Scientia Iranica, Vol. 14, No. 2, pp 118–125
© Sharif University of Technology, April 2007

SCIENTIA
IRANICA

Effect of the Attraction Range of Pair Potential on the Thermodynamic Properties of Fluids

G.A. Parsafar* **and I. Ahadzadeh**[1]

Recently, a new potential model has been proposed for the intermolecular interactions of model pure fluids and it was shown that the derived Equation Of State (EOS), based on this potential, can properly predict the thermodynamic properties of these fluids. In addition to simplicity and, to some extent, the realistic form, this potential has a parameter (α) which controls the range of the attraction tail. In the first part of this study, the proposed potential and derived EOS are extended to binary mixtures of model fluids. In a similar manner to that of the pure fluids, the results obtained are consistent with the data available from simulation studies. In the second part, after modification of the model potential through finding a general temperature dependency for α, the modified potential is used to calculate some equilibrium thermodynamic properties of real pure fluids and their binary mixtures. Again, it was found that the modified potential can suitably predict the thermodynamic properties for pure, as well as binary, mixtures of real fluids.

INTRODUCTION

Understanding the true nature of intermolecular and interatomic forces and their origin, as well as their behavior, is a tedious task. Also, the quantum mechanical calculations for obtaining even a rough representation of the pair potential function is time consuming and inevitably requires the assistance of suitable high-performance computers, capable of undertaking the necessary calculations at a reasonable rate. Therefore, from a practical point of view, in order to calculate the properties of fluids, use is made of various model potential functions. Although it is desirable that a potential model be able to represent the intermolecular forces for various kinds of fluids as accurately as possible, it must still be simple from a mathematical point of view, so that one is able to deduce the thermodynamic properties of the system without engaging in complicated mathematics. However, having these desirable factors simultaneously seems to be impossible.

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

Recently, a new analytical EOS was developed to predict the properties of hard-core model pure fluids [1]. The approach is based on the Barker-Henderson (BH) perturbation theory, along with a new pair potential function [2]. Even though their proposed potential function is as simple as the square well (SW) potential, it is more flexible than the SW, Hard-Core Lennard-Jones (HCLJ) and Lennard-Jones (LJ) potentials.

In the current study, the aim is to extend the proposed potential function, first, to model binary mixtures, then, modifying it in such a way that it can be used for predicting the equilibrium thermodynamic properties of real fluids, as well as their binary mixtures.

POTENTIAL FUNCTION

The proposed model pair potential function is a new extended SW potential function and, in fact, is a compromise between simplicity, reality and flexibility [1].

---

*. *Corresponding Author, Department of Chemistry, Sharif University of Technology, Tehran, I.R. Iran.*

[1] *Department of Chemistry, Sharif University of Technology, Tehran, I.R. Iran.*

The mathematical form of the new pair potential function, is as follows:

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

where, $x = r/\sigma$ is the intermolecular distance in units of hard-sphere diameter, σ. The quantity, ε, represents the potential well depth (minimum potential energy), λ is the reduced well width and α is an additional parameter responsible for the further flexibility of the potential, through changing the steepness of the potential tail, i.e. controlling the range of the attraction tail. The cut-off of the potential for $x > 3$ is reasonable, because, according to the well known Lennard-Jones potential (which is theoretically valid at least for the spherically symmetric molecules), the attraction decreases with x; as $\frac{1}{x^6}$. It means that the attraction energy for $x > 3$ is less than 0.14 percent of that at $x = 1$.

Using the above illustrated potential function, along with the perturbation theory of BH, a new EOS for the hard-core model fluids was derived showing a good agreement with available simulation data for the compressibility factor (Z) of the model pure fluids [1]. The derived EOS, represented in full detail in [1], is, as follows:

$$\begin{aligned}Z=Z_0\quad&\frac{\varepsilon}{2kT}\left[y(\frac{\partial H}{\partial y})+8\lambda^3y\quad\frac{24\alpha Gy}{3\quad\lambda}\right]\\&\frac{6yH}{(kT)^2}\left(I+y\frac{\partial I}{\partial y}\right)\;\;6y^2\left(\frac{\partial H}{\partial y}\right)\left(\frac{1}{kT}\right)^2\left(I+y\frac{\partial I}{\partial y}\right)\\&6y^2H(\frac{1}{kT})^2\left(2\frac{\partial I}{\partial y}+y\frac{\partial^2 I}{\partial y^2}\right),\end{aligned}\tag{2}$$

in which:

