN of hard-sphere system to obtain it for SW model. We obtained the value of CN of the hard-core SW for some values of well width, and temperatures, for which the results are listed in Table 2 and compared with simulation data [27]. As may be seen, like the critical points, the best results are obtained within $1.50 \le R \le 1.70$, which is suitable for real fluids. Such a suitable result obtained with our model is due to the criterion we used for taking into account the radial distribution function, Equations (10) and (13c), for which the criterion is correct only at the aforementioned potential well width.

3.3. Internal energy and compressibility factor

There are two alternative formulas, Equations (18) and (19), to calculate the internal energy, E, of soft-sphere and hard-core SW potential model:

$$\frac{E}{NkT} = \frac{E^{id}}{NkT} + \frac{E^{ex}}{NkT} = \frac{3}{2} + \beta\frac{\partial}{\partial\beta}\left(\frac{\beta F^{ex}}{N}\right) \tag{18}$$

$$E = E^{id} + E^{ex} = \frac{3}{2}NkT + 2\pi N\rho\int_0^\infty U(r)g(r)r^2\mathrm{d}r \tag{19}$$

where E^{id} and E^{ex} are the ideal and excess internal energy, respectively. For simplicity we use Equation (19), for which one may obtain

$$\frac{E^{ex}}{NkT} = -\frac{1}{2T^*}\left(\frac{24\eta}{\gamma^3(T^*)}\right)\int_{\gamma(T^*)}^{R} g^{\mathrm{SW}}(x)x^2\mathrm{d}x = -\frac{N_C}{2}\frac{1}{T^*}. \tag{20}$$

The value of excess energy for the hard-core SW model is calculated by using Equation (20), see Table 3, and compared with simulation data [20,21].

By using the derivative of Equation (14b), one may obtain other thermodynamic properties, such as the equation of state:

$$Z = \rho\left(\frac{\partial(\beta F/N)}{\partial\rho}\right)_\beta = \eta\left(\frac{\partial(\beta F/N)}{\partial\eta}\right)_\beta. \tag{21}$$

For the limit of hard-core SW potential, comparison of our calculated compressibility factor values with those computed from the equations reported by Lee and Chao (LC) [28], Lee and Sandler (LS) [29], Guo *et al.* (GWL) [30], Shen and Lu (SL) [31], and the MC data [20,21] is presented in Table 4. One may notice from Table 4 that the results obtained from this work are comparable with the simulation data and also other EOSs. However, this work has the advantage over the other EOSs that it does not use any complicated expression for the radial distribution function.

4. Dependencies of the critical point, liquid-vapor equilibrium, coordination number, and second virial coefficient on the steepness parameter (*n*)

The shape of the coexistence curve and the location of the critical point with variation of attractive range of the SW potential model are extensively investigated [3,23], and as we showed in the preceding section, our results are reasonable at least qualitatively in comparison with other theoretical approaches and simulation data. We tend to investigate how the coexistence curve, coordination number, and second virial coefficient can be influenced by the repulsive quantities such as steepness of SCSW potential model.

In Table 5, the effect of the steepness parameter on the critical parameters is listed. As may be seen, by reducing the *n*, the critical temperature increases. Such dependency is smoother than the dependency of critical parameters to the well width. Like the critical temperature, the critical density and pressure are almost not affected by the steepness parameter. In Figure 1, the coexistence curve for different values of *n* when $R = 1.60$ is shown. As may be seen, the effect of repulsion softness parameter on the

Table 2. Calculated coordination number N_C for the hard-core SW potential model compared with simulation data.

