

A New Analytical Expression for the Free Energy of Hard-Core Fluids

Hussein FARROKHPOUR¹ and Gholamabbas PARSAFAR^{2*}

¹*Isfahan University of Technology, Isfahan, Iran*

²*Sharif University of Technology, Tehran, Iran*

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A new potential function, which can in a simple and reasonable manner represent the molecular interaction of many kinds of hard-core fluids by varying the value of its parameter, is proposed. For prediction of thermodynamic properties of hard-core fluids such as the square-well (SW) and hard core Lennard–Jones (HCLJ), a simple perturbed equation of state (EOS) is derived by using the new potential function along with the Barker–Henderson perturbation theory. This method yields a simple and general analytical expression for each thermodynamic property of such fluids. The most important feature of these expressions is that they have no adjustable parameter and in some regions in which there is no simulation data for such hard-core fluids, such equation may be used to predict the needed data. The derived EOS in this work was successfully applied to predict thermodynamic properties of the SW and HCLJ fluids, for which the simulation data are available. The predicted results are in good agreement with both the computer simulation data and the well-known equations of state.

KEYWORDS: Barker–Henderson perturbation theory, equation of state, hard-sphere fluid, radial distribution function

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1. Introduction

The theory of simple fluids with spherical potentials is rather well developed and little remains to be done as far as improving the agreement with the known models involve an extensive numerical computation and are often not practical for obtaining quick and accurate results for the fluids. It is therefore of great interest to condense the numerical results of the long tables into some simple analytical expressions that are simpler to handle, from which even a physical insight may be provided and therefore application and extension to more complicated fluid systems becomes possible.

Reliable models for the accurate correlation and prediction of thermodynamic properties of pure fluids and their mixtures are much in demand for process design and material handling. In the chemical and petroleum industries, much effort has been given to the development of simple analytical equation of state to meet such a demand.

With the development of statistical thermodynamics of fluid, many equations of state have been developed in terms of parameters, which characterize the intermolecular forces. Such works include various equations of state based on the perturbed-hard-chain theory,¹⁾ the generalized van der Waals theory,²⁾ and the generalized perturbation theory.³⁾ However, all these equations have attractive terms that are based on either the SW, HCLJ, or Lennard–Jones (LJ) potentials and are not sufficiently flexible; that is due to the fact that the universal constants of these equations are frequently obtained from the simulation data for the specified potential.

Recently, an analytical expression for the first coordination shell of the radial distribution function (RDF) of the hard-sphere fluid has been derived.⁴⁾ This expression has as many as 153 parameters. If we use such an expression along with the Barker–Henderson perturbation theory for either the SW or SU fluid yields a very complicated equation of state

with 153 parameters which is not easy to handle.^{4,5)}

In this paper, we have developed a new analytical EOS to predict the properties of hard-core fluids. Our approach is based on the Barker–Henderson perturbation theory along with the new potential function. Even though the proposed potential function is as simple as the SW potential, it is more flexible than the SW, HCLJ, and LJ potentials for practical use. We have used this potential to derive a new equation of state, which is capable of predicting the thermodynamic properties of the hard-core fluids such as the SW and HCLJ fluids.

2. Potential Function

Potential functions, such as the hard sphere (HS), SW, LJ, and HCLJ are empirical in nature, and approximate to the intermolecular forces in real fluid.⁶⁾ Although it is desirable that a potential function be able to represent the intermolecular forces for various kinds of fluids as accurately as possible, it must still be simple in mathematical form. However it is difficult to have a potential function that satisfies these requirements simultaneously.

In this work, a new extended SW potential function is proposed which is a compromise between simplicity, reality and flexibility. The function is

$$u(x) = \begin{cases} \infty & x < 1 \\ -\varepsilon & 1 \leq x \leq \lambda \\ \alpha\varepsilon \frac{x-3}{(3-\lambda)} \left(\frac{1}{x}\right)^6 & \lambda < x \leq 3 \\ 0 & x > 3 \end{cases} \quad (1)$$

In this expression, $x = r/\sigma$ is the intermolecular separation in units of the hard-core diameter σ . The quantity ε is the well depth (minimum potential energy), λ is the reduced well width, and α is an additional parameter introduced to make the potential more flexible by changing the steepness of the potential tail. It is clear that this potential can be reduced to different hard-core potential models, depending on the value of α , for making the potential more flexible.