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

$$G=\frac{1}{2\lambda^2}\quad\frac{1}{\lambda^3}\quad\frac{1}{54},\tag{4}$$

$$\begin{aligned}I=\frac{\varepsilon^2}{24y}(H+8\lambda^3y\quad 1)\quad&\frac{\alpha^2\varepsilon^2}{(3\quad\lambda)^2}\Big(\frac{1}{13024}\quad\frac{1}{\lambda^9}\\&+\frac{3}{4\lambda^8}\quad\frac{1}{7\lambda^7}\Big),\end{aligned}\tag{5}$$

$$H=\frac{(1\quad y)^4}{1+4y+4y^2\quad 4y^3+y^4},\tag{6}$$

where Z denotes the compressibility factor and $y = \frac{\pi}{6}\rho\sigma^3$ (where $\rho = \frac{N}{V}$ is the number density) stands for the so-called packing fraction. It must be noted that one can regard λ as an adjustable parameter, as is the case in dealing with, for example, the SW model; but, for the model to become more simple and in order to reduce the mathematical work required, such as reported in other cases [3], a constant value was assigned for λ, chosen here to be 1.4, i.e., throughout the work $\lambda = 1.4$. This chosen value for λ is solely based on similar studies on the SW fluid properties.

EXTENSION OF THE EOS TO MODEL BINARY MIXTURES

In order to investigate both binary and multicomponent mixtures of fluids, customarily, a total understanding of thermodynamic properties is obtained, based on corresponding ones for each component in its pure state. In other words, a relationship is set between the thermodynamic properties of pure fluids and their mixtures using the so-called mixing rules as a bridge [4]. For binary, as well as ternary, mixtures of real and model fluids, extensive and detailed mixing rules were proposed and investigated in [5]. Using one pair of the simplest mixing rules, i.e., Lorentz-Berthelot approximation [6], the position was reached to test the applicability of the proposed new potential model and deduced EOS in predicting the compressibility factor of the model binary mixtures of hard-core fluids for which Monte Carlo simulation data are available [7]. According to Berthelot-Lorentz mixing rules, the unlike diameter, σ_{ij}, and unlike potential well, ε_{ij}, may be expressed in terms of those of the like parameters as:

$$\sigma_{ij}=\frac{\sigma_i+\sigma_j}{2},\qquad \varepsilon_{ij}=(\varepsilon_i\varepsilon_j)^{\frac{1}{2}}.\tag{7}$$

The variable of the packing fraction for a mixture was defined as:

$$y_{\text{mix}}=\frac{\pi}{6}\rho\sigma^3_{\text{mix}}=\frac{\pi}{6}\rho\left(\sum_i x_i\sigma_i^3\right)=\frac{\pi}{6}\rho^*.\tag{8}$$

Equation 8, for a binary mixture, takes the form, as below:

$$y_{\text{mix}}=\frac{\pi}{6}\rho(x_1\sigma_1^3+x_2\sigma_2^3),\tag{9}$$

where, x_1 and x_2 indicate the molar fraction of the components 1 and 2, respectively.

Based on assumptions made in Equations 7 and 9, to the first order of the BH perturbation theory, one can obtain the following EOS for model binary mixtures:

$$\begin{aligned}Z_{\text{mix}}=Z_0\quad&\sum_{i,j=1}^{2}x_ix_j(\frac{\varepsilon_{ij}}{2kT})\Big[y_{ij}(\frac{\partial H_{ij}}{\partial y_{ij}})+8\lambda^3y_{ij}\\&\frac{24\alpha Gy_{ij}}{3\quad\lambda}\Big],\end{aligned}\tag{10}$$

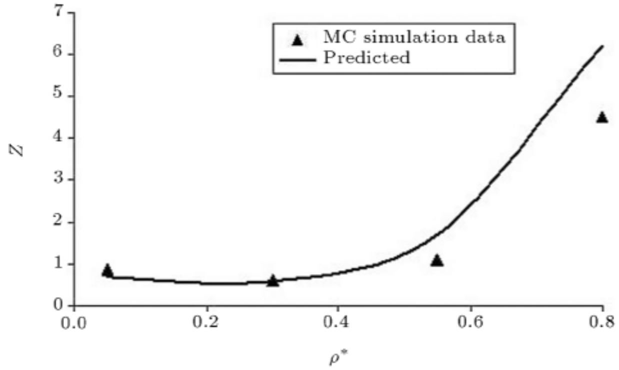

Figure 1. Compressibility factor of the model binary mixture with $\sigma_1 = \sigma_2$, $\frac{kT}{\varepsilon_{11}} = 2$ and $x_1 = 0.5$.