		$T^* = kT/\varepsilon$				
R	$\rho\sigma^3$	1.0	1.5	2.0	3.0	5.0
1.3	0.20	2.06 (2.47)	1.81 (1.89)	1.67 (1.68)	1.54 (1.50)	1.44 (1.38)
	0.30	2.94 (3.50)	2.67 (2.82)	2.53 (2.57)	2.38 (2.36)	2.25 (2.21)
	0.40	3.80 (4.48)	3.54 (3.78)	3.39 (3.53)	3.23 (3.30)	3.09 (3.14)
	0.50	4.64 (5.42)	4.39 (4.80)	4.25 (4.56)	4.09 (4.35)	3.95 (4.19)
	0.60	5.47 (6.41)	5.24 (5.92)	5.11 (5.71)	4.96 (5.51)	4.83 (5.37)
	0.70	6.29 (7.55)	6.09 (7.15)	5.97 (6.97)	5.83 (6.79)	5.71 (6.65)
	0.80	7.11 (8.84)	6.93 (8.49)	6.82 (8.33)	6.70 (8.16)	6.59 (8.03)
1.5	0.20		3.30 (3.4)	3.04 (3.04)	2.77 (2.73)	2.57 (2.53)
	0.30		4.75 (4.89)	4.45 (4.45)	4.15 (4.12)	3.91 (3.91)
	0.40		6.13 (6.22)	5.84 (5.85)	5.52 (5.56)	5.26 (5.37)
	0.50		7.49 (7.59)	7.20 (7.32)	6.89 (7.08)	6.62 (6.90)
	0.60		8.80 (9.06)	8.53 (8.85)	8.24 (8.64)	7.98 (8.47)
	0.70		10.09 (10.56)	9.85 (10.36)	9.58 (10.15)	9.35 (9.99)
	0.80		11.37 (11.89)	11.16 (11.71)	10.92 (11.53)	10.71 (11.38)
1.6	0.20		4.05 (4.50)	3.75 (3.84)	3.46 (3.45)	3.22 (3.20)
	0.30		5.78 (6.16)	5.46 (5.51)	5.13 (5.12)	4.86 (4.87)
	0.40		7.45 (7.57)	7.13 (7.13)	6.78 (6.81)	6.51 (6.59)
	0.50		9.07 (9.08)	8.76 (8.80)	8.45 (8.55)	8.17 (8.35)
	0.60		10.67 (10.71)	10.40 (10.49)	10.09 (10.27)	9.82 (10.08)
	0.70		12.27 (12.29)	12.01 (12.08)	11.73 (11.87)	11.48 (11.70)
	0.80		13.82 (13.67)	13.61 (13.47)	13.36 (13.28)	13.14 (13.11)
1.8	0.20			5.41 (5.98)	5.06 (5.13)	4.78 (4.76)
	0.30			7.82 (8.12)	7.44 (7.41)	7.13 (7.08)
	0.40			10.18 (10.08)	9.81 (9.67)	9.49 (9.40)
	0.50			12.52 (12.22)	12.17 (11.92)	11.86 (11.69)
	0.60			14.85 (14.38)	14.52 (14.10)	14.23 (13.87)
	0.70			17.16 (16.44)	16.87 (16.14)	16.61 (15.90)
	0.80			19.47 (18.38)	19.21 (18.06)	18.98 (17.80)

Simulation data [27] given in parentheses.

Table 3. Calculated excess internal energy, E^{ex}/NkT, compared with those of Monte Carlo simulation data, for given values of R, T^* and ρ^*.

R	$T^* = kT/\varepsilon$	$\rho^* = \rho\sigma^3$				
1.5		0.4	0.5	0.6	0.7	0.8
	0.57		−4.37	−8.68	−9.69	−10.69 (−10.03)
	0.67		−4.26	−7.31	−8.19	−9.06 (−8.59)
	0.80		−4.14	−5.95	−6.71 (−6.29)	−7.45 (−7.16)
	1.0		−3.96(−4.07)	−4.63 (−4.27)	−5.25 (−5.03)	−5.86 (−5.73)
	$1.\bar{3}$		−3.81(−3.89)	−3.34 (−3.2)	−3.83 (−3.77)	−4.30 (−4.30)
	2.0		−3.60(−3.64)	−2.13 (−2.13)	−2.46 (−2.51)	−2.79 (−2.86)
	4.0		−3.36(−3.48)	−1.01 (−1.07)	−1.18 (−1.26)	−1.35 (−1.43)
1.625						
	0.8	−5.43		−7.45		−9.40 (−9.33)
	1.25	−3.21 (−3.22)		−4.55 (−4.55)		−5.86 (−5.72)
	2	−1.87 (−1.87)		−2.73 (−2.73)		−3.57 (−3.51)
	3	−1.19 (−1.18)		−1.77 (1.78)		−2.34 (−2.31)

Simulation data [20,21] given in parentheses.

phase region is marginal. It means that the steepness parameter (unlike the well width parameter) as an additional parameter for non-conformal fluids isn't a suitable variable for the acenteric factor [3].

