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Critical and reduced properties of real fluids: Sutherland potential

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ABSTRACT

In this paper, the critical and reduced properties of several real fluids such as *Ne*, *N₂*, *CO*, and *etc.*, are studied. For this goal, the Sutherland potential model and the perturbed virial expansion are applied. We also use three

different compressibility factors ($\frac{P}{\rho k_B T}$) and show their influence to calculate the reduced and critical temperatures and densities of the fluids.

According to the obtained results, it is deduced that the critical and reduced properties for some fluids (no all) are in good agreement with experimental data. This means that the Sutherland potential model can not be used to determine the critical and reduced properties of any real fluids.

We also found that the best results can be obtained when the Sutherland potential model has been applied with the second compressibility factor.

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KEYWORDS

Critical property;
Reduced property;
Sutherland potential.

INTRODUCTION

Statistical mechanics provides a means of determining the structure, thermodynamical properties, and therefore the macroscopic properties of the fluids based on information about underlying forces acting between the atoms or molecules^[1]. Using the statistical mechanics formalism, one can explain the physical properties of matter in bulk on the basis of the dynamical behavior of its microscopic constituents. The scope of the statistical mechanics formalism is interesting and almost as unlimited as the very range of the natural phenomena; for in principle it is applicable to matter in any state whatsoever.

An equation of state (EOS) is a formula for de-

scribing the interconnection between various macroscopically measurable properties of a fluid^[2]. EOS only presents the behavior of physical states of matter, not the conversion from one state to another. This equation usually relates the various thermodynamic variables such as pressure, volume, temperature, and number of atoms to one another^[3].

The most prominent use of an EOS is to predict the state of gases and liquids. So far, many efforts have been performed to describe equations of states such as van der Waals, Redlich-wong, Peng-Robison, virial and *etc*^[4-7]. The virial equation of state is a standard approach used to represent experimental data of real gases. Unlike other EOS such as the van der Waals (which is, at best, very approximate) and the Beattie-

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Bridgeman (which is now rarely used), the virial EOS can be derived from exact statistical mechanic theory.

The virial expansion of the pressure of an imperfect gas is a power series in the number density^[7].

$$\frac{P}{\rho k_B T} = 1 + B_2 \rho + B_3 \rho^2 + \dots \quad (1)$$

Where B_i is called the i th virial coefficient and ρ is the number density. At not too high densities the third and higher order terms might be neglected. Furthermore, at high densities many terms of the series must be included to obtain satisfactory accuracy, and this means that many parameters have to be determined experimentally. It is to be noted that the virial coefficients can be calculated by using a numerical method.

From the theoretical point of view, the virial expansion can be used to determine an EOS when an intermolecular potential model is given. Basically, the interaction between particles in a real fluid is very complex. Since the long, many scientists have tried to predict the intermolecular potentials in fluids using physics laws. Therefore, the various potential models were presented to describe the interaction between particles in fluids. They also tried to formulate the models by the simple mathematical expressions. Hence, much intermolecular potential have discussed^[1,8].

After giving an intermolecular potential model, the virial coefficients can be calculated. Hitherto, the first few virial coefficients have been calculated for various potential models such as hard sphere, hard disk, hard-cube model, Lennard-Jones, square-well potential and real fluids^[9-11].

It is worth mentioning that the usefulness of the virial expansion has been a little broader. The virial expansion can be employed to predict the critical and reduced properties of fluids^[12,13]. So far, many works have been made in studying the critical points using the virial expansion and different potential models^[14-16].

With respect to importance of virial coefficients, we intend to calculate the critical and reduced temperatures and densities for several real fluids. For this goal, we use the Sutherland potential model and the perturbed virial expansion to obtain these properties.

The article is organized as follows: In Sec. 2, the Sutherland potential model and its second virial coefficient is presented. In Sec. 3, calculation method of the

critical and reduced properties is briefly described. In Sec. 4, the results are shown and discussed. Finally, the conclusion is presented in Sec. 5.

SUTHERLAND POTENTIAL MODEL

The interaction between molecules naturally depends on structure and shape of the molecules. For simplicity, we shall only consider the interaction between simple molecules^[1].

The general form of the interaction between atoms or molecules comprises a repulsive part at short distances and attractive part at large distances. The Sutherland potential is often used as an analytical representation of the interaction. For non-polar fluids consist of spherical particles, the Sutherland potential model can be used which may be considered as a fairly sufficient potential model.

In the Sutherland potential model, the short-distance repulsion approximates the interaction as a hard core. The attractive tail is described by the conventional dipolar r^{-6} law. However, it is instructive and possible to consider a generalization of this model whereby the long-range attraction is described by a general power $r^{-\gamma}$ law^[1,17,18].

