Modified Van der Waals equation and law of corresponding states(*)

Wei Zhong¹⁾, and Changming Xiao^{1)(**)}

Yongkai Zhu²⁾

1) Department of Physics, Hunan Normal University, Changsha, China, 410081

2) Department of Physics, Guangxi University, Nanning, China, 530004

Abstract

It is well known that the Van der Waals equation is a modification of the ideal gas law, yet it can be used to describe both gas and liquid, and some important messages can be obtained from this state equation. However, the Van der Waals equation is not a precise state equation, and it does not give a good description of the law of corresponding states. In this paper, we expand the Van der Waals equation into its Taylor's series form, and then modify the fourth order expansion by changing the constant Virial coefficients into their **analogous ones**. Via this way, a more precise result about the law of corresponding states has been obtained, and the law of corresponding states can then be expressed as: in terms of the reduced variables, all fluids should obey the same equation with **the analogous Virial coefficients**. **In addition, the system of ^3He with quantum effects has also been taken into consideration with our modified Van der Waals equation, and it is noted that, for a normal system without quantum effect, the modification on ideal gas law from the Van der Waals equation is more significant than the real case, however, for a system with quantum effect, this modification is less significant than the real case, thus a factor is introduced in this paper to weaken or strengthen the modification of the Van der Waals equation, respectively.**

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Introduction

It is well known that the Van der Waals equation is an equation of state for a fluid composed of particles that have a non-zero volume and a pairwise attractive

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(**) Corresponding author, Email: cmxiao@hunnu.edu.cn

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inter-particle force. The equation is based on a modification of the ideal gas law, and it approximates the behavior of real fluids, taking account of the nonzero size of molecules and the attraction between them [1]. It is found that, above the critical temperature, the Van der Waals equation is an improvement of the ideal gas law, and for lower temperatures the equation is also qualitatively reasonable for both the liquid state and the low-pressure gaseous state. Furthermore, many phenomena, including supercooling and superheating, were correctly predicted with the assistance of the van der Waals equation [2]. On the other hand, the law of corresponding states [3,4] suggests that, in the framework of reduced temperature, different substances have the same liquid-gas coexistence curve. Pertinent researches indicated that a qualitatively correct result was obtained by the Van der Waals equation, but the discrepancy between the Van der Waals results and the experiments data is significantly large. Obviously, the Van der Waals equation is not a precise state equation, and a modification of it is needed. In fact, a lot of modifications were made on it in the past decades. Most of modification on the Van der Waals equation are based on modifying the dispersion term, $a(T)/V_m^2$ [5], even the term $(V_m - b)^{-1}$ was also modified [6]. G. Schmidt and H. Wenzel [7] created a cubic equation of the Van der Waals type and S. H. Horab [8] tried to join another new parameter (the compressibility factor) to modify the Van der Waals equation so as to make the results fit the corresponding experimental results. Meanwhile H. Wenzel and G. Schmidt's another paper [9] extended the Van der Waals equation to contain a solid phase. Besides all above, M. Rossy and F. Hensel [10] constructed a two-state Van der Waals equation with a density-dependent cohesive energy, it led to compositional fluctuations and its calculations predicted that Hg and the alkali metals would exhibit similar behavior near the critical point. While the liquid-gas phase transition theory has been used in many other fields, such as the nuclear system, [11,12] in which a great progress in the simulation was made. [13] In addition, the universality of liquid-gas phase transition was also researched through Molecular Dynamics (MD), [14,15] and lots of results that are in good agreement to experiments were obtained in this way, [16-18] and a

review of gas-liquid critical phenomena was reported in Ref. [19] recently. This reminds us a further modification on the Van der Waals equation is needed.

In this paper, according to the law of corresponding states, we firstly expand the Van der Waals equation into the Taylor series, and just keep its first fourth order; then the Van der Waals equation is modified by changing the coefficients of the Taylor series into adjustable variables that are related to the density of the state. Obviously a more accurate description of the liquid-gas coexistence curve will be obtained.