*To whom correspondence should be addressed.
E-mail: parsafar@Sharif.edu

Equation (1) is obviously more realistic than both the HS and SW potentials, owing to the presence of the tail, and also more realistic than the Sutherland (SU) and triangular well potentials, due to the presence of the non-zero well width. Due to the term $(1/x)^6$ in the tail, the potential is more realistic than the trapezoidal-well (TW) potential. Owing to the fact that different values can be attributed to the parameter α of the potential in addition to the parameters σ , ε , and λ ; it becomes more flexible than the HS, SW, SU, TW, LJ, and HCLJ potentials. Finally it is less complicated than the HCLJ and LJ potentials, due to the simple expression for the tail portion of the potential.

3. A New Analytical EOS for the Hard-Core Fluid based on Perturbation Theory

In this section, we develop a new equation of state for the proposed potential, based on a perturbation theory. According to the perturbation theory, the Helmholtz free energy is given as,⁷⁾

$$\frac{A}{NkT} = \frac{A_0}{NkT} + \frac{12y}{kT} \int_1^\infty u(x)g_0(x)x^2 dx - \frac{6yH}{(kT)^2} \frac{\partial}{\partial y} \left[y \int_1^\infty u(x)^2 g_0(x)x^2 dx \right] \quad (2)$$

where A_0 and $g_0(r)$ refer to the Helmholtz free energy and the RDF of the reference fluid, respectively. The variable $y = (\pi/6)\rho\sigma^3$ is the packing fraction, and kT has its usual meaning. The integrals appear in eq. (2) depend on y , for which an expression will be derived. We use the HS fluid as the reference in this work. For this reason, A_0 may be derived from the Carnahan–Starling equation as,⁸⁾

$$\frac{A_0}{NkT} = \frac{4y - 3y^2}{(1 - y)^2} \quad (3)$$

and, $g_0(x)$ is simply given by,

$$g_0(x) = \begin{cases} 0 & x < 1 \\ g_1(x) & 1 \leq x \leq \lambda \\ 1 & x > \lambda \end{cases} \quad (4)$$

In eq. (4) we have considered a general form for $g_0(x)$ and there is no need to know the mathematical form of the $g_1(x)$. The expression for H is given by Barker–Henderson as,⁷⁾

$$H = \frac{(1 - y)^4}{1 + 4y + 4y^2 - 4y^3 + y^4} \quad (5)$$

The fact that $g_0(x) = 1$ for $x > \lambda$, we require the following approximation that,

$$24y \int_\lambda^\infty [g_0(x) - 1]x^2 dx = 0 \quad (6)$$

Using eq. (6) along with the isothermal compressibility equation,⁹⁾

$$\frac{6kT}{\pi\sigma^3} \left(\frac{\partial y}{\partial p} \right) = 1 + 24y \int_0^\infty [g(x) - 1]x^2 dx \quad (7)$$

we may obtain the following result,

$$24y \int_1^\lambda g_0(x)x^2 dx = H + 8\lambda^3 y - 1 \quad (8)$$

Substitution of eqs. (1), (4), and (8) into eq. (2) yields,

$$\frac{A}{NkT} = \frac{A_0}{NkT} - \frac{\varepsilon}{2kT} \left(H + 8\lambda^3 y - 1 - \frac{24\alpha Gy}{3 - \lambda} \right) - 6y \frac{H}{(kT)^2} \left(I + y \frac{\partial I}{\partial y} \right) \quad (9)$$

where,

$$I = \frac{\varepsilon^2}{24y} (H + 8\lambda^3 y - 1) + 8.650 \times 10^{-3} \alpha^2 \varepsilon^2 \quad (10)$$

and,

$$G = \frac{1}{2\lambda^2} - \frac{1}{\lambda^3} - \frac{9}{486} \quad (11)$$

Using eq. (9) for the Helmholtz free energy, the compressibility factor Z for the proposed potential may be obtained as,

$$Z = Z_0 - \frac{\varepsilon}{2kT} \left[y \left(\frac{\partial H}{\partial y} \right) + 8\lambda^3 y - \frac{24\alpha Gy}{3 - \lambda} \right] - \frac{6yH}{(kT)^2} \left(I + y \frac{\partial I}{\partial y} \right) - 6y^2 \left(\frac{\partial H}{\partial y} \right) \left(\frac{1}{kT} \right)^2 \times \left(I + y \frac{\partial I}{\partial y} \right) - 6y^2 H \left(\frac{1}{kT} \right)^2 \left(2 \frac{\partial I}{\partial y} + y \frac{\partial^2 I}{\partial y^2} \right) \quad (12)$$

where,

$$Z_0 = \frac{(1 + y + y^2 - y^3)}{(1 - y)^3} \quad (13)$$

Therefore, on the basis of the proposed potential, the perturbed EOS, eq. (12) is derived.