As mentioned before coordination number may have a significant effect on some thermodynamic properties such as equation of state, internal energy, and heat capacity. Every EOS based on one particle

Table 4. Comparison of calculated compressibility factor with Monte Carlo simulation data and those obtained from other equations of state for given values of R, T^* and ρ^*.

R	$T^* = kT/\varepsilon$	$\rho^* = \rho\sigma^3$	MC	LC	LS	GWL	SL	This work
	1.75	0.05	0.916	0.926	0.878	0.920	0.958	0.925
1.5	1.75	0.10	0.853	0.875	0.792	0.855	0.913	0.869
	1.75	0.30	0.736	0.880	0.798	0.760	0.856	0.834
	1.75	0.50	1.052	1.088	1.489	1.091	1.320	1.329
	1.75	0.65	2.073	1.690	2.730	1.898	2.366	2.385
	1.75	0.80	4.616	3.935	5.100	3.683	4.556	4.557
	2.50	0.05	0.959	0.991	0.960	0.987	1.004	0.989
	2.50	0.10	1.081	0.999	0.945	0.985	1.011	0.990
	2.50	0.30	1.097	1.211	1.163	1.132	1.189	1.177
	2.50	0.50	1.691	1.716	2.008	1.724	1.902	1.902
	2.50	0.65	2.909	2.623	3.355	2.766	3.137	3.135
	2.50	0.80	5.529	5.041	5.839	4.838	5.514	5.492
	3.00	0.05	1.013	1.014	0.989	1.011	1.022	1.011
	3.00	0.10	1.035	1.044	1.000	1.032	1.049	1.035
	3.00	0.30	1.265	1.339	1.302	1.275	1.319	1.310
	3.00	0.50	1.930	1.966	2.213	1.975	2.129	2.127
	3.00	0.65	3.168	2.996	3.608	3.114	3.436	3.430
	3.00	0.80	5.956	5.480	6.140	5.302	5.887	5.861
	4.00	0. 50	2.310	2.283	2.473	2.292	2.412	2.409
	4.00	0.60	3.130	2.967	3.349	3.047	3.250	3.244
	4.00	0.70	4.490	4.132	4.632	4.180	4.495	4.482
	4.00	0.80	6.470	6.036	6.526	5.894	6.353	6.326
1.625								
	1.25	0.4	−0.270					−0.223
	1.25	0.6	0.150					0.144
	1.25	0.8	3.44					2.138
	2.00	0.4	0.720	0.629	1.224	0.495	0.800	0.796
	2.00	0.6	1.66	0.726	2.464	0.945	1.642	1.657
	2.00	0.8	5.38	3.097	5.402	2.773	4.188	4.175
	3.00	0.4	1.35					1.368
	3.00	0.6	2.59					2.519
	3.00	0.8	5.71					5.342

Simulation data from [20,21,30].

Table 5. Effect of steepness parameter on critical parameters.

n	$T_C/(\varepsilon/k)$	$\rho_C\sigma_{HS}^3$	$P_C\sigma_{HS}^3/\varepsilon$
10	1.5735	0.2534	0.1383
12	1.5504	0.2535	0.1363
15	1.5292	0.2535	0.1344
18	1.5159	0.2536	0.1332
27	1.4953	0.2536	0.1314
36	1.4856	0.2537	0.1305
54	1.4763	0.2537	0.1297
Infinity	1.4587	0.2538	0.1281

effective potential, CN plays a pivotal role on its deriving process, either experimentally as a linear isotherm regularity EOS [32,33], or theoretically as a GvdW EOS [25] By using Equations (17a), (17b) and (13c). we have obtained the theoretical value of the CN for different values of reciprocal n (softness), which are shown schematically at different densities and temperatures in Figure 2. As seen in this figure, N_C behaves linearly as a function of $1/n$ with a suitable coefficient of determination, $R^2 = 0.9998$, from which one may obtain the hard-core value from the intercept. For $T^* = 2$, and $\rho^* = 0.2$, 0.5, and 0.8 the value of intercept is 3.746, 8.758, and 13.58, respectively, which are comparable with the corresponding values obtained from simulation (Table 2). Another feature of Figure 2 is that at higher densities and temperatures, the more significant of the steepness parameter, which is reasonable, since at higher density and temperature particles spend most time at the repulsive branch of the potential. Using this argument, one may infer that first, the expansion mechanism in fluid arises from the reducing of CN, whereas in the solid state it is due to the anharmonistic vibrations of particles, and second, for a constant density for which we expect that CN to be constant as well, the softer the model potential, leads to a less pressure or compressibility factor.