Modified Van der Waals equation

It is well known that, in molar volume, the Van der Waals equation can be written in the form

$$(P + a/V_m^2)(V_m - b) = RT \quad (1)$$

where P , V_m , T denote the pressure, molar volume and temperature of the system, respectively. At the critical point, we have

$$\left. \partial P / \partial V_m \right|_T = 0 \quad \left. \partial^2 P / \partial V_m^2 \right|_T = 0 \quad (2)$$

As a result, the corresponding critical values are determined as follows,

$$V_{mC} = 3b, \quad P_C = a / (27b^2), \quad RT_C = 8a / (27b) \quad (3)$$

For convenience, the reduced dimensionless variables t , π and ρ are introduced as follows,

$$t = T / T_C, \quad \pi = P / P_C, \quad \rho = V_{mC} / V_m = \rho' / \rho_c \quad (4)$$

then the Van der Waals equation turns into the universal form

$$(\pi + 3\rho^2)(1/\rho - 1/3) = 8t/3 \quad (5)$$

Obviously Eq. (5) is universal in that there are no system-specific quantities, and all fluids should obey the same equation. This is known as the law of corresponding states, i.e., when the critical volume, temperature and pressure of a system are known then in terms of the reduced variables all fluids should obey the same equation. With the assistance of Maxwell construction, the liquid-gas coexistence curve can be determined through Eq. (5), and the results are shown in Fig. 1a. In order to test the

correctness of the results obtained from the universal form of Van der Waals equation (5), the experimental data of coexistence for a number of substances plotted in reduced form, originally by Gugenheim [3], are also shown in Fig. 1a. It tells us clearly that the law of corresponding states is qualitatively correctly described by the Van der Waals equation, but it does not give a good description of the universal behavior, and the difference between the calculations and experiments are very large. So a proper modification on the Van der Waals equation is needed.

Fig. 1, Liquid-gas coexistence lines. (a), Liquid-gas coexistence curve determined by the experiments and the Van der Waals equation (described by the dotted line) [3]; (b), The coexistence curves of experiments and different state equations: red line noted by 1 is the result of Van der Waals equation, black line 2 the experiment's result, the two lines of 3 and 4 are the results of Eqs. (7) and (6), respectively.

To modify the Van der Waals equation, we would like to make sure where its error comes from. Firstly, the Van der Waals equation is expanded into the Taylor series. For convenience, both the second and fourth order of Taylor series of Van der Waals equation are under consideration, and they can be rewritten as follows, respectively,

$$\frac{P}{RT} = \frac{1}{V_m} + \frac{1}{V_m^2} \left(b - \frac{a}{RT} \right) + \frac{b^2}{V_m^3} \quad (6)$$

$$\frac{P}{RT} = \frac{1}{V_m} + \frac{1}{V_m^2} \left(b - \frac{a}{RT} \right) + \frac{b^2}{V_m^3} + \frac{b^3}{V_m^4} + \frac{b^4}{V_m^5} \quad (7)$$

In fact, Eqs. (6) and (7) are also the Virial expansion, and the coefficients are just the Virial coefficients [20]. Obviously, two liquid-gas coexistence curves can be

determined by the same way of Maxwell construction through Eqs. (6) and (7), respectively, and the results are demonstrated in Fig. 1b. While the experimental data and the result of the Van der Waals equation (5) are shown in Fig. 1b once more. From Fig. 1b, it is clear that, both the results obtained from the second and fourth order expansion of Van der Waals equation are better than that obtained from the Van der Waals equation itself; Furthermore, it also tells that the results of the second order expansion of Van der Waals equation are in good agreement to the experiments when the parameter ρ falls into the interval (0.2984, 1.4533), including the critical point of $\rho = 1$. But the difference between the second order expansion and the experimental data increases quickly with the increase of ρ when $\rho > 1.4533$, or with the decrease of ρ when $\rho < 0.2984$, and the value of this difference changes from negative to positive. However, the case of the fourth order expansion is just on the contrary: the values of most points of its coexistence curve are smaller than that of the experiments. In addition, compared the two crossing points near $\rho \approx 1.4533$ and 0.2984 of the second order expansion, there are also two crossing points of the fourth order expansion with $\rho \approx 0.08$ and 2.15, respectively. Obviously, only near its crossing points, the fourth order expansion will be more accurate than the second order expansion.