4. Calculation of the Thermodynamic Properties of Hard-Core Fluids Using the Derived EOS

The resultant EOS can be easily applied to many kinds of hard-core fluids, for the prediction of their thermodynamic properties, because of the flexibility of the proposed potential function. The applications of the proposed EOS to the SW and HCLJ fluids is presented as follows.

4.1 Square-well fluid

The resultant equation of state may be used to calculate the compressibility factor Z of the square-well fluid. The value of λ in eq. (12) was taken to be 1.5, which has been used by many researchers to simulate the properties of this fluid.^{10,12)}

To calculate the properties of this fluid, the value of α in eq. (12) should be taken equal to zero, since there is no tail for the SW potential. At any reduced density $\rho^* = \rho\sigma^3$ and temperature $T^* = kT/\varepsilon$, the value of the fluid compressibility factor can be easily calculated from eq. (12) without requiring any additional parameter. For comparison, the value of Z may be compared with that given by the 27-constant expression of Alder *et al.*,¹⁰⁾

$$Z = Z_0 + \sum_{m=1} \sum_{n=1} m A_{nm} \left(\frac{\varepsilon}{kT} \right)^n \left(\frac{V_0}{V} \right)^m \quad (14)$$

Table I. Calculated compressibility factor of the SW fluid, compared to that given by different equations of state and the simulation data.

ρ^*	T^*	AN ^{a)}	LLS ^{d)}	LS ^{e)}	GWL ^{f)}	This work	Simulation data
0.50	1.00	0.055	-0.096	0.270	-0.405	0.077	-0.450 ^{b)}
0.60	1.00	0.385	0.399	0.877	-0.272	0.412	-0.210 ^{b)}
0.70	1.00	1.097	1.335	1.878	0.145	1.120	0.590 ^{b)}
0.80	1.00	2.403	2.918	3.463	1.020	2.420	2.340 ^{b)}
0.50	1.33	0.815	0.762	0.960	0.445	0.827	0.460 ^{b)}
0.60	1.33	1.309	1.364	1.631	0.759	1.324	0.700 ^{b)}
0.70	1.33	2.195	2.393	2.704	1.390	2.210	1.820 ^{b)}
0.80	1.33	3.684	4.056	4.374	2.524	3.697	3.840 ^{b)}
0.05	1.75	0.929	0.904	0.878	0.920	0.927	0.916 ^{c)}
0.10	1.75	0.875	0.828	0.792	0.855	0.870	0.853 ^{c)}
0.30	1.75	0.865	0.787	0.798	0.760	0.864	0.736 ^{c)}
0.50	1.75	1.382	1.378	1.489	1.091	1.389	1.052 ^{c)}
0.65	1.75	2.445	2.560	2.730	1.898	2.454	2.073 ^{c)}
0.80	1.75	4.635	4.193	5.100	3.683	4.642	4.616 ^{c)}
0.05	2.50	0.990	0.972	0.960	0.987	0.989	0.959 ^{c)}
0.10	2.50	0.992	0.962	0.945	0.985	0.990	1.081 ^{c)}
0.30	2.50	1.194	1.159	1.163	1.132	1.193	1.097 ^{c)}
0.50	2.50	1.933	1.956	2.008	1.724	1.936	1.691 ^{c)}
0.65	2.50	3.176	3.273	3.356	2.766	3.180	2.909 ^{c)}
0.80	2.50	5.553	5.746	5.839	4.838	5.556	5.529 ^{c)}
0.05	3.00	1.012	0.997	0.989	1.011	1.011	1.013 ^{c)}
0.10	3.00	1.036	1.012	1.000	1.032	1.034	1.035 ^{c)}
0.30	3.00	1.322	1.300	1.302	1.275	1.321	1.265 ^{c)}
0.50	3.00	2.150	2.178	2.213	1.975	2.153	1.930 ^{c)}
0.65	3.00	3.464	3.551	3.608	3.114	3.466	3.168 ^{c)}
0.80	3.00	5.914	6.075	6.140	5.302	5.916	5.956 ^{c)}

a) ref. 13. b) ref. 11. c) ref. 12. d) ref. 2. e) ref. 15. f) ref. 12.

