A mathematical recursive model for accurate description of the phase behavior in the near-critical region by Generalized van der Waals Equation

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Abstract. Recently, related studies on Equation Of State (EOS) have reported that generalized van der Waals (GvdW) shows poor representations in the near critical region for non-polar and non-sphere molecules. Hence, there are still remains a problem of GvdW parameters to minimize loss in describing saturated vapor densities and vice versa. This paper describes a recursive model GvdW (rGvdW) for an accurate representation of pure fluid materials in the near critical region. For the performance evaluation of rGvdW in the near critical region, other EOS models are also applied together with two pure molecule group: alkane and amine. The comparison results show rGvdW provides much more accurate and reliable predictions of pressure than the others. The calculating model of EOS through this approach gives an additional insight into the physical significance of accurate prediction of pressure in the near-critical region.

1. Introduction

Even before the GvdW EOS [1], there were a large number of studies [2-6] have been proposed for accuracy of fluids. In those, "Modified Cubic Equation of States (MC EOS)" is the first advanced theory, which based on the van der Waals (vdW) EOS [7]. However, these approaches have limitations on accuracy for near critical region.

As recently published, GvdW EOS is based on the interaction of particles and has potential by setting the thermodynamic theory based on the physical unit. GvdW EOS induced highly simplified EOS which builds on the inter-molecular interactions in Dieterici’s form. Nevertheless the results of, extrapolated to other fluids, the GvdW EOS’s accuracy declines [8].

For the reason that declines accuracies with GvdW EOS, this paper shows a mathematical recursive model for accurate description in the critical region which named rGvdW EOS. In the supposed process, EOSs tested with various substances for comparing results with well-known EOSs called GvdW, PR (Peng Robinson) [9], MPR (Modified Peng Robinson) [9] EOS. Verifying the accuracy of them, saturated alkane(C\textsubscript{n}H\textsubscript{2n+2}) and saturated amine(RNH\textsubscript{2}) are selected for experiment, respectively.

We first describe the theoretical background about rGvdW EOS for the analysing. In the experimental section, we show the volume change with supposed rGvdW EOS for each experiment to confirm the accuracy with various molecules that has linearity and polarity, and finally concluded.
2. Theoretical background

2.1. Mathematical recursive model for GvdW EOS

In this section, introducing a method that has a recursive process to get more accurate performance and optimized results which named rGvdW EOS. As mentioned, the fore study noted that iteration processes can be omitted, but that makes large errors in estimation for critical point. In rGvdW EOS, the recursive processes are performed automatically and exactly by PC with each equation (eq. 1~4).

By the process, calculating cycle begins with $Z_{cc}$ data of each substance. After that, whole calculating processes are started and being terminated with $c_c$ parameter which can be seen milestone for three parameters. In the iteration process, from initialize to complete values which more than 50 times of each parameter are saved and compared values to find a repeated period. And finally, determines to optimize three values with only averaged repeated parameters more than 10 times.

Finally, confirmed parameter values by mean calculating procedure, that can present most precise critical values and those results can be found in section 3. The whole process for accurate calculation starts with $Z_{cc}$ value to find initialized $c_c$ value ($k=0$) with the equation in eq. (1) in only the first time.

$$c_{c,0} = 2Z_{cc} + \sqrt{4Z_{cc}^2 + 1}$$  \hspace{1cm} (1)

After the initializing $c_c$, it can be possible to find $a_c$ and $b_c$ which expressible by $k$ in eq. (2) and (3).

$$a_c = \left(\frac{c_{c,k} + 1}{c_{c,k} - 1}\right)^{c_{c,k+1}} 	imes P_c, \quad k = 0,1,2...$$ \hspace{1cm} (2)

$$b_c = \left(\frac{c_{c,k} - 1}{c_{c,k} + 1}\right)^{c_{c,k+1}} 	imes V_c, \quad k = 0,1,2...$$ \hspace{1cm} (3)

At that time, the definition process for initial values is done to start recursive calculation for accurate $a_c$, $b_c$ and $c_c$ with substitution $a_c$ and $b_c$ values in eq. (4).

$$c_c = \frac{\ln\left(\frac{RT_c}{V_c - b_{c,k-1}} - P_c\right) - \ln a_{c,k-1}}{\ln b_{c,k-1} - \ln V_c}, \quad k = 1,2,3...$$ \hspace{1cm} (4)

And the whole process for calculating accurate parameter values to estimate critical point is performed with a PC which instructed compare values for every procedure to clustering statistical results.

3. Simulation results and discussion

3.1. Characteristics for alkane group which have linearity the optimized parameters

Normal saturated alkanes can be a milestone for other hydrocarbon-based materials. From the results in Table 2, alkanes, there are obvious differences between GvdW and rGvdW EOS nonetheless the same formula. In the result of GvdW EOS, there was no iteration process and can make a large error contrary to rGvdW EOS for near the critical point.