We may use either the statistical mechanical analytical expression or the first derivative of compressibility factor to obtain an analytical expression for the second virial coefficient [34]:

$$B_2(T) = -2\pi \int_0^\infty \left(e^{-\beta u(r)} - 1\right) r^2 \mathrm{d}r$$
$$B_2(T) = \left(\frac{\partial Z}{\partial \rho}\right)_{\rho\to 0} = \lim\left(\frac{Z-1}{\rho}\right)_{\rho\to 0}. \qquad (22)$$

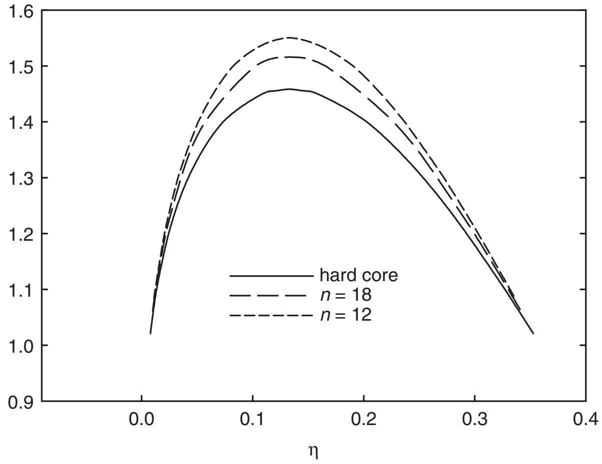

Figure 1. Effect of the softness parameter (1/n) on the coexistence curve, where $\eta = \pi\rho\sigma_{\mathrm{HS}}^3/6$.

Using both forms of Equation (22), the reduced form of the second virial coefficient, $B_2^*(T^*) = B_2/b_0$ where $b_0 = (2\pi/3)N_0\sigma^3$, may be obtained in terms of the reduced temperature, well width, and steepness, as

$$B_2^*(T^*) = \gamma^3(T^*)\left(1 - \left(e^{1/T^*} - 1\right)\left(\frac{R^3}{\gamma^3(T^*)} - 1\right)\right). \qquad (23)$$

In Figure 3, the reduced second virial coefficient as a function of reduced temperature for some different values of steepness, hard-core limit of the potential model, vdW co-volume (b_0), and effective vdW co-volume ($b(T^*)$) are depicted. As expected and shown in this figure, $B_2^*(T^*)$ of the hard-core fluid doesn't pass through any inversion temperature, whereas three other forms behave like that of real fluids [35,36]. Variation of the Boyle and inversion temperatures and also their ratio for some different values of steepness parameter and well width of SCSW potential model are listed in Table 6. By inspection of Figure 3 and Table 6, one obtains the following results: (1) The soft repulsive part of the potential model associated with the attractive range has two especial effects on the second virial coefficient, the attractive characteristic of the potential increases monotonically, and the repulsive branch decrease monotonically, and at low temperatures the former dominates the second virial coefficient, whereas at a specific temperature known as the inversion temperature,

