The two-parameter equation of state the van der Waals type.

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Abstract

In this work the new two-parameter equation of state was proposed for real gases, which is inferior to Redlich-Kwong equation in the description quality. It is shown that from this equation can be easy obtained the three-parameter equation of state, which is described the fluid behaviour in the wide area of state parameters.

Introduction

In spite of that from the time when van der Waals determinate the equation of state for fluid (1873) come more then 125 years, this equation, and ideas to put in it, until used for description of the thermodynamic properties of the substances and mixtures. This equation done a strong influence on the development of the physics and physic-chemistry of the isotropy phase (see, for example, [1]). The van der Waals equation of state a true qualitative describe of the thermal fluids properties in the wide area of state parameters with exception of the nearby vicinity of critical point of liquid-gas.

However the van der Waals equation of state gives only qualitative describe of the fluid behaviour. In the quantitative terms this equation is not enough suitable for description of thermal properties even the simple substances such as argon. In literature there are many attempt to modernise, to improve the van der Waals equation of state (see, for example, review [2]) in order to obtain a best agreement those equation with experimental data without loss of simplicity and obviousness that inherent to these

wonderful equation. As a rule these attempt lead to either serious complication of the obtained equations in comparison with initial one or considerable limitation of the use area.

Result and discussion

We take the van der Waals equation

$$\left(p_{vW} + \frac{a}{v^2}\right)(v-b) = RT\ , \tag{1}$$

from which

$$p_{vW} = \frac{RT}{v-b} - \frac{a}{v^2}\ . \tag{2}$$

Here R is a gas constant of substance, T is temperature, p is pressure, v is specific volume, a and b are van der Waals constant of substance.

At great v the second term $\frac{a}{v^2}$ in (2) can be neglected, especially as the constant a decrease when temperature increase. Then

$$p_{vW1} = \frac{RT}{v-b} = \frac{RT}{v_f}\ . \tag{3}$$

That is we obtained in this approach the ideal gas equation of state in which the "free" volume v_f=v-b appear instead the absolute volume though.

Another well-known equation that now used for description of thermodynamic and kinetic properties of fluids is a hard sphere equation of state

$$p_{hs} = \frac{RT}{v}\left(1 + b\rho + 0.625\, b^2\rho^2 + \ldots\right) = \frac{RT}{v} f(\rho)\,. \tag{4}$$

At the present it is known the numeric values about 10 first terms of this equation. The fact to attract attention that both in the van der Waals equation (2) and in the hard sphere equation the coefficient b is equal to quadruplicate molecule volume (calculated on one particle): $b = \frac{2}{3}\pi\sigma^3$, where σ is molecule diameter.

At present work to make the attempt obtain the equation of state which combine the merits of the van der Waals and hard sphere equations. At first we demand that the hard sphere equation of state was fulfil for "free" volume v_f, that is superpose the equations (3) and (4):

$$p_1 = \frac{RT}{v_f} f(\rho). \tag{5}$$

We come back to van der Waals equation (2), that is keep the term $\frac{a}{v^2}$ at small v, we obtain:

$$p_2 = \frac{RT}{v_f} f(\rho) - \frac{a}{v^2} \tag{6}$$

and if we neglected in the hard sphere equation in the function $f(\rho)$ all terms except of linear on ρ and 1, we obtain:

$$p = \frac{RT}{v-b}(1+b\rho) - \frac{a}{v^2} = \frac{RT}{v}\frac{v+b}{v-b} - \frac{a}{v^2}, \tag{7}$$

or

$$\left(p + \frac{a}{v^2}\right)(v-b) = \frac{RT}{v}(v+b). \tag{7a}$$

The critical point condition used: $(\partial p/\partial v)_T = 0$ and $\left(\partial^2 p/\partial v^2\right)_T = 0$, it is easy can be obtained the values of coefficients of the equation (7):