Nevertheless the differences in results, GvdW and rGvdW EOS have a similar characteristic which the linearity increases in molecules, $Z_{cc}$ and $c_c$ parameters are decreased and increasing number of carbon particles in each molecule are make grows of $b_c$ parameter by 12~13 cm$^3$ which be setted void volume.

3.2. Characteristics of alkyl amine group that have a complex intermolecule action

Ammonia, the basic material of amine, has non-shared electron pair which does not participate in the combination with hydrogen, and that makes fast (23.79 GHz) nitrogen inversion due to the instability.
Because of the thermodynamic data obtained by these conditions, the impact of dipole moment may be ignored and it is possible to apply to general liquid with defined as the materials have nonideality only. And the frequency declines after ethylamine in the series of unsaturated amines and be known that the dipole moment are reflected in thermodynamic characteristic, directly [11]. Therefore, the access of these materials is confined only between the liquid region and the critical point [12, 13].

Representatively for many other molecules, Figure 1 shows the comparative results with real gas phase of methylamine and ethylamine on the near critical point for many EOS’s estimation results.

| Table 1. Parameters used in GvdW and rGvdW EOS for some molecules in alkane group. |
|----------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Molecule            | CP         | GvdW EOS | Parameters for GvdW EOS | rGvdW EOS | Parameters for rGvdW EOS |
|                     |            | c_c     | a_c(bar) | b_c(cm^3)     | c_c     | a_c(bar) | b_c(cm^3)     |
| Methane             | 46.04      | 45.97709273 | 1.7366 | 1668.9000 | 26.9159 | 46.04005852 | 1.731579 | 1682.733521 | 26.594791 |
| Ethane              | 48.80      | 48.80075209 | 1.7127 | 1829.2000 | 38.6428 | 48.800008059 | 1.718714 | 1816.825317 | 39.098545 |
| Propane             | 42.49      | 42.02750340 | 1.6914 | 1628.6000 | 51.7242 | 42.48999198 | 1.707249 | 1608.767822 | 53.006143 |
| Butane              | 37.97      | 46.36485079 | 1.6911 | 1472.8000 | 62.7483 | 37.97007322 | 1.687660 | 1480.938477 | 65.218254 |
| Methylamine         | 74.58      | 74.58248992 | 1.8310 | 2397.0310 | 45.2045 | 74.58002757 | 1.830993 | 2397.050537 | 45.204254 |
| Ethylamine          | 56.24      | 56.22631679 | 1.6761 | 1663.2420 | 71.6897 | 56.23985481 | 1.676138 | 1663.621765 | 71.684521 |
| Propylamine         | 47.42      | 47.46031094 | 1.7614 | 1480.0643 | 86.0239 | 47.42005870 | 1.761324 | 1480.293825 | 86.014461 |

| Table 2. Calculated values for alkane and amine group with each EOSs on critical point |
|----------------------------------|-----------------|-----------------|-----------------|-----------------|
| Molecule            | Formula | CP         | GvdW EOS | rGvdW EOS | PR EOS | MPR EOS |
|                     |            |            | c_c     | a_c(bar) | b_c(cm^3)     | c_c     | a_c(bar) | b_c(cm^3)     | c_c     | a_c(bar) | b_c(cm^3)     |
| Methane             | CH₄       | 46.04      | 45.97709273 | 46.04005852 | 46.05212995 | 45.05205110 |
| Ethane              | C₂H₆      | 48.80      | 48.80075209 | 48.800008059 | 48.82483887 | 48.82475463 |
| Propane             | C₃H₈      | 42.49      | 42.02750340 | 42.48999198 | 42.52569942 | 42.52562560 |
| Butane              | C₄H₁₀     | 37.97      | 46.36485079 | 37.97007322 | 38.03609805 | 38.03603144 |
| Methylamine         | CH₅N      | 74.58      | 74.58248992 | 74.58002757 | 74.57463383 | 74.57451399 |
| Ethylamine          | C₂H₇N     | 56.24      | 56.22631679 | 56.23985481 | 56.38225744 | 56.38215833 |
| Propylamine         | C₃H₉N     | 47.42      | 47.46031094 | 47.42005870 | 47.42129416 | 47.42121458 |
| Butylamine          | C₄H₁₁N    | 42.00      | 42.02503523 | 42.00001466 | 42.00162568 | 42.00155502 |
4. Conclusion

In this paper, to improve performance of the GvdW EOS on near the critical region that be known, it has an accuracy to represent without correction of three parameters $a_c$, $b_c$ and $c_c$, the recursive mathematical calculation method (rGvdW EOS) is suggested which can be based on computer that automatically compensates parameters on it is dealt with. To compare the accuracy of the suggested rGvdW EOS with others which are well known we use some molecules that have single, double and triple carbon bond. Especially complex interactions also applies to a linear saturated derivative at the critical region than in the other state equations could be seen that virtually no errors. Thus, using rGvdW EOS, it can provide accurate characteristics in the near critical point by the auto-calibration of $a_c$, $b_c$ and $c_c$ parameters.

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