The mathematical term for this model is following as

$$V(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon r^{-\gamma} & r > \sigma \end{cases} \quad (2)$$

Where the parameter γ is usually taken to be 6. Using this potential, one can obtain the second virial coefficient as

$$B_2(T) = -b_0 \sum_{m=0}^{\infty} \frac{1}{m!} \left(\frac{3}{m\gamma - 3} \right) \left(\frac{\epsilon}{\sigma^\gamma k_B T} \right)^m \quad (3)$$

Where $b_0 = 2\pi\sigma^3/3$ is the hard-sphere second virial coefficient.

THE CRITICAL AND REDUCED TEMPERATURES

The extent to which the PVT behavior of gas is non-ideal depends upon its P and T . The term "critical point" is sometimes used to denote specifically the vapor-liquid critical point of a material. The vapor-liquid

critical point denotes the conditions above which distinct liquid and gas phases do not exist. The thermal motion of the molecules prevents them from sticking together. We could gradually compress this gas until it has attained the density of a liquid without it ever condensing^[19].

To calculate the critical properties of a fluid, we use the perturbed virial expansion. The perturbed virial expansion can be obtained from expanding the compressibility factor of both the fluid interest and a suitable reference fluid in powers of density,

$$\frac{P}{\rho k_B T} = \left(\frac{P}{\rho k_B T}\right)_{\text{ref}} + \sum_{i \geq 2} \Delta B_i \rho^{i-1} \quad (4)$$

Where $\left(\frac{P}{\rho k_B T}\right)$ is the compressibility factor and ΔB_i are the residual virial coefficients, $\Delta B_i = B_i - B_{\text{ref},i}$. The dimensionless terms^[20] $B_{\text{ref},i}$ are known analytically for $i=1, 2, 3$. The obvious choice of reference fluid in this case is hard-sphere (HS) fluid of diameter σ , with the few first virial coefficients being

$$B_{\text{HS},2} = b_0, B_{\text{HS},3} = 0.625b_0^2, B_{\text{HS},4} = 0.2906b_0^3 \quad (5)$$

To calculate the fluid critical points, we apply the different compressibility factor instead of the first term of Eq.(5)^[1, 21, 22].

$$\phi_v^{\text{PY}} = \left(\frac{P}{\rho k_B T}\right)_{\text{ref};1} = \frac{1 + 2\eta + 3\eta^2}{(1 - \eta)^2} \quad (6)$$

$$\phi_C^{\text{PY}} = \left(\frac{P}{\rho k_B T}\right)_{\text{ref};2} = \frac{1 + \eta + \eta^2}{(1 - \eta)^3} \quad (7)$$

$$\phi^{\text{CS}} = \left(\frac{P}{\rho k_B T}\right)_{\text{ref};3} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (8)$$

Where $n = \pi\sigma^3/6$ is the packing fraction. Using this method, we intend to show the influence of compressibility factor for predicting the critical points.

On a pressure-density diagram, the critical point is an inflection point. Thus, the following conditions should be satisfied to obtain the critical points.

$$\left(\frac{\partial P}{\partial \rho}\right)_c = 0, \left(\frac{\partial^2 P}{\partial \rho^2}\right)_c = 0 \quad (9)$$

These relations can be used to evaluate two parameters for an equation of state in terms of the critical properties.

The unique relationship between the compress-

ibility factor and the reduced temperature, T_r and the reduced pressure, P_r was first recognized by van der Waals in 1873 and is known as the two-parameter principle of corresponding states^[23]. We introduce new variables P_r, T_r , and ρ_r as the reduced variables that relate P, T , and ρ in terms of critical constant, P_c, T_c , and ρ_c . Therefore, the reduced parameters are defined as

$$T_r = \frac{T}{T_c}, \rho_r = \frac{\rho}{\rho_c} \quad (10)$$

RESULTS AND DISCUSSION

In this part, we intend to examine the critical and reduced properties of several real fluids like Ne, N_2, CO, NO , and O_2 by using the aforementioned theory in previous section. For this purpose, we use the Eqs. (4)- (9) to determine the critical properties. Then, using Eq. (10), one can obtain the reduced properties of the real fluids.

TABLE 1 shows the critical density for several real fluids using the Sutherland potential model. In this TABLE, we have applied Eqs. (6)- (8) as Ref1, Ref2, and Ref3. The obtained results have also been com-

TABLE 1 : Critical density of real fluids obtained by using the perturbed virial expansion and the Sutherland potential model [using the Eqs. (6) to (8)]. Our results have been compared with experimental data^[23] (Exp.).