in which,

$$y_{ij} = \frac{\pi}{6}\rho\sigma_{ij}^3. \tag{11}$$

Using Equation 10, the compressibility factor of model binary mixtures of hard-core fluids was calculated. Figure 1 shows the results, along with data produced by the Monte Carlo simulation technique [7]. As can be seen from this figure, overall agreement is fairly good, i.e., the proposed model is capable of reproducing Z for the model binary mixtures as accurately as that for the model pure fluids [1].

EXTENSION OF THE EOS TO REAL PURE FLUIDS

The derived EOS (Equation 2) may be expanded in a Taylor series, in order to obtain a virial type EOS for which the second virial coefficient is, as follows:

$$B(T) = b_0\Big(1 \quad \frac{1.744\varepsilon}{kT} \quad \frac{0.24\varepsilon\alpha}{kT} \quad \frac{0.872\varepsilon^2}{(kT)^2} \quad \frac{0.00652\varepsilon^2\alpha^2}{(kT)^2}\Big), \tag{12}$$

where, b_0 is the second virial coefficient of the hard-sphere model [6].

After using the dimensionless reduced parameters of $T^* = \frac{kT}{\varepsilon}$ and $B^*(T^*) = B(T^*)/b_0$, Equation 12 can be rewritten as:

$$B^*(T^*) = 1 \quad \frac{1.744}{T^*} \quad \frac{0.24\alpha}{T^*} \quad \frac{0.872}{T^{*2}} \quad \frac{0.00652\alpha^2}{T^{*2}}. \tag{13}$$

The first derivative of Equation 13 with respect to T^* is as below:

$$\frac{dB^*}{dT^*} = \frac{1.744}{T^{*2}} + \frac{0.24\alpha}{T^{*2}} + \frac{1.744}{T^{*3}} + \frac{0.01304\alpha^2}{T^{*3}}. \tag{14}$$

Due to the fact that $\frac{dB^*}{dT^*} > 0$, the graph of B^* versus T^* does not exhibit any maximum as do other hard-core potentials [6]. However, this is not the case with real fluids for which, at a high temperature (so-called inversion temperature), the second virial coefficient passes through a maximum. Therefore, it is reasonable to suppose that α, which is responsible for the range of the attraction tail of the pair potential, is not in fact a constant, but a function of the temperature, i.e.:

$$\alpha = \alpha(T^*). \tag{15}$$

It must also be noted that some studies have dealt with the effect of temperature on pair potential parameters [8]. In fact, only when this interaction is regarded as being effective, i.e. only when one considers an effective pair potential, does the effect of temperature and state of the system on potential parameters become physically meaningful [9]. This reasoning has its roots in the fact that temperature makes no physical sense in a system consisting of only two interacting particles.

However, the logic behind assigning a temperature dependency for the parameter α is rather different from the above mentioned reasoning. Due to the fact that molecules are not perfectly rigid but to some extent can be regarded as possessing a hard core surrounded by a rather penetrable outer shell, at high temperatures, especially near the above introduced inversion temperature, molecules have a significant kinetic energy. So, molecules at such temperatures can penetrate each other to a further or lesser extent at the instant of collision, resulting in a pair potential interaction model, in which the diameter (σ) of each molecule is explicitly temperature dependent. But, the model in hand (Equation 1) is a hard-core one. The term hard-core means that the molecules behave as totally rigid spheres with, necessarily, a fixed value for their diameter. Therefore, the above mentioned penetrability is no longer possible. On the other hand, hard-core potentials are well-developed in literature, with many beneficial aspects [10]. Because hard-core potential models are of great importance in fluid theories, due to the following facts, one should make use of the new pair potential, (Equation 1):

(i) Fluid properties may be expressed analytically,

(ii) They are used as a reference state in the perturbation theory of simple liquids,

(iii) The behavior of all simple liquids approaches that of the hard-core fluids at high density and temperature.

However, in order to mimic the behavior of real fluids, especially at high temperatures, a more flexible attraction may be assumed in this range, by assigning a temperature dependency for α.