where $V_0 = N\sigma^3/\sqrt{2}$; the Aim-Nezbeda's (AN) equation,¹³⁾

$$Z = Z_0 - \frac{\varepsilon}{kT} \left[\frac{(4y + 10y^2 - 2y^3)(1 - y^3)}{D^2} - 4y\lambda^3 \right] - 6 \left(\frac{\varepsilon}{kT} \right)^2 \left[yCI + y^2I \frac{\partial C}{\partial y} + y^2C \frac{\partial I}{\partial y} \right] \quad (15)$$

where

$$D = 1 + 4y + 4y^2 - 4y^3 + y^4, \\ C = (1 - y)^4/D$$

and

$$I = (\lambda^3/3) + (C - 1)/24y;$$

the Lee *et al.*'s (LLS) equation,¹⁴⁾

$$Z = Z_0 - \frac{Z_m V_0 [\exp(\varepsilon/2kT) - 1]}{V + V_0 [\exp(\varepsilon/2kT) - 1]} \quad (16)$$

with $Z_m = 18$; the Lee-Sandler (LS) equation¹⁵⁾ as presented by Guo *et al.*¹²⁾

$$Z = Z_0 - \frac{N_0}{2f} \left[-\frac{f'}{f} \ln \left(1 + \frac{\rho^*(\Omega - 1)}{\sqrt{2}} \right) + \frac{\Omega(1 + f'\rho^*/T^*) - 1}{\sqrt{2} + \rho^*(\Omega - 1)} \right] \quad (17)$$

with

$$N_0 = 18\rho^*, \quad f = 1 - \rho^*/\sqrt{2}, \quad f' = -1/\sqrt{2}, \\ \Omega = \exp\left(\frac{\bar{\varepsilon}}{kT}\right), \quad \bar{\varepsilon} = (1 - \rho^*/\sqrt{2})\varepsilon$$

and the Guo *et al.*'s equation (GWL),¹²⁾

$$Z = Z_0 - \frac{N_0}{2f} \left[\left(\frac{0.58}{1 + 0.58\rho^*} - \frac{f'}{f} \right) \ln(1 + \rho^*(\Omega - 1)) + \frac{\Omega(1 + f'\rho^*/T^*) - 1}{1 + \rho^*(\Omega - 1)} \right] \quad (18)$$

where

$$N_0 = (4\pi/3)(\lambda^3 - 1)(1 + 0.58\rho^*)\rho^*, \\ f = 1 - \rho^*/\sqrt{2}, \quad f' = -1/\sqrt{2}.$$

Such a comparison is given in Table I and also shown in Fig. 1. The simulation data are taken from ref. 11 at $T^* = 1.00$ and 1.33, and from ref. 12 at $T^* = 1.75, 2.50$ and 3.00. In Table II, the calculated results are compared with the simulation data reported by Henderson *et al.*¹⁶⁾ and also with the results obtained from the Lee and Chao (LC),¹⁷⁾ GWL, and LS equations of state for various values of λ .

Recently an analytical expression for the first coordination shell of the RDF for the hard-sphere fluid has been derived,⁴⁾ which is given as

$$g_1(x) = \frac{1}{x^2} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} I_{nm} \frac{n(x - 1.5)^{n-1}}{(1 - y)^{n+1}} y^m \quad (19)$$

where the parameters I_{nm} s are constant. The values of I_{nm} s up to $n = 8$ and $m = 16$ are reported in ref. 4. This expression has as many as 153 parameters. Such expression, along with the Barker-Henderson perturbation theory for both the SW and SU fluids, are used to derive a complicated

