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RESEARCH NOTES

Generalization of vdW Type of Equations of State

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1 INTRODUCTION

Because of importance of equations of state (EOS) in science and industry, hundreds forms of EOS have been presented since latter 19 th century. It seems impossible to develop a general equation covering various kinds of EOS. But for cubic EOS, several general equations have been reported already.

Martin presented the first general equation which is following[1]

$$p = \frac{RT}{v} - \frac{\alpha(T)}{(v+\beta)(v+\gamma)} + \frac{\delta(T)}{v(v+\beta)(v+\gamma)} \tag{1}$$

Kumar *et al.* presented an equation called the most general form of a density-cubic or, alternatively, volume-cubic mathematical equation, the form of which is as follows[2]

$$Z = \frac{1 + d_1\rho + d_2\rho^2}{1 + d_3\rho + d_4\rho^2 + d_5\rho^3} \tag{2}$$

Abbott[3] gave another equation which is similar to Eq. (2)

$$p = \frac{RT(v^2 + \alpha v + \beta)}{v^3 + \lambda v^2 + \mu v + \nu} \tag{3}$$

From the above general equations, most prevailing cubic equations of state can be derived.

Main character of all the previous general equations is that they generalize the cubic EOS just from the viewpoint of pure mathematics. They give no hint about why the capabilities of the cubic EOS are different from each other. In other words the reason why some cubic EOS are better than others can not be found with the help of the previous general equations of state. In fact, those equations can not be used as tools to value or compare the various cubic EOS, and therefore they give little access to improving old EOS or developing a new EOS.

2 NEW GENERAL EQUATION FOR vdW TYPE OF EOS

Nearly all prevailing cubic equations of state (EOS) could be regarded as the results of reforming the original vdW EOS. The form of the original vdW EOS is

$$p = \frac{RT}{v-b} - \frac{a_w}{v^2} \tag{4}$$

Where b, a_w are constants independent of temperature and volume, subscript w means the vdW EOS. The accuracy of the vdW EOS is so low that in fact it is of little practical use for engineering calculations.

In today's vdW type of EOS, the original assumption given by van der Waals has scarcely been changed, and the original form of repelling term is retained too. The improvements on original vdW EOS focused on the attractive term. There are many types of forms of improved attractive term of EOS. The rules and the relations among these improved attractive term can be revealed by following comparisons and discussions.

RKS EOS is the first one which is of practical use in engineering[4]

$$p = \frac{RT}{v-b} - \frac{a_{RKS}}{v(v+b)} \tag{5}$$

where a_{RKS} is dependent on temperature.

Assuming that a_w is not a constant, and making Eq. (4) equal to Eq. (5), *i.e.*

$$\frac{a_w}{v^2} = \frac{a_{RKS}}{v(v+b)} \tag{6}$$

then, after rearranging, the a_w can be calculated as

$$a_w = \frac{a_{RKS}}{1 + b/v} = \frac{a_{RKS}}{\pi_{RKS}(v)} \tag{7}$$

where $\pi(v)$ is a new function which expresses the influence of volume on the attractive parameter a_w.

By the same approach, for PR EOS[5]

$$p = \frac{RT}{v-b} - \frac{a_{PR}}{v(v+b) + b(v-b)} \tag{8}$$

the a_w can be expressed as

$$a_w = \frac{a_{PR}}{1 + 2b/v - b^2/v^2} = \frac{a_{PR}}{\pi_{PR}(v)} \tag{9}$$

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Similarly, for Martin EOS[1]

$$p=\frac{RT}{v-b}-\frac{a_{\rm M}}{(v+c)^2} \tag{10}$$

$$a_{\rm w}=\frac{a_{\rm M}}{1+2c/v+c^2/v^2}=\frac{a_{\rm M}}{\pi_{\rm M}(v)} \tag{11}$$

For PT EOS[6]

$$p=\frac{RT}{v-b}-\frac{a_{\rm PT}}{v(v+b)+(v-b)c} \tag{12}$$

$$a_{\rm w}=\frac{a_{\rm PT}}{1+(b+c)/v-cb/v^2}=\frac{a_{\rm PT}}{\pi_{\rm PT}(v)} \tag{13}$$

For ALS EOS[7]

$$p=\frac{RT}{v-b_1}-\frac{a_{\rm ALS}}{(v-b_2)(v+b_3)} \tag{14}$$

$$a_{\rm w}=\frac{a_{\rm ALS}}{1+(b_3-b_2)/v-b_2b_3/v^2}=\frac{a_{\rm ALS}}{\pi_{\rm ALS}(v)} \tag{15}$$

From Eq. (5)—Eq. (15), it is easy to conclude that today's various improvements on the attractive term of original vdW EOS in fact are improvements on the attractive parameter $a_{\rm w}$. As for the influence of volume on $a_{\rm w}$ being introduced, the improvements are realized by various forms of $\pi(v)$ functions which can be generalized by following equation

$$\pi(v)=1+k/v+l/v^2+\cdots \tag{16}$$

So various vdW type of EOS can be generalized as follows

$$p=\frac{RT}{v-b}-\frac{a_{\rm w}}{\pi(v)v^2} \tag{17}$$

3 COMPARISON OF EOS BY USING $\pi(v)$ FUNCTION

When being used to calculate fluid phase behaviors, especially saturated liquid volumes and saturated vapor volumes, vdW type of EOS with different forms of attractive term give different accuracy. There must be some reasons and rules which could account for why some forms of attractive term give better calculating results than others do.