In order to obtain a crude insight about the trend of variation of $\alpha(T^*)$ with T^*, the reported values of $B_2(T)$ [11] and the corresponding values of σ and ε

for the Lennard-Jones potential [12] for the five gases He, N_2, O_2, CO and NO, have been used in order to reduce the temperature and reported values of $B_2(T)$. Then, by solving Equation 13 for $\alpha(T^*)$ the following is obtained:

$$\alpha = \quad 18.4T^* + 0.06135$$
$$\times \sqrt{130750T^{*2} \quad 40750B^*(T^*)T^* \quad 71068T^* \quad 35534}. \tag{16}$$

It should be noted that the reported values for $B_2(T)$ at high temperatures are not, in fact, direct experimentally obtained values, but derived from high energy molecular beam scattering investigations, along with an accurate correlation, based on the principle of corresponding states [11].

Using Equation 16, the trend of α versus T^* can now be presented. The general trend of the variation of α with T^* for the two fluids N_2 and O_2 is shown in Figure 2. After some trials, along with making use of the statistical software, Table Curve, through fitting with various functional forms, the best general function for $\alpha(T^*)$, simultaneously applicable to all studied fluids, was found to be:

$$\alpha(T^*) = 0.34 + 0.4T^* + 0.46T^* \ln T^*. \tag{17}$$

The criteria for selecting this function are threefold, namely:

a) Seeking a general function relying on the validity of the principle of corresponding states, due to the structural simplicity of the studied fluids;

b) Good reproduction of the reported second virial coefficient within the whole temperature range involved and, finally;

c) Reasonable prediction of the inversion temperature.

Substituting this general function for $\alpha(T^*)$ into Equation 13 gives a general expression for the second virial coefficient of the real fluid in a reduced form, as follows:

$$B^*(T^*) = 1 \quad \frac{1.744}{T^*} \quad \frac{0.24\alpha(T^*)}{T^*} \quad \frac{0.872}{T^{*2}}$$
$$\frac{0.00652[\alpha(T^*)]^2}{T^{*2}}, \tag{18a}$$

or:

$$B(T) = \left(\frac{2\pi N_A \sigma^3}{3}\right)\Big(1 \quad \frac{1.744\varepsilon}{kT} \quad \frac{0.24\varepsilon\alpha(T)}{kT}$$
$$\frac{0.872\varepsilon^2}{k^2T^2} \quad \frac{0.00652\varepsilon^2[\alpha(T)]^2}{k^2T^2}\Big). \tag{18b}$$

The reported values of $B_2(T)$ for all studied gases have been well fitted into the final expression, as shown in Figure 3. Parameters of the modified potential, obtained on the basis of second virial coefficient data, are given in Table 1.

In order to calculate the value of the inversion temperature, the first derivative of Equation 18, with respect to the reduced temperature, was set equal to zero and, via numerical solution, it was found that the inversion temperature at which Equation 18 has its maximum, corresponds to a value of $T^* = 14.06 \pm 0.02$. In the case of the Lennard-Jones model, use was made of the tabulated values of $B^*(T)$ versus T^* to get the inversion temperature at $T^* = 35.25 \pm 0.01$ [12].

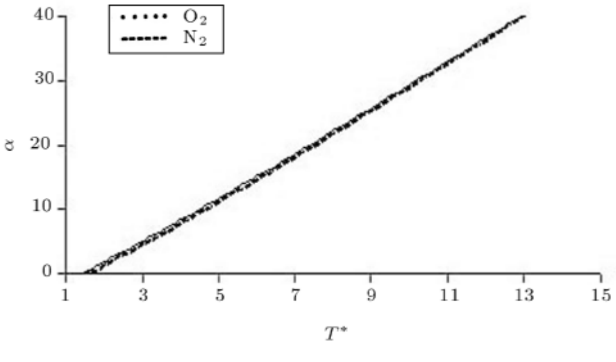

Figure 2. Variation of α with T^* for O_2 and N_2.