Fluid	Ref (1)	Ref (2)	Ref (3)	Exp.
Ne	0.0340	0.0325	0.0330	0.0238
N ₂	0.0128	0.0123	0.0124	0.0111
O ₂	0.0158	0.0151	0.0153	0.0137
CO	0.0125	0.0120	0.0121	0.0108
NO	0.0148	0.0141	0.0143	0.0172

TABLE 2 : Critical temperature of real fluids obtained by using the perturbed virial expansion and the Sutherland potential model [using the Eqs. (6) to (8)]. Our results have been compared with experimental data^[23] (Exp.).

Fluid	Ref (1)	Ref (2)	Ref (3)	Exp.
Ne	49.8	49.0	49.3	44.4
N ₂	130.1	128.1	128.6	126.2
O ₂	160.2	157.5	158.3	154.6
CO	140.2	138.0	138.5	132.9
NO	165.4	168.4	166.3	180.2

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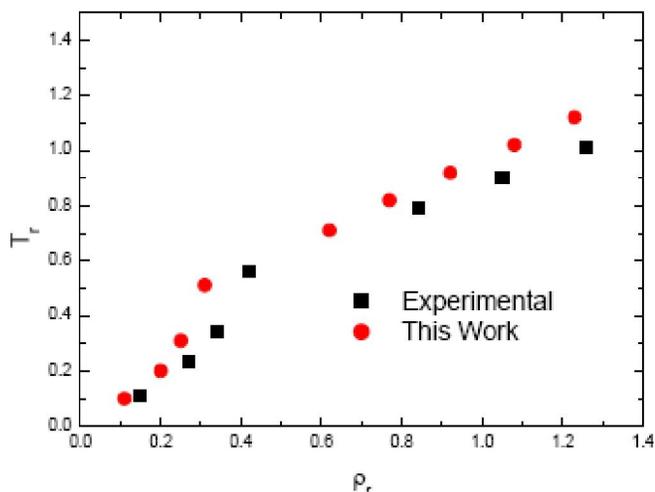


Figure 1 : Reduced temperature as a function of reduced density for Ne [using the Ref2].

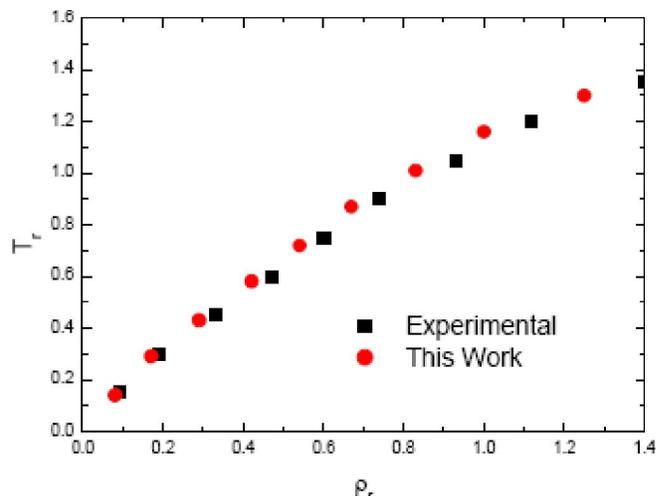


Figure 4 : The same as Figure 1, but for CO.

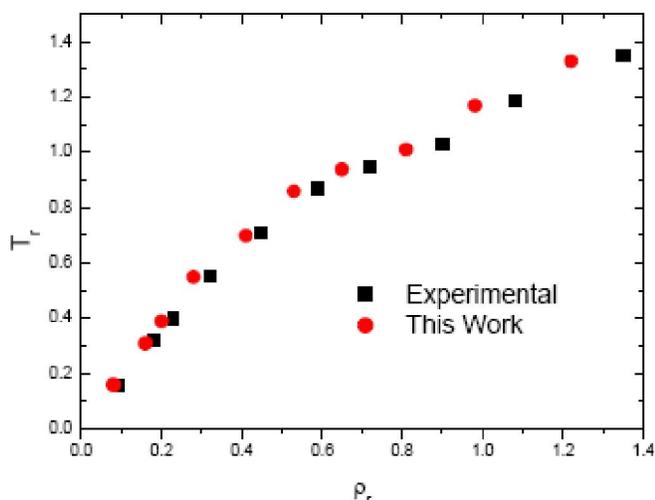


Figure 2 : The same as Figure 1, but for N₂.