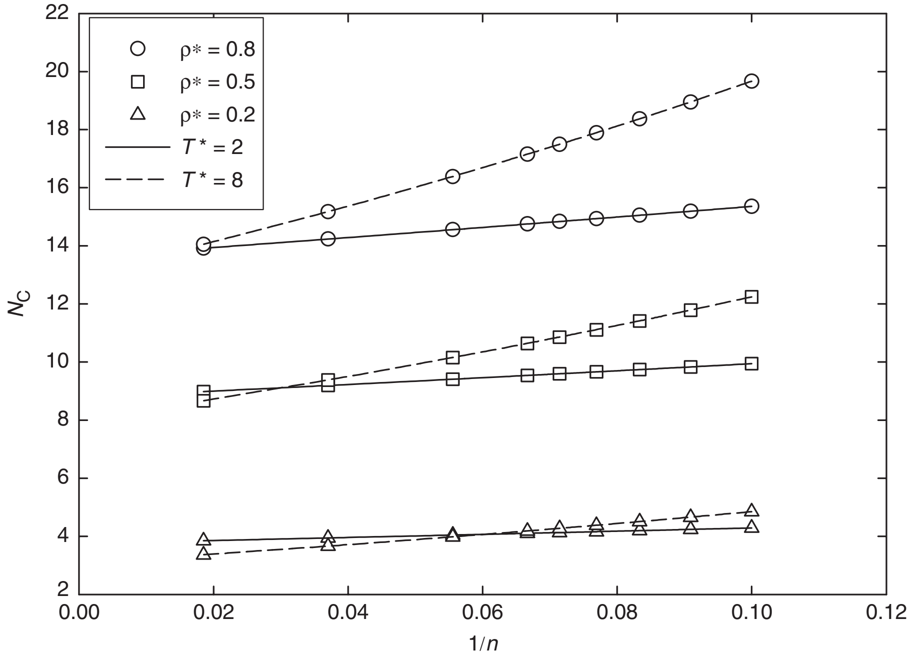

Figure 2. Steepness dependency of the coordination number at given values of temperature and density.

these two effects balance each other; finally at very high temperatures the latter effect dominates. (2) For a given value of the steepness, the Boyle and inversion temperatures increase with increasing well width, but their ratio remains almost constant. (3) For a fixed value of well width, with increasing steepness parameter, the inversion temperature rises, since there is the characteristic distance at this temperature where two opposite effects balance each other, hence for attaining to such distance, system needs a higher thermal energy, but it has marginal effect on the Boyle temperature. These effects make the ratio rise when the steepness parameter increases. (4) The hard-core potential model shows an inversion temperature at infinity. It is worth noting that for real fluid this ratio is 6.5–7.8 [36].

Table 6. Boyle and inversion temperatures and their ratio for some given values of well width and steepness of SCSW potential model.

R	n	T^*_{B}	T^*_{I}	$T^*_{\mathrm{I}}/T^*_{\mathrm{B}}$
1.3	12	1.8396	11.718	6.370
1.4	12	2.6052	16.830	6.460
1.5	12	3.5245	22.927	6.505
1.6	12	4.6224	30.166	6.526
1.7	12	5.9235	38.701	6.533
1.8	12	7.4534	48.696	6.533
1.6	10	4.9355	28.4116	5.757
1.6	12	4.6224	30.1656	6.526
1.6	15	4.3531	33.2650	7.642
1.6	18	4.1937	36.5916	8.725
1.6	27	3.9576	46.9328	11.859
1.6	54	3.7525	77.9238	20.766
1.6	Hard-core limit	2.8458	Infinity	Infinity

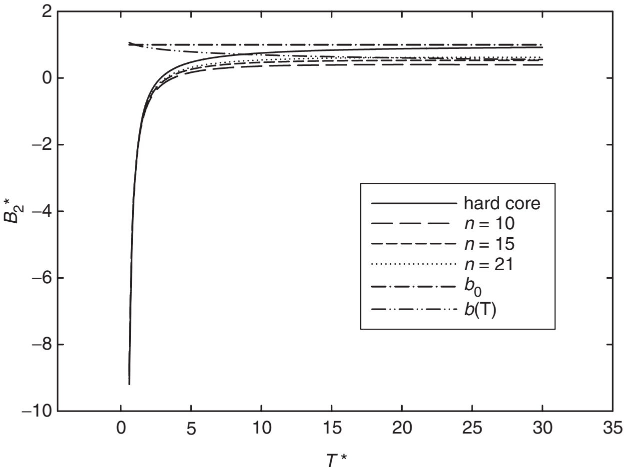

Figure 3. Second virial coefficient for the soft-core and hard-core potential models and also for vdW and effective vdW co-volume, for some given values of n.

5. Conclusions

Owing to the fact that, the intermolecular potential model with two common parameters, σ and ε, does not show potential shape and thermodynamic quantities accurately, and other dimensionless parameters are needed, we chose the steepness of the repulsive branch of the potential model as an additional parameter to investigate its influence on thermodynamic properties. In this work, by using the WCA theoretical model, we have shown with a suitable effective hard-sphere criterion, that one may use the step function approximation for soft-core potential models and then investigate the influence of the steepness parameter on some properties of interest. Regarding the fact that, there are extensive simulation data for the hard-core SW potential model, and also that one is able to derive a simple closed expression without using a complicated form of the radial distribution function, and coordination number, we have focused on the equation of state of the square well fluid. In order to investigate the appropriateness of the new expression, Equation (14a), we have chosen different values of R from 1.25 to 2 as an input for the hard-core model to calculate the critical parameters and coordination number, and as shown in Tables 1 and 2, our new model is suitable for well width $1.55 \le R \le 1.70$. As shown in Figures 1, 2 and 3, the steepness of the potential model is an important variable for the coordination number and second virial coefficient at high temperatures, at which penetration of two particles into each other is significant, but not for the coexistence curve, in which the attraction term and thermal fluctuation both play very significant roles.