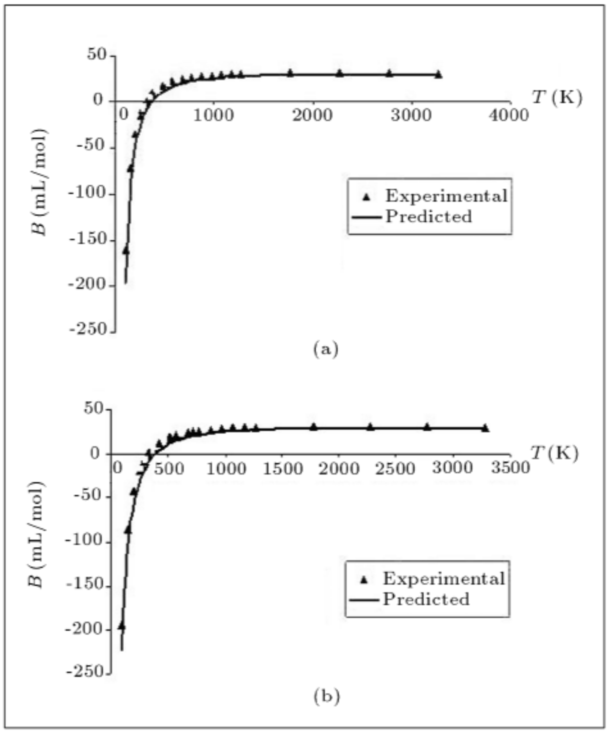

Figure 3. The second virial coefficient of a) N_2 and b) CO as predicted by the modified model, Equation 18b.

Table 1. Modified potential parameters obtained from the second virial coefficient data.

Fluid	ε/k **(K)**	σ **(Å)**	b_0 **(mL/mol)**
He	10.1	2.70	25.0
CO	143.4	3.70	64.3
NO	172.5	3.55	56.5
$\mathbf{O_2}$	162.4	3.48	53.4
$\mathbf{N_2}$	134.4	3.69	63.6

Table 2 gives the inversion temperature as predicted by the modified as well as Lennard-Jones (6-12) potentials along with the reported values [11]. It can be seen that the modified model (i.e., when assigning a temperature dependency to the parameter, α, according to Equation 17) can reproduce the inversion temperature accurately, whilst the Lennard-Jones (6-12) potential gives very high values for this temperature.

Also, to obtain an expression for the second virial coefficient, Equation 18 was used to calculate the Joule-Thomson coefficient (μ_{JT}) at zero pressure, via the following well-known thermodynamic relation:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P \quad V\right], \tag{19}$$

or, equivalently, by using its relation with the second virial coefficient in its reduced form [12]:

$$\mu_{JT} = \frac{b_0}{C_P^0}\left(T^*\frac{dB^*}{dT^*} \quad B^*\right), \tag{20}$$

where, C_p^0 is the constant pressure heat capacity at zero-pressure limit, whose values were taken from [13]. Results are shown in Figure 4. As can be seen from this figure, overall agreement in the case of μ_{JT} is reasonable.

One may use the obtained value of ε, along with Equation 17 for α to calculate the compressibility factor and internal energy (U) of any real fluid as a function of the packing fraction (or, equivalently, pressure) via:

$$Z = Z_0 \quad \frac{\varepsilon}{2kT}\left[y(\frac{\partial H}{\partial y}) + 8\lambda^3 y \quad \frac{24\alpha G y}{3 \quad \lambda}\right], \tag{21}$$

and:

$$U = \frac{3}{2}kT \quad \frac{\varepsilon}{2}\left[y(\frac{\partial H}{\partial y}) + 8\lambda^3 y \quad \frac{24\alpha G y}{3 \quad \lambda}\right]. \tag{22}$$

For two fluids, the results are shown in Figures 5 and 6. Experimental values are taken from [13].