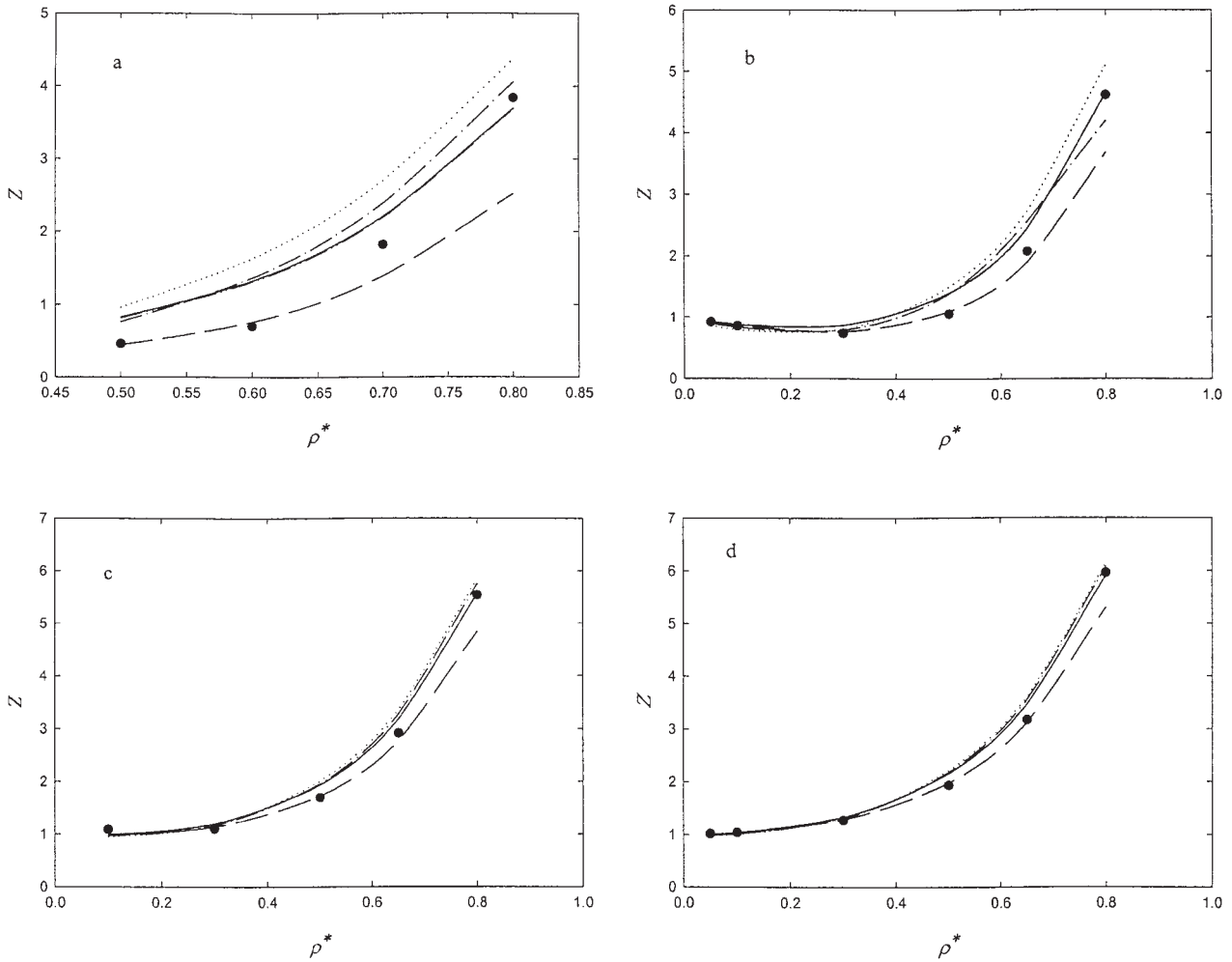


Fig. 1. Compressibility factor calculated by AN (— · — · —), LLS (---), LS (·····), GWL (—) and simulation data (●) for (a) $T^* = 1.33$, (b) $T^* = 1.75$, (c) $T^* = 2.5$, (d) $T^* = 3.00$.

Table II. Calculated compressibility factor of the SW fluid at various values of λ compared to that given by different equations of state and the simulation data.

λ	T^*	ρ^*	LC ^(a)	LS ^(b)	GWL ^(c)	This work	Simulation data
1.125	1.00	0.40	2.049	-0.052	2.005	1.521	1.390 ^(d)
1.125	1.00	0.60	3.416	0.877	3.470	2.702	2.230 ^(d)
1.125	1.00	0.80	6.601	3.463	6.549	5.538	3.530 ^(d)
1.375	1.50	0.40	1.306	0.792	1.212	1.214	0.970 ^(d)
1.375	1.50	0.60	2.018	1.906	2.159	2.265	1.680 ^(d)
1.375	1.50	0.80	4.777	4.710	4.594	4.980	4.000 ^(d)
1.625	2.00	0.40	0.629	1.224	0.495	0.845	0.720 ^(d)
1.625	2.00	0.60	0.726	2.464	0.945	1.725	1.660 ^(d)
1.625	2.00	0.80	3.097	5.402	2.773	4.272	5.380 ^(d)
1.750	1.43	0.40	-0.940	0.708	-1.213	-0.395	-0.220 ^(d)
1.750	1.43	0.60	-2.169	1.800	-1.769	-0.142	0.160 ^(d)
1.750	1.43	0.80	-0.726	4.580	-1.233	1.724	3.030 ^(d)
2.000	6.00	0.40	1.160	2.090	1.083	1.806	1.480 ^(d)
2.000	6.00	0.60	1.676	3.656	1.835	3.197	2.820 ^(d)
2.000	6.00	0.80	4.359	6.923	4.063	6.281	5.500 ^(d)

a) ref. 17. b) ref. 15. c) ref. 12. d) ref. 16.