$$b = \left(2-\sqrt{3}\right)v_c \approx 0.268 v_c, \tag{8}$$

$$a = \frac{1}{2} RT_c v_c \frac{\sqrt{3}-1}{2-\sqrt{3}} \approx 2.732 RT_c v_c; \tag{9}$$

from this we obtained that $p_c = \frac{RT_c}{v_c}\left(\sqrt{3} - \frac{1}{2}\frac{\sqrt{3}-1}{2-\sqrt{3}}\right) = \frac{\sqrt{3}-1}{2}\frac{RT_c}{v_c}$ and a compressibility factor in the critical point be equal to:

$$Z_c = \frac{p_c v_c}{RT_c} = \frac{\sqrt{3}-1}{2} \approx 0.366, \tag{10}$$

and according to the van der Waals equation $Z_C \approx 0.375$.

Among the more successful two-parameter equation of state usually related the Redlich-Kwong equation [3]:

$$p_{RK} = \frac{RT}{v-b} - \frac{a}{T^{\frac{1}{2}} v(v+b)}. \tag{11}$$

From critical condition it is follow [3] that in equation (11)

$$b \approx 0.0866 \frac{RT_c}{p_c},\ a \approx 0.4275 \frac{R^2 T_c^2}{p_c}, \text{ and } Z_c \approx 0.333. \qquad (12)$$

The experimental values of the compressibility factor in the critical point are near to 0.3 for many substances. Thus the Redlich-Kwong equation gives values Z_c more close to experimental in comparison with equations (1) and (7).

If we obtain the constant a and b in equations (7) and (11) by the experimental (tabulated) data processing that is give the approximately equal description by those equations.

On figure 1 as an example the results of calculations of the compressibility factor on the new equation (7) and Redlich-Kwong equation (11) are correlated with tabulated data at different temperatures for carbon dioxide [4]. In the equation (7) for $a = 1.833 \cdot 10^{-4}$ MPa·m^6/kg^2, $b = 0.58865 \cdot 10^{-3}$ m^3/kg, p – in MPa, T – in K, v – in m^3/kg. From the figure 1 it is seen that in the wide area of the condition parameters the proposed equation (7) is as good as the Redlich-Kwong equation (11) in accuracy. The similar results was obtained at $p - v - T$ data processing on methane, inert gases and other nonpolar substances. Notice that at our opinion the equation (7) rather simpler then the Redlich-Kwong equation (11).

Conclusion

In conclusion we to mark off the next case. When the equation (7) was deduced we to take a decision that the constant b in the van der Waals equation (1) and the hard sphere equation (4) has a same values as it is follows from the theory. But if we take, at least formally, that those constants in equations (1) and (4) are distinguish i.e. $b_{vW} \neq b_{hs}$ and the equation (7) can be written as (with accuracy of designation):

$$p = \frac{RT}{v} \frac{v + b1}{v - b} - \frac{a}{v^2}, \qquad (13)$$

and substitute $b1 = c - b$, we obtain

$$Z = 1 + \frac{c}{v - b} - \frac{a}{vRT}, \qquad (14)$$

where a, b and c are three individual substance constants. As our preliminary calculation shown the inserting one adjustable constant in the equation (7) yields a large dividend in accuracy of the description $p - v - T$ data in the wide area of state parameters.

The equations (13) and (14) go into van der Waals equation (1) when $c = b$ and into equation (7) when $c = 2b$. The values of individual constants of the equation (14) and $\delta Z = \frac{\sqrt{(Z - Z_{calc})^2}}{N - 1}$ for different substances resulted in the table, those were calculated on base tabulated data from [4-9] by least-square method. As it seen from the table the ratio c/b even near to *2* but it is individual parameter for each substance and changes from *1.84* (methane) to *3.31* (carbon dioxide). In this connection the equation (7) is a very rough approximation to the more accurate equation (13). On figure 2 as example the results of calculation on the equation

$$p = \frac{RT}{v}\left(1 + \frac{c}{v - b}\right) - \frac{a}{v^2}, \tag{15}$$

were related to the tabulated data [7] for carbon dioxide, the constant values equation (15) given in table. The correlation between calculated values of pressure on the equation (15) with tabulated ones may be considered for simple three-parameter equation of state as satisfactory (with the exception of region nearby the critical point).