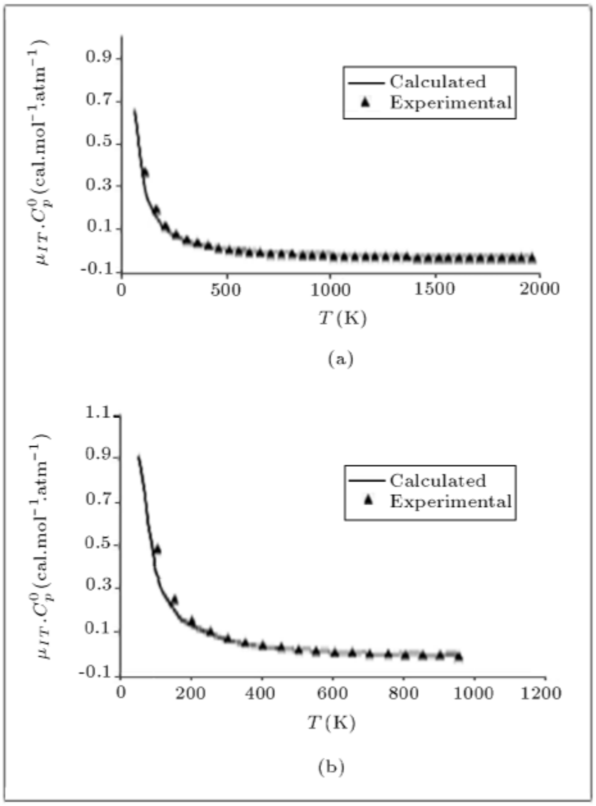

Figure 4. The zero-pressure Joule-Thomson coefficient of a) N_2 and b) O_2 as a function of temperature.

Table 2. The inversion temperature of the studied fluids (reported values for T_i are calculated using the data of [11]).

Fluid	T_i **(K) Reported**	T_i **(K) Predicted**	T_i **(K) LJ(6-12)**	**% Error of the Modified Model**
He	170 ± 10	162 ± 15	378 ± 25	4.7
$\mathbf{N_2}$	2150 ± 130	2160 ± 150	2533 ± 110	0.46
$\mathbf{O_2}$	2650 ± 150	2610 ± 120	4356 ± 150	1.5
CO	2230 ± 130	2304 ± 125	3707 ± 120	3.3
NO	2750 ± 140	2772 ± 155	4847 ± 180	0.8

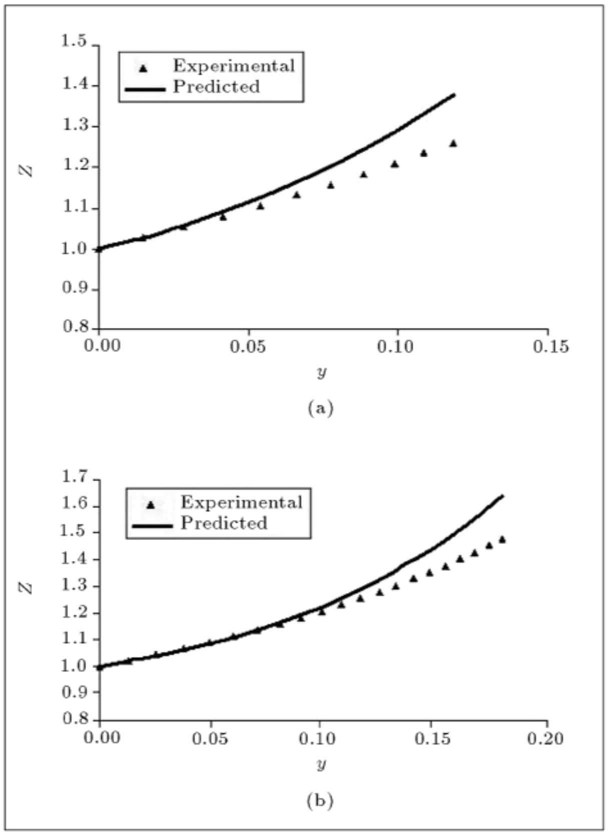

Figure 5. The compressibility factor of a) He at 500 K and b) CO at 700 K versus packing fraction.

EXTENSION OF THE EOS TO REAL BINARY MIXTURES

In this section, the extended EOS in virial form, i.e. Equation 18, along with the simple mixing rules of Lorentz-Berthelot, were used to predict the second virial coefficient of equimolar mixtures of N_2+O_2, N_2+NO and N_2+CO. The second virial coefficient for a binary mixture, assuming a random distribution of species, can be written as [6]:

$$B_{\text{mix}}(T) = x_1^2B_1(T) + 2x_1x_2B_{12}(T) + x_2^2B_2(T), \qquad (23)$$

where, B_{ij} stands for the second virial coefficient of the pair, i and j.

