An Extension of the Van der Waals Equation of State

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Abstract
In this paper, we extend the Van der Waals equation of state to a universal form and find that the Van der Waals equation of state is a special condition of this form. Then a good form of equation of state for a balanced liquid-gas coexistence canonical argon-like system is given. The localization of this universal form is mentioned out in the end.
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1 INTRODUCTION
Much attention has been paid in recent years to the hard core Yukawa (HCY) potential as a model for the pair interactions of fluids[1]. The liquid state theories such as the Mean Spherical Approximation (MSA) and the Self Consistent Ornstein-Zernike Approximation (SCOZA) are proposed. Recent studies of the HCY fluid can be found in [2,3] and references therein. But the Van der Waals equation of state

\[ P = \frac{k_B T}{v - b} - \frac{a}{v^2} \]  

was less mentioned recently. Here \( a \) and \( b \) are parameters, \( k_B \) is the Boltzmann constant, and \( v = V/N \). In PART 2 of this paper, we extend the VDW equation

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of state to a universal form and find that the VDW equation of state is a special case of this form. In PART 3, we state the localization of this universal form by applying it to the liquid-gas phase transition to one order.

2 Theory

We define particle number density by

$$n = \frac{N}{V} = \frac{1}{v}. \quad (2)$$

Then Eq.(1) can be expressed as

$$P = \frac{Nk_B T}{V - Nb} - an^2. \quad (3)$$

Now we extend the VDW equation of state to such a form as

$$P = \frac{Nk_B T}{V - Nb} - \sigma Bn^{\sigma + 1}. \quad (4)$$

B and σ are parameters, too. When σ = 1, B = a, Eq.(4) reads the VDW equation of state. Now we sign

$$T^* = \frac{T}{T_c}, \quad (5)$$

$$n^* = \frac{n}{n_c}, \quad (6)$$

$$P^* = \frac{P}{P_c}, \quad (7)$$

with $T_c$ the critical temperature, $P_c$ the critical pressure, $n_c$ the critical particle number density.

At critical point, the function $P = P(V, T, N)$ has such qualities as

$$\left. \frac{\partial P}{\partial V} \right|_{T_c} = 0, \quad (8)$$

$$\left. \frac{\partial^2 P}{\partial V^2} \right|_{T_c} = 0. \quad (9)$$

Thus we get the critical data from Eq.(4) by solving Eq.(8) and Eq.(9). They are

$$n_c = \frac{\sigma}{(\sigma + 2)b}, \quad (10)$$

$$k_B T_c = \sigma(\sigma + 1)\left(\frac{2}{\sigma + 2}\right)^2 Bn_c^\sigma, \quad (11)$$

$$P_c = \frac{\sigma^2}{\sigma + 2} Bn_c^{\sigma + 1}, \quad (12)$$
\[ C = \frac{n_ck_BT_c}{P_c} = \frac{4(\sigma + 1)}{\sigma(\sigma + 2)} \]  

Letter C represents the critical coefficient. Substituting Eq.(10-12) to Eq.(4), we get the reduced equation of state:

\[ P^* = \frac{4n^*T^* (\sigma + 1)}{((\sigma + 2) - n^*\sigma)\sigma} - \frac{(\sigma + 2)n^* (\sigma+1)}{\sigma}. \]  

When \( \sigma = 1 \), Eq.(4) reads

\[ P = \frac{Nk_B T}{V - n_b} - Bn^2, \]  

which is just the form of the VDW equation of state. Data in Eq.(10-13) read

\[ n_c = \frac{1}{3b}, \]
\[ k_B T_c = \frac{8B}{27b}, \]
\[ P_c = \frac{B}{27b^2}, \]
\[ C = \frac{n_c k_B T_c}{P_c} = 8/3. \]  

We are very familiar with these results, which are the data from the VDW equation of state. Eq.(14) reads

\[ P^* = \frac{8n^*T^*}{(3 - n^*)} - 3n^*^2, \]  

which is the reduced form of the VDW equation of state. From Eq.(3), Eq.(4) Eq. (14) and Eq.(20), we see that the original form of the VDW equation of state is

\[ P = \frac{Nk_B T}{V - n_b} - 1 \ast an^{1+1}. \]  

When \( \sigma = 0.7432 \), Eq.(4) reads

\[ P = \frac{Nk_B T}{V - n_b} - 0.7432Bn^{1.7432}. \]  

Eq.(10-13) reads

\[ n_c = 0.2709b^{-1}, \]
\[ k_B T_c = 0.2609Bb^{-0.7432}, \]
\[ P_c = 0.0207Bb^{-1.7432}, \]
\[ C = \frac{n_c k_B T_c}{P_c} = 3.4201. \]
Eq.(14) reads

\[ P^* = \frac{9.3821n^*T^*}{(2.7432 - 0.7432n^*)} - 3.6911n^*^{1.7432}. \] (27)

Eq.(26) offers the critical coefficient of argon approximatively.