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Table

The coefficients of the equation (14) for different substances.

Substance	a, J·m^3/kg^2	b, m^3/kg	c, m^3/kg	c/b	δZ
Carbon dioxide [4]	240	$0.5451 \cdot 10^{-3}$	$1.8053 \cdot 10^{-3}$	3.31	$1.485 \cdot 10^{-3}$
Argon [5]	90	$0.5406 \cdot 10^{-3}$	$1.0434 \cdot 10^{-3}$	1.93	$8.832 \cdot 10^{-4}$
Methane [6]	905.8	$1.7857 \cdot 10^{-3}$	$3.2836 \cdot 10^{-3}$	1.84	$1.819 \cdot 10^{-3}$
Propane [7]	561.6	$1.2304 \cdot 10^{-3}$	$3.2593 \cdot 10^{-3}$	2.65	$5.732 \cdot 10^{-3}$
Oxygen [8]	138.04	$0.6569 \cdot 10^{-3}$	$1.2675 \cdot 10^{-3}$	1.93	$2.125 \cdot 10^{-3}$
Ammonia [9]	1262	$1.0732 \cdot 10^{-3}$	$2.5324 \cdot 10^{-3}$	2.36	$2.377 \cdot 10^{-3}$

Figure captions

Figure 1. The deviation between of the tabulated compressibility factor Z_{tabl} of carbon dioxide [4] and those calculated on the new equation (7) - (+), and Redlich-Kwong equation (11) - ( ); $T = 220…1000$ K, $p = 0.1…100$ MPa.

Figure 2. The isotherms of the carbon dioxide.
The points are tabulated values [4], the solid lines are calculated from the equation (15), the dash line is vapor-liquid equilibria.
1 - *230* K, 2 - *260* K, 3 - *290* K, 4 - *305* K, 5 - *330* K, 6 - *350* K, 7 - *400* K, 8 - *500* K, 9 - *600* K, 10 - *800* K, 11 - *1000* K.

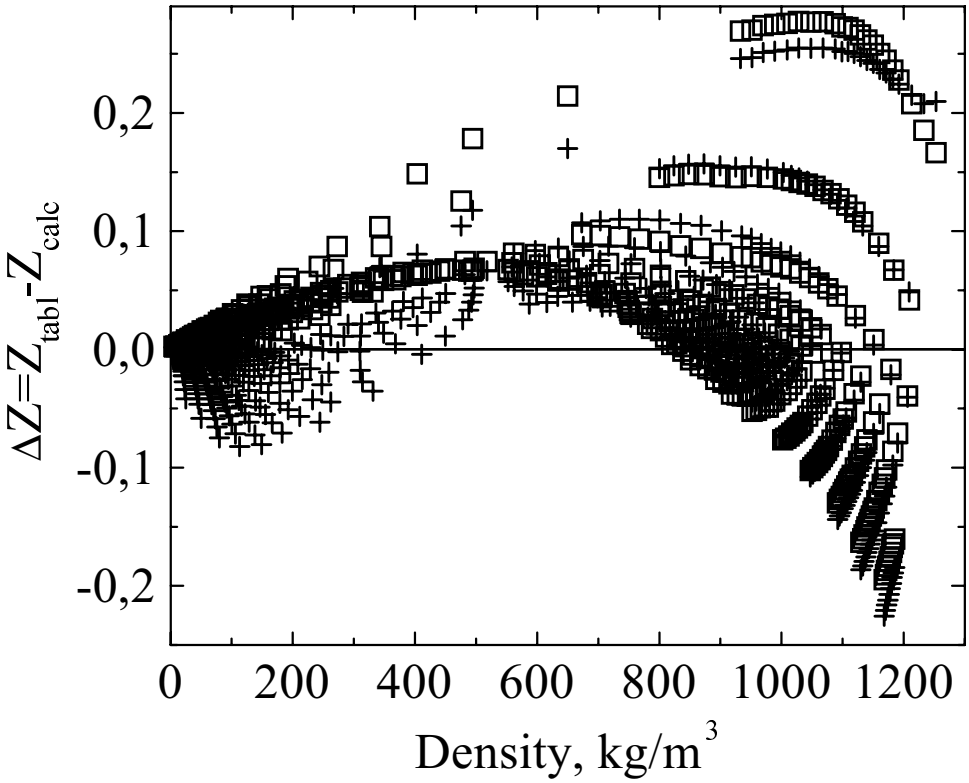
0,2
0,1
0,0
-0,1
-0,2
ΔZ=Z_tabl-Z_calc
0
200
400
600
800
1000
1200
Density, kg/m3