In order to calculate the cross second virial coefficient, $B_{12}(T)$, one may again use the simple mixing rules of Lorentz-Berthelot i.e.:

$$\varepsilon_{12} = \sqrt{\varepsilon_1\varepsilon_2}, \qquad \sigma_{12} = \frac{\sigma_1+\sigma_2}{2},$$

$$b_{0(12)} = \frac{2}{3}\pi N_A\sigma_{12}^3. \qquad (24)$$

A sample result is shown in Figure 7. Again, the agreement with reported values [14] is good. In Table 3, the reported values of the inversion temperature, as well as those predicted by the modified model and LJ (6-12) potentials, were depicted. As in the case with pure fluids, the modified model represents a much better prediction than those of the LJ (6-12) potential. Also, the predicted value of T_i for some other binary mixtures for which no reported values are available, is given in the same table. Even though it is believed that the second virial coefficient is not sensitive enough to differentiate between unrealistic model potentials [6], this is true only for a small temperature range. In fact, it has recently been shown that, if the temperature range is very large, in such a way that covers the inversion temperature, the second virial coefficient may be considered useful criterion for the model potential [15].

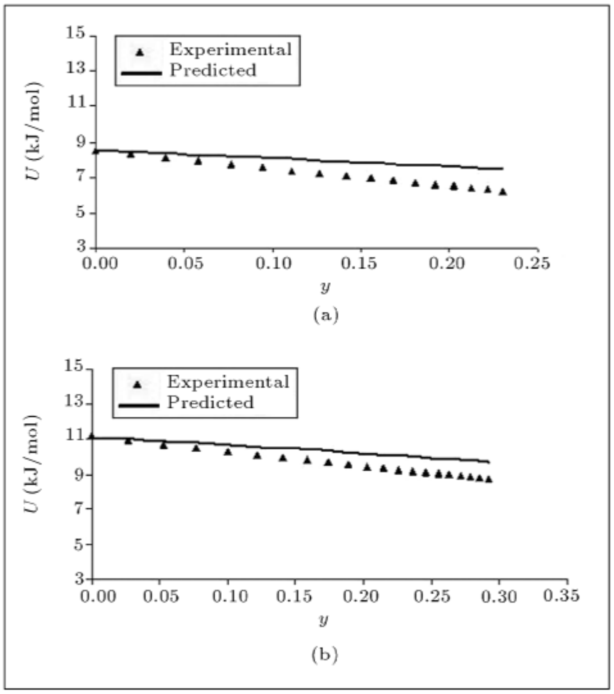

Figure 6. Internal energy of a) O_2 at 250 K and b) CO at 200 K versus packing fraction.

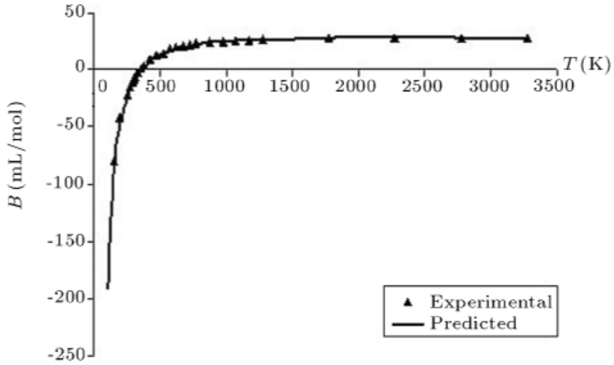

Figure 7. The same as Figure 3 but for an equimolar binary mixture of N_2+O_2.

Table 3. The inversion temperature of binary mixtures (reported values for T_i are calculated using the data of [11]).

Mixture	**T_i (K) Reported**	**T_i (K) Predicted**	**T_i (K) LJ (6-12)**
N_2+NO	2200 ± 110	2273 ± 115	4150 ± 210
N_2+O_2	2160 ± 113	2260 ± 115	3920 ± 180
N_2+CO	2270 ± 114	2273 ± 117	3620 ± 150
He+N_2	—	1850 ± 95	2670 ± 160
He+O_2	—	1900 ± 95	2700 ± 140
He+CO	—	1900 ± 95	2670 ± 135
He+NO	—	1850 ± 90	2750 ± 135
O_2+CO	—	2150 ± 110	3970 ± 190
O_2+NO	—	2273 ± 115	4100 ± 210
CO+NO	—	2200 ± 110	4150 ± 210