In 1975, W.G. Hoover, etc, generalized the Van der Waals mean-field attraction by choosing the attractive potential energy proportional to the \( S \)th power of the density[4]. Its per-particle partition function has the form[4]:

\[ z = \frac{V_e}{N!^s} \exp\left[ -\frac{\phi_0}{Nk_BT} - \frac{3\varepsilon\phi}{Nk_BT} + \frac{B}{k_BT}n^S \right]. \] (28)

Parameters are interpreted there. \( S \) is the exponent of \( n \). We all know that the equation of state can be obtained by

\[ P = kT \left( \frac{\partial}{\partial V} \ln z \right)_{T,N}. \] (29)

Then we can integrate Eq.(4) to get its corresponsive per-particle partition function. The result is

\[ z_0 = f(T,N,m)(V - Nb)^N \exp \left( \frac{B}{k_BT}n^\sigma \right), \] (30)

with \( f \) a function independent with \( V \). Here \( m \) is the mass of one particle. The equation of state obtained from Eq.(28) is complex. It is difficult to get its reduced form. Relatively, Eq.(4) is easier to be operated.

If we replace the Van der Waals repulsion term in Eq.(4) with the Carnahan-Starling hard-sphere repulsion term[5,6], the equation of state is written as

\[ P = \frac{Nk_BT}{V} \left[ 1 + \frac{4y - 2y^2}{(1 - y)^3} \right] - \sigma Bn^{\sigma + 1}, \] (31)

with \( y = g/(4V_m) \). Here \( g \) is the covolume of Carnahan-Starling hard-spheres[5], and \( V_m \) is \textit{mol} – volume. The critical data of Eq.(31) and the reduced form of Eq.(31) are difficult to be solved. We do not discuss it in this paper.

3 Discussion

Here we only study the balanced liquid-gas phase coexistence canonical system with Eq.(4) and Eq.(14).

In 1945, E.A. Guggenheim collected the data of this system from experiments and gave out the correlation of \( \rho_1^* \), \( \rho_2^* \) and \( T^* \) by the empirical equations[7] below

\[ \rho_1^* = 1 + 0.75(1 - T^*) - 1.75(1 - T^*)^{1/3}, \] (32)
In Eq. (32-35), \( \rho^* \) is the reduced density of the gases and \( \rho_2^* \) is the reduced density of the liquids. As far as an argon system is concerned, the inaccuracy of these two equation is generally only one or two parts per thousand of \( \rho_2^* \) or of \( \rho_1^* \) when \( T^* > 0.60T_c[7] \). So, it is acceptable to consider the data of \((T^*, n_1^*(T^*), n_2^*(T^*))\) from Eq.(36) and Eq.(37) as the experimental ones in this temperature region when the balanced liquid-gas coexistence argon-like system is considered. In Eq.(34-35), \( m \) is the mass of one particle. E.A. Guggenheim gave a numerical analytic result of the relation between the reduced temperature and the reduced pressure from experiments by equation[8]

\[
P_e^* = \exp(5.29 - 5.31/T^*),
\]

which best fits the experimental data for argon when \( T^* > 0.56T_c \) except a tiny region near the critical point[8]. Thus it is acceptable to consider the data of \((P_e^*, T^*)\) from Eq.(38) as the experimental ones, too. Substituting the data \((T^*, n_1^*(T^*))\) from Eq.(36) to Eq.(14), we get the data of the reduced pressure of the gases when \( \sigma \) is fixed. Then we compare these data with the ones gotten from Eq.(34) to see the accuracy of Eq.(14) when \( \sigma \) is chosen to be this value. Table.(1) illustrates the data with \( \sigma = 0.7432, \sigma = 0.8, \sigma = 1, \) and \( \sigma = 1.5 \). \( P_e^* \) is the reduced pressure of the gases gotten by substituting the data \((T^*, n_1^*(T^*))\) in Eq.(36) to Eq.(14). And \( P_2^* \) is the reduced pressure of the liquids gotten by substituting the data \((T^*, n_2^*(T^*))\) in Eq.(37) to Eq.(14). From Table 1, we can see

- \( |P_1^* - P_e^*|_{\sigma=0.7432} < |P_1^* - P_e^*|_{\sigma=0.8} < |P_1^* - P_e^*|_{\sigma=1} < |P_1^* - P_e^*|_{\sigma=1.5} \) when \( T^* > 0.8 \).
- \( |P_2^* - P_e^*|_{\sigma=0.7432} < |P_2^* - P_e^*|_{\sigma=0.8} < |P_2^* - P_e^*|_{\sigma=1} < |P_2^* - P_e^*|_{\sigma=1.5} \) when \( T^* > 0.8 \).
- \( |P_1^* - P_e^*|_{\sigma T^*} < |P_2^* - P_e^*|_{\sigma T^*} \) when \( T^* \) are fixed in the region \( 0.7 \leq T^* \leq 0.99 \).