Fig 1

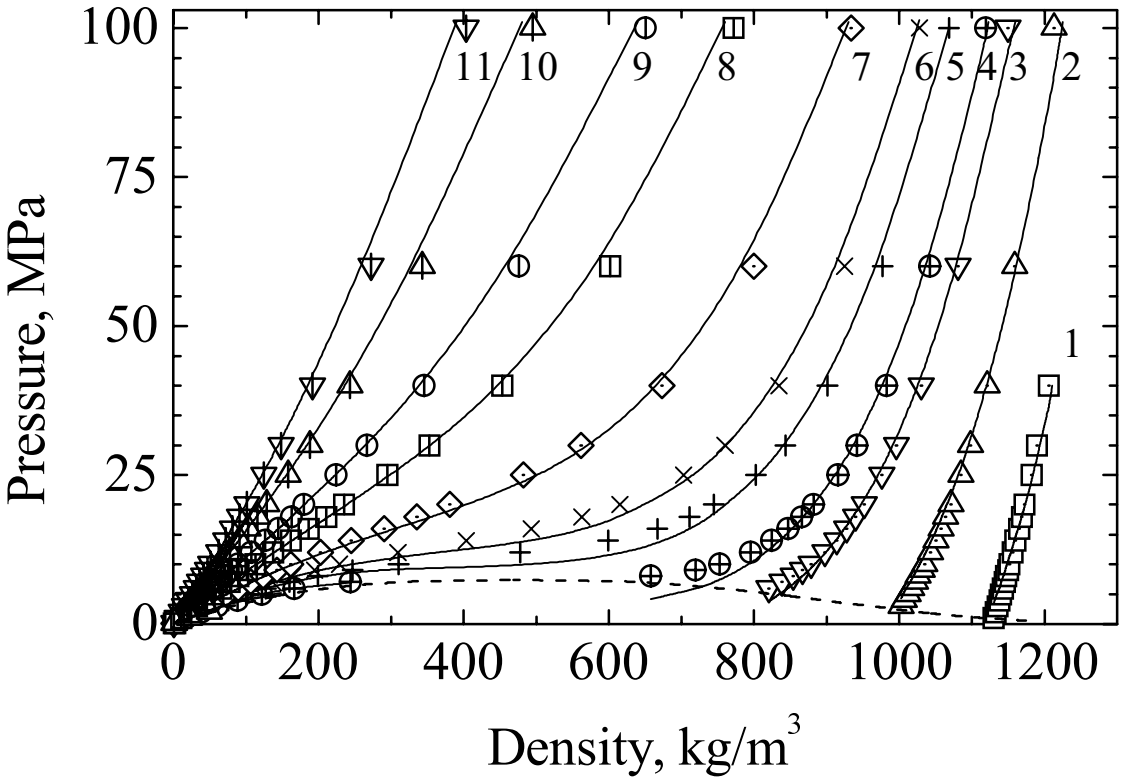
Pressure, MPa
Density, kg/m3
0
25
50
75
100
0
200
400
600
800
1000
1200
11
10
9
8
7
6
5
4
3
2
1

Fig 2