CONCLUSION

Due to the simplicity of the mathematical form and, to some extent, the reality and flexibility of the proposed pair potential and the derived EOS, on the basis of the BH perturbation theory and its capability to predict the thermodynamic properties of model and real pure fluids, as well as their binary mixtures, the modified potential can be used whenever thermodynamic data are not available. For simplicity of calculation, the authors wished to use this hard-core model, but, in such a way that it can predict the observed behavior of the second virial coefficient and the inversion temperature. Therefore, in this study, parameter α is considered to be temperature dependent, so that, at higher temperatures, the contribution of the attraction tail in the potential increases. As mentioned earlier, the inversion temperature corresponds to a temperature at which, due to high kinetic energy, molecules can penetrate each other to some extent. A larger value for this inversion temperature can be considered as the larger kinetic energy required by molecules to penetrate into the repulsive branch of the pair potential, so, it can be stated that, according to Table 2, the Lennard-Jones (6-12) potential expresses a sharper or steeper repulsion branch compared with the real potential. The inappropriateness of such a well known potential, suitable mainly for spherically symmetric molecules (at least qualitatively), has been pointed out by some recent studies [16-19].

As can be seen in Figures 1, 5 and 6, the calculated values for Z and U are in good agreement with experimental data at low and moderate densities. However, the agreement is poor at high densities. Such behavior is expected, because of the fact that the unperturbed state is chosen at $\rho \rightarrow 0$. When ρ increases, the contributions of the higher order terms, which are neglected throughout this work, become significant.

REFERENCES

1. Farrokhpour, H. and Parsafar, G.A. "A new analytical expression for the free energy of hard-core fluids", *Journal of the Physical Society of Japan*, **72**(11), pp 2747-2753 (2003).
2. Barker, J.A. and Henderson, D. "Perturbation theory and equation of state for fluids: The square-well potential", *J. Chem. Phys.*, **47**(8), pp 2856-2861 (1967).
3. Alder, B.J. et al. "Studies in molecular dynamics. Corrections to the augmented van der Waals theory for the square-well fluid", *J. Chem. Phys.*, **56**, p 3013 (1972).
4. Ghotbi, C. and Vera, J.H. "Performance of three mixing rules using different equations of state for hard-spheres", *Fluid Phase Equilibria*, **187-188**, pp 321-336 (2001).
5. Šindelka, M. et al. "Simulations in ternary hard-sphere mixtures", *Fluid Phase Equilibria*, **143**, pp 13-27 (1998).
6. McQuarrie, D.A., *Statistical Mechanics*, Harper Collins Publishers (1976).
7. Lee, R.J. and Chao, C.K. "Coordination number and thermodynamics of square-well fluid mixtures", *Molecular Physics*, **A**, pp 1431-1442 (1987).
8. Nasehzadeh, A. et al. "The effect of temperature on the Lennard-Jones (6-12) pair potential function", *Journal of Molecular Structure*, **589-590**, pp 329-335 (2002).
9. Keshavarzi, E. et al. "The state dependency of the effective pair potential parameters", *Polish. J. Chem.*, **78**, pp 1893-1906 (2004).

10. Zhang, Z.Y. et al. “The use of statistical associating fluid theory to improve the BACK equation of state, I. pure fluids”, *Fluid Phase Equilibria*, **172**(2), pp 111-127 (2000).

11. Boushehri, A. et al. “Equilibrium and transport properties of polyatomic gases”, *J. Phys. Chem. Ref. Data*, **16**(3), pp 448-458 (1987).

12. Hirschfelder, J.O. et al., *Molecular Theory of Gases and Liquids*, John Wiley, New York (1964).

13. http://webbook.nist.gov/chemistry/fluid.

14. Bzowski, J. et al. “Equilibrium and transport properties of gases at low density: Eleven polyatomic gases and five noble gases”, *J. Phys. Chem. Ref. Data*, **19**(5), pp 1179-1232 (1990).

15. Parsafar. G.A. et al. “Calculation of equilibrium and transport properties using modified hard-core potential models”, *Chem. Phys.*, **326**, pp 257-534 (2006).

16. Girifalco, L.A. “Molecular properties of C_{60} in the gas and solid phases”, *J. Chem. Phys.*, **96**, pp 858-861 (1992).

17. Ashcroft, N.W. “Elusive diffusive liquids”, *Nature*, **365**, pp 387-388 (1993).

18. Sandler, S.I. “Quantum mechanics: A new tool for engineering thermodynamics”, *Fluid Phase Equilibria*, **210**, pp 147-160 (2003).

19. Garrison, S.L. and Sandler, I.I. “Ab initio pair potential and phase equilibria predictions for hydrogen chloride”, *J. Chem. Phys.*, **118**, pp 4086-4093 (2003).