EOS with 153 parameters which is not simple to be handled.^{4,5)} For example, the compressibility factor of the SW fluid can be written as,

$$Z = Z_0 + \frac{Z_1}{T^*} + \frac{Z_2}{T^{*2}} \quad (20)$$

where Z_0 is the compressibility factor for the hard-sphere fluid and

$$Z_1 = -12 \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} I_{nm} [1 + m + (n - m)y] y^{m-1} \frac{(\lambda - 1.5)^n}{(1 - y)^{n-2}} \quad (21)$$

and

$$Z_2 = -\frac{kT}{\sigma^3} \frac{36}{\pi} y \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} I_{nm} \left\{ \left(\frac{\partial y}{\partial p} \right)_0 \left[-1 - 3n + m^2(1 - y) - n^2(1 + y) + 2m(1 + ny) + \frac{2 + 3n + n^2}{1 - y} \right] + \frac{\partial}{\partial y} \left(\frac{\partial y}{\partial p} \right)_0 [1 + m + (n - m)y] y \right\} \frac{(\lambda - 1.5)^n}{(1 - y)^{n-2}} y^m \quad (22)$$

It is to be noted that eq. (12) is simpler than all compared equations of state, except for the LLS equation. As we shall see in the next section, eq. (12) is not limited to the SW fluid. It is to be noted that eq. (12) has three advantages over eq. (20); first is the number of parameters, second is the generality of the EOS, and finally there is no need to any explicit mathematical expression for the RDF for deriving eq. (12).

4.2 Hard-core Lennard–Jones fluid

The HCLJ potential is more realistic but more complex than the SW potential. This potential is given as,¹⁸⁾

$$u(x) = \begin{cases} \infty & x < 1 \\ -\varepsilon & 1 \leq x \leq 2^{1/6} \\ 4\varepsilon \left[\left(\frac{1}{x} \right)^{12} - \left(\frac{1}{x} \right)^6 \right] & x > 2^{1/6} \end{cases} \quad (23)$$

In order to apply eq. (12) to the HCLJ fluid, the potential parameters have to be obtained in a suitable manner. In general, the parameters of an equation of state which are used to calculate the fluid properties are considered as adjustable parameters, and their values chosen in such a way that it gives the best fit with the simulation data. This fitting procedure usually makes the theoretically developed equation of state lose its original physical meaning. In this work, an analytical method is proposed to obtain the values of the potential parameters. Strictly speaking, the value of λ in eq. (12) should vary with density.⁹⁾ However, the exact variation of λ with density is not known, and therefore, its density dependency is discarded. In our calculation λ is taken to be 1.3 which nearly satisfies eq. (6) for all densities. In addition we have assumed that σ in eq. (1) is equal to that of eq. (23). The values of α and $\varepsilon/\varepsilon_{\text{HCLJ}}$ are determined in a straightforward analytical procedure, as explained below. This procedure is also applicable to fluids other than the HCLJ fluid with a hard-core repulsion.

For a given fluid, whose potential function, $u_d(x)$, is known, we require that the following two equal-area constraints to be approximated as,

$$\int_1^\lambda u(x) dx = \int_1^\lambda u_d(x) dx \quad (24)$$

$$\int_\lambda^3 u(x) dx = \int_\lambda^3 u_d(x) dx \quad (25)$$

For the HCLJ fluid, we substitute eqs. (23) and (1) into eqs. (24) and (25). If we use $\lambda = 1.3$ and solve eqs. (24) and (25) simultaneously, we would get $\varepsilon/\varepsilon_{\text{HCLJ}} = 0.914$ and $\alpha = 4.849$.

These values for the parameters were used to calculate the reduced internal energy and the compressibility factor for the HCLJ fluid. The calculated values of $Z = p/\rho RT$ are compared with the simulation data of Sowers and Sandler³⁾ in Table III. We have used eq. (9) to calculate the reduced internal energy of the HCLJ fluid, the results of which are compared with those of the simulation data and eq. (27) in Table IV. The Sowers and Sandler EOS (SS) is given as,

$$Z = \frac{1 + y + y^2 - y^3}{(1 - y)^3} - \frac{Z_m [\exp(1/2T^*) - 1] y}{\pi \sqrt{2}/6 + [\exp(1/2T^*) - 1] y} + 2a \frac{1}{T^*} \exp(-\sqrt{T^*}) \rho^* + \left[b_1 \left(\frac{1}{T^*} \right) + b_2 \left(\frac{1}{T^*} \right)^2 \right] \rho^* \quad (26)$$

from which,

$$\frac{E}{N\varepsilon_{\text{HCLJ}}} = \frac{-Z_m y \exp(1/2T^*)}{2[\pi \sqrt{2}/6 + [\exp(1/2T^*) - 1] y]} + a \rho^{*2} \exp(-\sqrt{T^*}) (1 + \sqrt{T^*}/2) + \left(b_1 + 2b_2 \frac{1}{T^*} \right) \rho^* \quad (27)$$

where $T^* = kT/\varepsilon_{\text{HCLJ}}$, $\rho^* = \rho \sigma_{\text{HCLJ}}^3$, and Z_m is the maximum coordination number. The quantities a , b_1 , and b_2 are adjustable parameters, whose values are obtained by fitting the simulation data into eq. (26). In Table IV, the calculated internal energy is compared with that of eq. (27) and simulation data.³⁾

One may notice from Tables III and IV that the results obtained from this work are comparable with those obtained from eqs. (26) and (27). However, eq. (12) has an advantage over the SS EOS, which is the absence of any adjustable parameter in this EOS.