So we can conclude that \( \sigma = 0.7432 \) is the best one of these four values in the temperature region \( 0 > T^* > 0.8 \) and Eq.(14) fits the gas phase better than the liquid phase.
Here we will ask whether a proper $\sigma = \sigma_0$, which can bring right academic forecast to the experimental data $P^*, n_1^*, n_2^*$ and $T^*$, exists. Now we suppose that such a proper $\sigma_0$ exists. Then Eq.(14) is fixed to be the form of

$$P^* = 4n^*T^* (\sigma_0 + 1) \frac{(\sigma_0 + 2) n^*(\sigma_0 + 1)}{\sigma_0}.$$  \hspace{1cm} (39)

Thus we have

$$y = y(T^*, \sigma_0) = P^*(n_1^*, T^*, \sigma_0) - P^*(n_2^*, T^*, \sigma_0) = 0,$$ \hspace{1cm} (40)

where $n_1^*$, $n_2^*$ and $T^*$ are the experimental ones in Eq.(36) and Eq.(37). According to our supposition, at two different reduced temperature $T_1^*$ and $T_2^*$, Eq.(40) will be true. Fig.(1) is the curve of $y = y(T_1^* = 0.8, \sigma)$. Fig.(2) is the curve of $y = y(T_2^* = 0.85, \sigma)$. From the figures, we know that $y = y(T_1^* = 0.8, \sigma) = 0$ when $\sigma = \sigma_0(T_1^* = 0.8) = 1.7050$, $y = y(T_2^* = 0.85, \sigma) = 0$ when $\sigma = \sigma_0(T_2^* = 0.85) = 1.9190$. For $\sigma_0(T_1^* = 0.8) \neq \sigma_0(T_2^* = 0.85)$, the proper $\sigma = \sigma_0$ we try to find does not exist.

In 1990, J.M.Kincaid, etc, representated the pure fluid coexistence curves by series expansion successfully[9]. Detailed description about pure fluid coexistence curves such as argon’s can be seen there. Our result here is not as good as theirs, but is more simple in calculation.

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Figure 1: The curve of $y = y(T^*_1 = 0.8, \sigma)$ versus $\sigma$. The dotted line is beeline $y = 0$ which is a reference here.

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Figure 2: The curve of $y = y(T_1^* = 0.85, \sigma)$ versus $\sigma$. The dotted line is beeline $y = 0$ which is a reference here.
Table 1: Data

| $T^*$   | $\sigma$  | $\sigma$  | $\sigma$  | $\sigma$  | $\sigma$  |
|---------|-----------|-----------|-----------|-----------|-----------|
| 0.7     | 0.7432    | 0.7432    | 0.7432    | 0.7432    | 0.7432    |
| 0.8     | 0.1075    | 0.1042    | 0.0931    | 0.0715    | 0.0715    |
| 0.8     | 0.0071    | 0.2249    | 5.0082    | 138.7650  | 138.7650  |
| 0.88    | 0.0071    | 0.0071    | 0.0071    | 0.0071    | 0.0071    |
| 0.88    | 0.0071    | 0.0071    | 0.0071    | 0.0071    | 0.0071    |
| 0.9     | 0.0071    | 0.0071    | 0.0071    | 0.0071    | 0.0071    |
| 0.9     | 0.0071    | 0.0071    | 0.0071    | 0.0071    | 0.0071    |
| 0.95    | 0.0071    | 0.0071    | 0.0071    | 0.0071    | 0.0071    |
| 0.97    | 0.0071    | 0.0071    | 0.0071    | 0.0071    | 0.0071    |
| 0.99    | 0.0071    | 0.0071    | 0.0071    | 0.0071    | 0.0071    |

$P^*_1$ | 0.1075    | 0.1042    | 0.0931    | 0.0715    | 0.0715    |
$P^*_2$ | 0.0071    | 0.2249    | 5.0082    | 138.7650  | 138.7650  |
$P^*_c$ | 0.0071    | 0.0071    | 0.0071    | 0.0071    | 0.0071    |
$|P^*_1 - P^*_c|$ | 0.0071    | 0.0071    | 0.0071    | 0.0071    | 0.0071    |
$|P^*_2 - P^*_c|$ | 0.0071    | 0.0071    | 0.0071    | 0.0071    | 0.0071    |

$\sigma = 0.7432$ $\sigma = 0.8$ $\sigma = 1$ $\sigma = 1.5$