Now a interesting and important point is found from the results of the expanded Van der Waals equation: near the the critical point, the experimental data are well discribed by the results of the second order expansion of Van der Waals equation, however, when the parameter ρ is out of the interval (0.2984, 1.4533), both the second and fourth order expansions do not describe the experimental data correctly, but the law of their deviations from the experimental data are in the opposite tendency. This reminds us that the deviation will be reduced if the two equations are combined in a way, and the correct equation from which the liquid-gas coexistence curve can be correctly described should lie between the second and fourth order of the Taylor

expansion of Van der Waals equation. To get a more precise liquid-gas coexistence curve, the correct way for us is to modify the fourth order Taylor expansion of Van der Waals equation by combining the second and fourth order expansions together. One of the most efficient ways to accomplish this task is to change the constant coefficients of the fourth order expansion of the Van der Waals equation into the adjustable variables. However, the Virial coefficients of Eq. (7) are only related to the temperature of the system. For a given temperature, they are constants [20]. To modify the Van der Waals equation, these coefficients must be variables, so the corresponding Virial coefficients will be substituted by the analogous Virial coefficients, and the only difference between them is that the former is related to the temperature, but the later will relate to both the temperature and density of the system. According to above ideal, corresponding to different values of density ρ , the Van der Waals equation should be modified to be the second, fourth order expansions, or their mixing, respectively, by changing its Virial coefficients into variables. Obviously these coefficients of the expanded Van der Waals equation are related to the difference between the calculation results and the experimental data. In addition, we noted that the two crossing points of the two coexistence curves of the second order expansion of Van der Waals equation and that of the experiments are at $\rho = 1.4533$, and 0.2984 , so the Van der Waals equation should not be modified at these two points; the other points of the coexistence curve of the fourth order expanded Van der Waals equation can be possibly modified as: keep the coefficients of the first three items to be constant, but the coefficients of the fourth and fifth items in the series are modified by timing another adjustable coefficient η , so Eq. (7) is rewritten as,

$$\frac{P}{RT} = \frac{1}{V_m} + \frac{1}{V_m^2} \left(b - \frac{a}{RT} \right) + \frac{b^2}{V_m^3} + \eta \left(\frac{b^3}{V_m^4} + \frac{b^4}{V_m^5} \right) \quad (8)$$

η is the new parameter introduced to reduce the difference between the calculation values from Eq. (8) and experimental data, and it takes different values for different densities. Due to η , Eq. (8) turns to be an empirical formula.

Results

A lot of values of the parameter η are determined through different crossing points of the coexistence curve of Eq. (8) with the experimental curve, and the results are shown in Table 1, in which ρ_g is corresponding to the case of gas when $\rho < 1$, and ρ_L is the case of fluid with $\rho > 1$.

Table.1: The relation between the parameter η and the density. ρ_g is corresponding to the case of gas when $\rho < 1$, and ρ_L is the case of fluid with $\rho > 1$.

η	ρ_g	ρ_L
0.0	0.29844	1.45329
0.1	0.19324	1.61905
0.2	0.16082	1.7617
0.3	0.15141	1.82492
0.4	0.12795	1.87879
0.5	0.11905	1.92641
0.6	0.11662	1.96793
0.7	0.10901	1.98401
0.8	0.10204	2.00437
0.9	0.10204	2.04082
1.0	0.0974	2.0671
2.0	0.07012	2.2788

From Table 1, it is known that, corresponding to $\rho_g \approx 0.2984$ or $\rho_L \approx 1.4533$, $\eta = 0.0$, Eq. (8) turns to be the second order expansion; when $\rho_g \approx 0.08$ or $\rho_L \approx 2.15$, $\eta = 1.0$, and then Eq. (8) turns to be the fourth second order expansion; Furthermore, making use of the data listed in table 1, the relation between the parameter η and the corresponding density of the state can also be determined. For the gas and liquid, their relations are described by the following two equations, respectively:

$$\eta = 0.02145 + 13.24883 \times e^{\left(-\frac{\rho}{0.03689}\right)} \quad \text{for } \rho < 0.3 \quad (9)$$

$$\eta = -0.21449 + 0.00199 \times e^{\left(\frac{\rho}{0.32434}\right)} \quad \text{for } \rho > 1.45 \quad (10)$$

Then the universal coexistence curve can now be determined by the combination of our modified Van der Waals equation Eq. (8) and the relations about the corresponding variable coefficients (9) and (10), and the results are shown in Fig. 3. For convenience of comparison, both the experimental data and the results of Van der Waals equation are also shown in Fig. 2. From Fig. 2, it is easy to know that our results are in good agreement with the experimental data, and the differences between the values of modified equation and the experimental data are demonstrated in Fig. 3. For convenient of comparison, both the differences between the experimental data and the second, fourth order expansions of Van der Waals equation are also demonstrated in Fig. 3. It is clear that, compared with the second and fourth order

Fig.2: The gas-liquid coexistence curve: the black one is the experimental data, and the blue one is the result obtained from the Van der Waals equation, while the red line is the result determined by our modified equation (eq.9).