5. Conclusion

We have proposed a new potential function for hard-core fluids that has at least three advantages over other hard-core potentials. These advantages are the reality, flexibility, and simplicity. For example, this potential is more realistic and flexible than the SW potential and more flexible and less complicated than the HCLJ potential. The most important advantage of this potential is the presence of the α parameter that makes the potential more flexible. It is clear that this potential can be reduced to different hard-core potential models, depending on the value of α . Using the proposed potential function along with the Barker–Henderson perturbation theory, a simple perturbed EOS is derived. This EOS has some advantages, the first advantage is the unique feature of the EOS is that it contains the same number of parameters and uses the same expression for different hard-core fluids that is due to the flexibility of the proposed potential function. Secondly, this EOS has no adjustable parameters, therefore, in some regions that there is no simulation data for such hard-core fluids, it may be used to

Table III. Calculated compressibility factor of this work compared to the simulation data and SS EOS at different reduced temperatures and densities for the HCLJ fluid.

ρ^*	T^*	This work	Simulation data ^{a)}	eq. (26)
0.05	1.350	0.844	0.841	0.863
0.100	1.350	0.703	0.716	0.733
0.200	1.350	0.487	0.496	0.503
0.300	1.350	0.373	0.353	0.333
0.400	1.350	0.383	0.258	0.258
0.500	1.350	0.568	0.299	0.331
0.600	1.350	1.014	0.528	0.634
0.700	1.350	1.853	1.206	1.294
0.800	1.350	3.296	2.516	2.517
0.900	1.350	5.691	4.996	4.644
0.05	1.750	0.912	0.912	0.916
0.100	1.750	0.836	0.855	0.841
0.200	1.750	0.738	0.752	0.728
0.300	1.750	0.736	0.711	0.687
0.400	1.750	0.860	0.749	0.753
0.500	1.750	1.167	0.993	0.981
0.600	1.750	1.741	1.364	1.454
0.700	1.750	2.713	2.288	2.300
0.800	1.750	4.293	3.771	3.725
0.900	1.750	6.827	6.213	6.072
0.05	2.000	0.940	0.939	0.939
0.100	2.000	0.890	0.904	0.888
0.200	2.000	0.843	0.845	0.827
0.300	2.000	0.889	0.854	0.842
0.400	2.000	1.064	0.975	0.970
0.500	2.000	1.423	1.229	1.266
0.600	2.000	2.051	1.773	1.813
0.700	2.000	3.079	2.760	2.739
0.800	2.000	4.717	4.290	4.250
0.900	2.000	7.310	6.995	6.692
0.05	3.000	1.001	0.999	0.994
0.100	3.000	1.012	1.022	1.001
0.200	3.000	1.083	1.090	1.064
0.300	3.000	1.247	1.223	1.215
0.400	3.000	1.542	1.470	1.491
0.500	3.000	2.026	1.883	1.947
0.600	3.000	2.783	2.554	2.667
0.700	3.000	3.944	3.667	3.780
0.800	3.000	5.716	5.405	5.492
0.900	3.000	8.444	8.193	8.147
0.05	4.000	1.030	1.027	1.023
0.100	4.000	1.071	1.079	1.060
0.200	4.000	1.202	1.207	1.186
0.300	4.000	1.426	1.415	1.405
0.400	4.000	1.784	1.719	1.755
0.500	4.000	2.331	2.233	2.290
0.600	4.000	3.154	3.022	3.095
0.700	4.000	4.380	4.172	4.298
0.800	4.000	6.219	6.124	6.105
0.900	4.000	9.015	8.813	8.863
0.05	6.000	1.058	1.054	1.052
0.100	6.000	1.129	1.133	1.119
0.200	6.000	1.320	1.322	1.309
0.300	6.000	1.606	1.598	1.596
0.400	6.000	2.027	1.990	2.017
0.500	6.000	2.639	2.576	2.629
0.600	6.000	3.527	3.447	3.514
0.700	6.000	4.820	4.736	4.801
0.800	6.000	6.729	6.648	6.699
0.900	6.000	9.589	9.392	9.550

a) ref. 3.