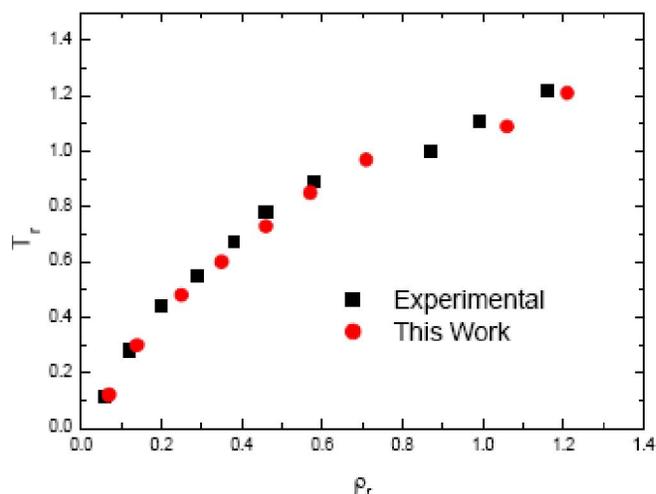


Figure 5 : The same as Figure 1, but for NO.

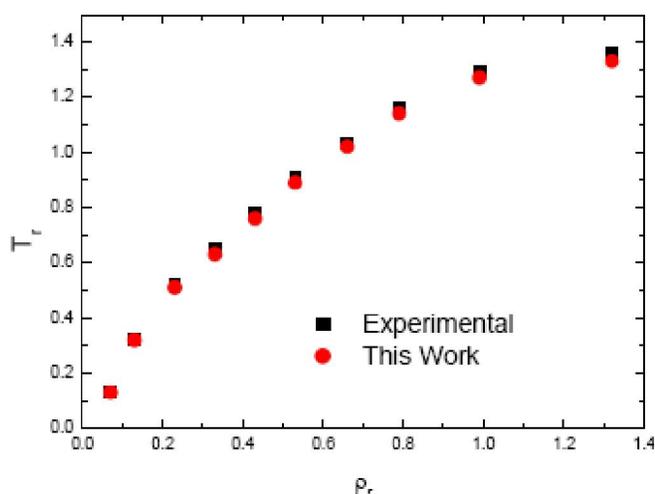


Figure 3 : The same as Figure 1, but for O₂.

pared with experimental data^[23]. In regard to the results reported in this TABLE, it is deduced that the best

values for critical density can be obtained using reference fluid 2 [Eq. (7)]. It is worth mentioning that we have calculated the critical density for some other fluids such as *He*, *Water*, *CH₄*, and etc. The obtained results for those fluids were not good. Therefore, we have not presented our results in the present work. It is observed from TABLE 1 that the Sutherland potential with sufficient compressibility can be applied to predict critical density of some real fluids.

In TABLE 2, we have presented the critical temperatures for several real fluids using Sutherland potential model. The results obtained using the different compressibility [Eq. (6) to (8)] as Ref1, Ref2, and Ref3. It is seen from the TABLE that the best values for critical temperatures can be obtained using Ref2 [Eq. (7)]. This shows that the Sutherland potential model can predict the critical temperature of some real fluids.

To better understanding, we have plotted several Figures for reduced properties. Figures 1 to 5 show the reduced temperature as a function of reduced density for several real fluids, Ne , N_2 , O_2 , CO , and NO , respectively. In all Figures, we have used Eq. (7) for compressibility factor. Because, in the critical properties, we have obtained the better results using Eq. (7)

It is seen from the Figures that, the obtained results for O_2 and NO are in good agreement with experimental data. For other fluids, the obtained results are in fairly agreement with experimental data. It is deduced that the intermolecular interaction between the particles in O_2 and NO are in the form of Sutherland potential. In general, the Sutherland potential can be used for the real fluids which are applied in this present work. At future studies, we intend to consider other terms in Eq. (4) and also other potential model to obtain the critical and reduced properties of real polar and non-polar fluids.

CONCLUSION

In the present work, we have used the perturbed virial expansion and the Sutherland potential model to calculate the critical and reduced properties of several non-polar real fluids. The paper includes two parts. In the first part, we changed the compressibility factor in the perturbed virial expansion. We have applied the various compressibility factors and studied its influence on critical properties of several real non-polar fluids. In second part, we have calculated the reduced density and temperature using the Sutherland potential. In regard to the results obtained in the present work, it is deduced that: **i)** the critical densities obtained using the Sutherland potential with Ref2 have been improved with respect to experimental data. **ii)** The critical temperatures obtained with the Sutherland potential with Ref2 have been improved with respect to experimental data. **iii)** The Sutherland potential is sufficient model to predict the critical and reduced properties of fluids which are applied in the present work. **iv)** The reduced properties for O_2 and NO are in good agreement with experimental data. But, for other fluids, the results are in fairly agreement with available data.

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