Fig.3: The red line is the difference line between the second order expansion of Van der Waals equation and the experimental data, the blue one is the difference line between the fourth order expansion of Van der Waals equation and the experimental data, while the green one is difference

between our modified equation and the experimental data.

expansions of Van der Waals equation, all the differences between the values of the modified equation and experimental data are very small. Obviously, the differences are successfully controlled in a small range by the parameter η . Instead of modifying the dispersion term, $a(T)/V_m^2$, or $(V_m - b)^{-1}$, in the Van der Waals equation, we just change the **Virial coefficients of the fourth and fifth items in the Taylor series into the analogous Virial coefficients**. Then the law of corresponding states can be modified as: in terms of the reduced variables all fluids should obey the same equation with **the analogous Virial coefficients**.

Discussion

Though the law of corresponding state is quite efficiently for most gas and liquid, it loses effectiveness for a system with quantum effects[1], which is clearly demenstrated in Fig. 1. Based on the same anlysis, the quantum effects of ^3He can also be fitted if the Van der Waals equation is modified as follows:

$$\frac{P}{RT} = \frac{1}{V_m} + \frac{1}{V_m^2} \left(b - \frac{a}{RT} \right) + \gamma(T) \left(\frac{b^2}{V_m^3} + \frac{b^3}{V_m^4} + \frac{b^4}{V_m^5} \right) \quad (11)$$

where $\gamma(T)$ is a new factor introduced to modify the Van der Waals equation, and it is a function of temperature. In fact, the difference between Eqs. (8) and (11) is that, for the former, the factor η is timed with the last two items, however, in Eq. (11), the new factor is timed with the last three items. While the relation between the new factor and temperature was determined by the same way mentioned above, and the results are written as follow

$$\gamma(T) = 10.04513 \exp\left(\frac{-T/T_c}{0.34834}\right) + 0.3988 \quad (12)$$

then the gas-liquid coexistence line of ^3He was also determined by Eqs. (11) and (12), and the results are shown in Fig. 4. It is found our results are also in good agreement to the experimental data. On the other hand, combined with Fig. 4 and Eqs. (1), (8), and (11), we noted that, for the normal state without quantum effects, the values of the

Fig.4 The gas-liquid coexistence lines including the result from helium 3. The experimental data for normal case is the red line, and the blue line is the calculating result from Van der Waals equation, while the black solid line is determined by our modified Van der Waals; besides, the stars and the purple line are coexistence lines of ^3He obtained by experiment and our modified Van der Waals equation, respectively.

gas-liquid coexistence line of Eq. (1) are smaller than that of the experimental data or the corresponding values determined from Eq. (8), but they are larger than that of the state with quantum effects or the coexistence line of Eq. (11). So the modification on ideal gas law from Van der Waals is not pertinent. It is reasonable to believe that, for a normal system without quantum effects, the modification from the Van der Waals equation is more significant than the real case, but this modification is less significant than the real case with quantum effects, thus a factor is introduced to weaken or strengthen the modification of the Van der Waals equation, or to re-modify the Van der Waals equation.

Though our result seems better, but there is still a few problems here. In the normal corresponding state, when the parameter ρ is too large or too small, our method becomes useless, because the parameter η will become very large, in these cases, maybe a properly modification on the higher order of expansion of Van der Waals equation is needed. Meanwhile, the physics of quantum effect about the corresponding state is not clear either. The mass of the particle and the temperature of the system will play important roles here, finally it will lead us to the interactions between the atoms.

Conclusion

The Van der Waals equation is expanded into its Taylor series form, and a parameter η is introduced to modify the fourth order item by changing its constant coefficients into variables. Obviously, the coexistence curve has been determined by the modified Van der Waals equation. It is found that our results are in good agreement with the experimental data, and it is also better than most of the other phenomenological equations. So our method seems to be very useful, and the most important fact is that we make use of the parameter η or analogous Virial coefficients to modify the expansion of Van der Waals equation. In fact, the modified Van der Waals equation is empirical, and it cannot be deduced from other formula. On the other hand, coexistence line of ^3He was also taken into consideration. It is found that, in general, for a normal system without quantum effects, the modification of the Van der Waals equation on the ideal gas law is more significant than the real case, however, for a system with quantum effect, the modification from the Van der Waals equation is less significant than the real case, that is why the factor η or γ is introduced to remodel the Van der Waals equation.

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