Table IV. Calculated reduced internal energy of this work compared to the simulation data and SS EOS at different reduced temperatures and densities for the HCLJ fluid.

ρ^*	T^*	This work	Simulation data ^{a)}	eq. (27)
0.100	1.350	-0.751	-0.848	-0.612
0.200	1.350	-1.4562	-1.628	-1.246
0.300	1.350	-2.1225	-2.344	-1.905
0.400	1.350	-2.7679	-3.044	-2.596
0.500	1.350	-3.4096	-3.758	-3.320
0.600	1.350	-4.0563	-4.541	-4.081
0.700	1.350	-4.710	-5.378	-4.883
0.800	1.350	-5.374	-6.253	-5.728
0.900	1.350	-6.049	-7.122	-6.617
0.100	1.750	-0.7135	-0.765	-0.637
0.200	1.750	-1.3997	-1.498	-1.305
0.300	1.750	-2.060	-2.212	-2.005
0.400	1.750	-2.7114	-2.941	-2.740
0.500	1.750	-3.360	-3.711	-3.511
0.600	1.750	-4.015	-4.513	-4.321
0.700	1.750	-4.679	-5.366	-5.171
0.800	1.750	-5.352	-6.240	-6.063
0.900	1.750	-6.032	-7.115	-6.998
0.100	2.000	-0.694	-0.737	-0.649
0.200	2.000	-1.371	-1.459	-1.330
0.300	2.000	-2.029	-2.172	-2.045
0.400	2.000	-2.682	-2.909	-2.795
0.500	2.000	-3.336	-3.680	-3.582
0.600	2.000	-3.996	-4.504	-4.407
0.700	2.000	-4.663	-5.360	-5.271
0.800	2.000	-5.340	-6.237	-6.176
0.900	2.000	-6.025	-7.112	-7.124
0.100	3.000	-0.6472	-0.685	-0.678
0.200	3.000	-1.253	-1.380	-1.387
0.300	3.000	-1.958	-2.097	-2.128
0.400	3.000	-2.616	-2.852	-2.902
0.500	3.000	-3.279	-3.648	-3.710
0.600	3.000	-3.651	-4.482	-4.551
0.700	3.000	-4.629	-5.352	-5.427
0.800	3.000	-5.314	-6.237	-6.338
0.900	3.000	-6.005	-7.105	-7.285
0.100	4.000	-0.6252	-0.662	-0.692
0.200	4.000	-1.268	-1.349	-1.412
0.300	4.000	-1.923	-2.070	-2.161
0.400	4.000	-2.581	-2.826	-2.937
0.500	4.000	-3.250	-3.636	-3.743
0.600	4.000	-3.927	-4.474	-4.578
0.700	4.000	-4.610	-5.342	-5.442
0.800	4.000	-5.301	-6.222	-6.336
0.900	4.000	-5.996	-7.099	-7.260
0.100	6.000	-0.603	-0.642	-0.706
0.200	6.000	-1.234	-1.321	-1.433
0.300	6.000	-1.886	-2.043	-2.181
0.400	6.000	-2.550	-2.810	-2.950
0.500	6.000	-3.219	-3.621	-3.741
0.600	6.000	-3.905	-4.467	-4.552
0.700	6.000	-4.590	-5.339	-5.385
0.800	6.000	-5.287	-6.222	-6.240
0.900	6.000	-5.983	-7.100	-7.116

a) ref. 3.

predict the needed data. Thirdly, for deriving EOS based on the perturbation theory there is no need to know any explicit mathematical form for $g_0(r)$ in the $1 < x < \lambda$ region.

As expressed by eqs. (24) and (25), the proposed equal area approach for determining the values of the parameters is straightforward. Using this EOS, we have calculated the compressibility factor for the SW and HCLJ fluids. The results are presented in Tables I, II, and III, and also shown in Fig. 1. As shown in these tables and Fig. 1, the results of the EOS are in good agreement with the simulation data. The reason for this good agreement may be due to the fact that value of the parameter α is chosen in such a way that the surface underneath of the new extended SW potential function is equal to that of the model potentials (like SW and HCLJ), see eqs. (24) and (25). According to eq. (2) the accuracy of such surface leads to the accurate Helmholtz free energy. In these tables and Fig. 1 the results of our EOS are compared with those of the others EOSs, from which we may conclude that this EOS is compatible with the mentioned equations of state. Therefore, the approximations we used in this work seem to be appropriate. Extension of this work to fluids with a soft repulsive branch of potential remains for the future.

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