Taking $a_{\rm w}$ as a constant is the fatal drawback of the original vdW EOS. The amendments given by numerous researchers for the $a_{\rm w}$ can be divided into two cases: (1) $a_{\rm w}$ is taken as a function of temperature only; (2) $a_{\rm w}$ is taken as a function dependent on both of the temperature and volume. The later seems to be done unconsciously and has not been pointed out clearly by previous researchers. However, in fact, it is an essential improvement on the vdW EOS to make $a_{\rm w}$ being dependent on both of the temperature and volume.

By comparing Eq. (7)—Eq. (15), it is easy to see that there are obvious differences among $\pi(v)$ functions of different vdW EOS. It is the form of $\pi(v)$ function that account for the differences among the capabilities of various vdW type of EOS.

It is known that the forms of $a(T)$ in PR and RKS EOS are the same,

$$a=a_{\rm c}\alpha(T_{\rm r}) \tag{18}$$

$$\alpha(T_{\rm r})^{0.5}=1+m(1-T_{\rm r}^{0.5}) \tag{19}$$

Where $a_{\rm c}$ and m are characteristic constants of substances. What makes PR EOS differ from RKS EOS is only the forms of $\pi(v)$ functions. Usually PR EOS has better accuracy than RKS EOS, especially for the calculation of liquid volume. The reason for this is that the form of $\pi_{\rm PR}(v)$

$$\pi_{\rm PR}(v)=1+2b/v-b^2/v^2 \tag{20}$$

is better than the form of $\pi_{\rm RKS}(v)$

$$\pi_{\rm RKS}(v)=1+b/v \tag{21}$$

The former is more competent for expressing the influences of volume.

The form of $\pi_{\rm M}(v)$ in Martin EOS is similar to $\pi_{\rm PR}(v)$ of PR EOS, so the accuracy of Martin EOS and PR EOS are about the same. Similarly, the reasons why the accuracy of PT EOS and ALS EOS are better than that of RKS and PR EOS can be found too. The forms of $\pi(v)$ in PT and ALS EOS are

$$\pi_{\rm PT}(v)=1+(b+c)/v-cb/v^2 \tag{22}$$

$$\pi_{\rm ALS}(v)=1+(b_3-b_2)/v-b_2b_3/v^2 \tag{23}$$

In comparison with the forms of $\pi_{\rm RKS}$ and $\pi_{\rm PR}(v)$, Eq. (22) and Eq. (23) are more elastic, more powerful, and so more competent for the regression of data. It is reasonable that by using of Eq. (22) and Eq. (23), PT EOS and ALS EOS would produce higher accuracy than RKS and PR EOS do.

4 DISCUSSION AND CONCLUSIONS

Comparing with the $\pi(v)$, *i.e.* Eq. (16), it is easy to see that the $\pi_{\rm RKS}(v)$ has only two terms, *i.e.* $\pi_{\rm RKS}(v)=1+b/v$, and the forms of $\pi(v)$ functions in other EOS have three terms. It is the fatal drawback of the RKS EOS which makes it to be a loser in competition with the later vdW types of EOS. The RKS EOS seems to be no longer a good candidate for the calculation of properties of fluids except for the calculation of vapor pressure of fluids.

Apart from the numbers of terms in $\pi(v)$, the relations between the parameter k, l, $\cdots$ in Eq. (16) could also influence the capability of EOS for data representation. The relations between the parameters k and l in $\pi_{PR}(v)$ and $\pi_M(v)$ are very strong which in fact limit the capabilities of PR and Martin EOS, while the relations between the parameters k and l in $\pi(v)$ of PT and ALS EOS are relatively weak which make them being better than PR, Martin, RKS and other EOS for the calculations of various properties of fluids[8].

Conclusions are: (1) vdW type of EOS are generalized by using of $\pi(v)$ function; (2) the new general equation could be used to value or compare vdW type of EOS, and by improving $\pi(v)$ function, it would be possible to develop a better vdW type of EOS.

NOMENCLATURE

a	attractive parameter of equations of state
b	volume parameter of equations of state
c	parameter of Martin's equation or PT's equation
d_1—d_5	parameters of Kumar's general equation
k, l	parameters of the new general equation
m	parameter of temperature function
p	pressure
R	gas constant
T	temperature
v	mole volume
Z	compressibility factor
α	temperature function or parameter of Martin's or Abbott's general equation
β	parameter of Martin's or Abbott's general equation
δ, γ	parameter of Martin's general equation
λ, μ, ν	parameter of Abbott's general equation
ρ	density
π	new function

Subscripts

ALS	ALS equation
c	critical
M	Martin equation
PR	Peng-Robinson equation
PT	PT equation
r	relative
RKS	RKS equation
W	van der Walls equation

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