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References

[1] D. Henderson, O.H. Scalise, and W.R. Smith, J. Chem. Phys. **72**, 2431 (1980).

[2] L.V. Enrique, D. Miguel, and L.F. Rull, J. Chem. Phys. **96**, 2296 (1992).

[3] A. Gil-Villegas, F.D. Rio, and A.L. Benavides, Fluid Phase Equilib. **119**, 97 (1996).

[4] J.A. Barker and D. Henderson, J. Chem. Phys. **47**, 2856 (1967).

[5] J.A. Barker and D. Henderson, Rev. Mod. Phys. **48**, 587 (1976).

[6] J. Chang and S.I. Sandler, Mol. Phys. **81**, 735 (1994).

[7] J. Chang and S.I. Sandler, Mol. Phys. **81**, 745 (1994).

[8] T. Hino and J.M. Prausnitz, Fluid Phase Equilib. **138**, 105 (1997).

[9] B.-J. Zhang, Chem. Phys. Lett. **296**, 266 (1998).

[10] B.-J. Zhang, Fluid Phase Equilib. **154**, 1 (1999).

[11] D. Ben-Amotz and G. Stell, J. Phys. Chem. B **108**, 6877 (2004).

[12] J.D. Weeks and D. Chandler, J. Chem. Phys. **54**, 5237 (1971).

[13] H. Andersen, J.D. Weeks, and D. Chandler, Phys. Rev. A **4**, 1597 (1971).

[14] D. Chandler and J.D. Weeks, Phys. Rev. Lett. **25**, 149 (1970).

[15] L. Boltzmann, *Lectures on Gas Theory*. (University of California Press, Berkeley, CA, 1964).

[16] F.O. Raineri, G. Stell, and D. Ben-Amotz, J. Phys. Condensed Matter **16**, S4887 (2004).

[17] F. Carnahan and K.E. Starling, J. Chem. Phys. **51**, 635 (1969).

[18] N.F. Carnahan and K.E. Starling, AIChE J. **18**, 1184 (1972).

[19] H. Farrokhpour and G.A. Parsafar, J. Phys. Soc. Jpn. **72**, 2747 (2003).

[20] D. Henderson, W.G. Madden, and D.D. Fitts, J. Chem. Phys. **64**, 5026 (1976).

[21] D. Henderson, O.H. Scalise, and W.R. Smith, J. Chem. Phys. **72**, 2431 (1980).

[22] J.R. Elliott and L. Hu, J. Chem. Phys. **110**, 3043 (1999).

[23] E.S. Pasching, A.L. Benavides, and R.C. Priego, J. Chem. Phys. **123**, 234513 (2005).

[24] R.J. Lee and J.C. Chao, Mol. Phys. **65**, 1253 (1988).

[25] J. Largo and J.R. Solana, Phys. Rev. E **67**, 66112 (2003).

[26] D.M. Heyes, J. Chem. Soc. Faraday Trans. **87**, 3373 (1991).

[27] J. Largo and J.R. Solana, Fluid Phase Equilib. **193**, 277 (2002).

[28] R.J. Lee and J.C. Chao, Mol. Phys. **61**, 1431 (1987).

[29] K.H. Lee and S.I. Sandler, Fluid Phase Equilib. **34**, 113 (1987).

[30] M. Guo, W. Wang, and H. Lu, Fluid Phase Equilib. **60**, 37 (1990).

[31] S. Shen and B.C.-Y. Lu, Fluid Phase Equilib. **84**, 9 (1993).

[32] G.A. Parsafar and E.A. Mason, J. Phys. Chem. **97**, 9048 (1993).

[33] M. Shokouhi and G.A. Parsafar, Fluid Phase Equilib. (In press).

[34] D.A. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, 1976).

[35] G.A. Parsafar, M. Khanpour, and A.A. Mohammadi, Chem. Phys. **326**, 527 (2006).

[36] G.A. Parsafar and M. Shokouhi, Mol. Phys. **104**, 3269 (2006).