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_nH_{2n+2}) and saturated amine(RNH_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.

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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.

$$c_{c,0} = 2Z_{cc} + \sqrt{4Z_{cc}^{\,2} + 1} \tag{1}$$

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).

$$a_c = \left(\frac{c_{c,k} + 1}{c_{c,k} - 1} \right)^{c_{c,k}+1} \times P_c, \qquad k = 0,1,2\ldots \tag{2}$$

$$b_c = \left(\frac{c_{c,k} - 1}{c_{c,k} + 1} \right)^{c_{c,k}+1} \times V_c, \qquad k = 0,1,2\ldots \tag{3}$$

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).

$$c_c = \frac{\ln\left(\frac{RT_c}{V_c - b_{c,k-1}} - P_c \right) - \ln a_{c,k-1}}{\ln b_{c,k-1} - \ln V_c}, \qquad k = 1,2,3\ldots \tag{4}$$

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. Characteristis 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.

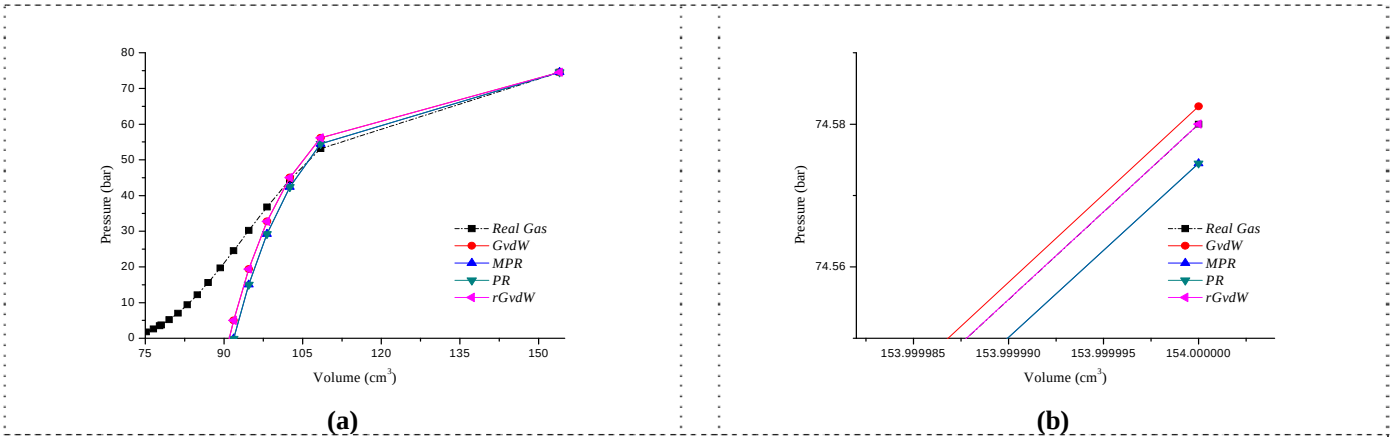
Because of the thermodynamic data obtained by these conditions, the impact of dipole moment may be ignored and it is possible to apply to general liquid with defined as the materials have nonideality only. And the frequency declines after ethylamine in the series of unsaturated amines and be known that 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	48.80008059	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	2233.5314	45.9812	56.23985481	1.676138	2233.395264	45.983124
Propylamine	47.42	47.46031094	1.7614	1663.2420	71.6897	47.42005870	1.761324	1663.621765	71.684521
Butylamine	42.00	42.02503523	1.7580	1480.0643	86.0239	42.00001466	1.757885	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
Methane	CH_4	46.04	45.97709273	46.04005852	46.05212995	45.05205110
Ethane	C_2H_6	48.80	48.80075209	48.80008059	48.82483887	48.82475463
Propane	C_3H_8	42.49	42.02750340	42.48999198	42.52569942	42.52562560
Butane	C_4H_{10}	37.97	46.36485079	37.97007322	38.03609805	38.03603144
Methylamine	CH_5N	74.58	74.58248992	74.58002757	74.57463383	74.57451539
Ethylamine	C_2H_7N	56.24	56.22631679	56.23985481	56.38225744	56.38215833
Propylamine	C_3H_9N	47.42	47.46031094	47.42005870	47.42129416	47.42121458
Butylamine	$C_4H_{11}N$	42.00	42.02503523	42.00001466	42.00162568	42.00155502



(a) **(b)**

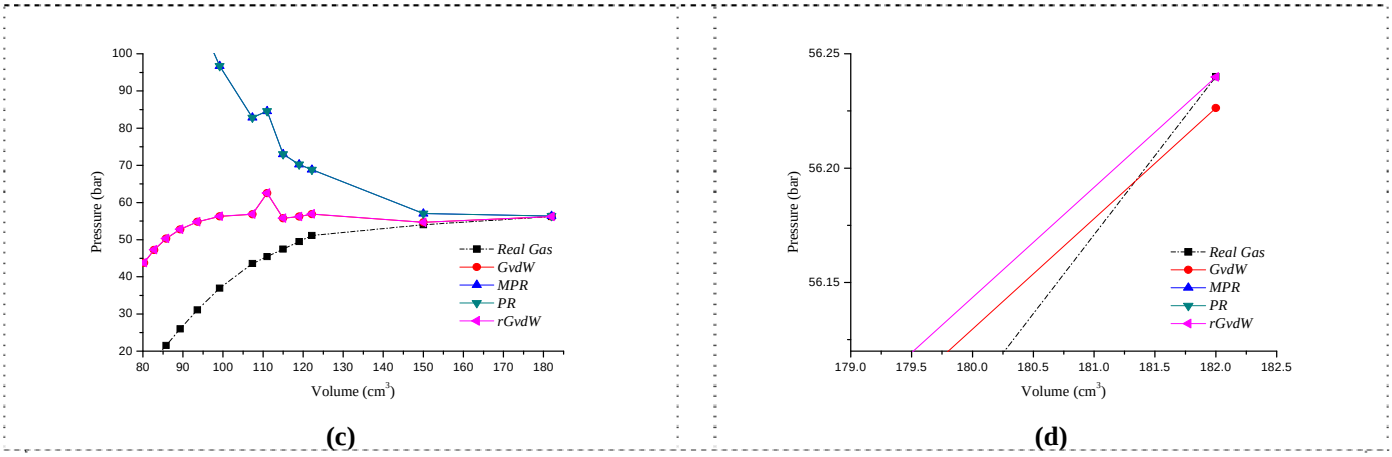


Figure 1. Result graphs for GvdW, rGvdW, PR and MPR with real gas data in near critical point.
(a) Methylamine; (b) Magnifying methylamine; (c) Ethylamine; (d) Magnifying ethylamine

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.

Acknowledgments

This work was supported by the Technology Innovation Program (10043787, Development of Ion Selective Membranes for redox Flow Battery) funded By the Ministry of Trade, industry & Energy (MI, Korea).

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