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Solid State Density in Equations of State for Fluids

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Abstract. — The correlation between the density of a substance at the critical point and in the solid state is examined in view of the amazing empirical feature that the ratio between the above two densities is a constant for most substances. This universal feature offers a new criterion for assessing some improved versions of van der Waals equation of state for fluids.

1. Introduction

The quest for a simple closed form analytical Equation Of State (EOS) has been persisting [1–6] ever since the proposal of van der Waals EOS in 1873. Its subsequent refinements and its relations to some modern approaches have been extensively discussed in a recent review [5]. Later, a new equation of state [7] has been proposed by a judicious combination of hard-sphere pressure term and attractive pressure term to fairly match the perturbed hard-sphere approach [8].

This note discusses the importance of the amazing empirical feature [9] that the ratio \((\rho_s/3\rho_c)\) between the solid state density \(\rho_s\) and the critical density \(\rho_c\) is a universal constant close to unity. In addition, it is demonstrated that the above empirical feature offers a new criterion for evaluating various two-constant equations of state [1–7] obtained by improving the van der Waals EOS.

2. Van der Waals Equation

In 1873, van der Waals proposed the following EOS [1–5] for fluids relating the pressure \(p\), molar volume \(V\) and the temperature \(T\):

\[
p = RT/(V - b) - a/V^2
\]  

(1)

Here, \(R\) is the universal gas constant, \(a\) is the parameter characterizing cohesion between the molecules and \(b\) is the correction factor of the intrinsic volume of the molecules equal to four times the hard-core volume of molecules in one mole of gas [4], viz.

\[
b = \mathcal{N}(2\pi d^3/3)
\]  

(2)

Here \(\mathcal{N}\) is the Avogadro number and \(d\) is the hard-core diameter of the molecules.
At the critical point, the conditions [1-5]

\[
\left( \frac{dp}{dV} \right)_{T=T_c} = 0
\]

and

\[
\left( \frac{d^2p}{dV^2} \right)_{T=T_c} = 0
\]

yield the critical parameters \( p_c, V_c \) and \( T_c \) in terms of \( a, b, \) and \( R, \) as well as the critical compressibility factor \( Z_c = p_c V_c / RT_c. \) As seen in Table I, the value of \( z_c = 0.375 \) predicted by van der Waals EOS is about 40% higher than the experimental values of \( Z_c \) for most substances [1-5] which lie around 0.27.

Table I. — Comparison of \( Z_c \) and \( (V_c/b) \) ratio for various EOS considering \( V_c = 3V_s \)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>van der Waals (Eq. (1))</th>
<th>Dieterici (Eq. (9))</th>
<th>Guggenheim (Eq. (10))</th>
<th>New [7] (Eq. (11))</th>
<th>Exptl. Ref. [1, 9]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Z_c )</td>
<td>0.375</td>
<td>0.271</td>
<td>0.36</td>
<td>0.252</td>
<td>0.27</td>
</tr>
<tr>
<td>( V_c )</td>
<td>3 b</td>
<td>2 b</td>
<td>1.975 b</td>
<td>0.75 b</td>
<td>—</td>
</tr>
<tr>
<td>( V_s/b )</td>
<td>1</td>
<td>2/3</td>
<td>0.66</td>
<td>0.25</td>
<td>—</td>
</tr>
</tbody>
</table>

3. Solid State Density

An important shortcoming of the van der Waals equation and its subsequent modifications [1-6] would become more apparent when consistency of their predictions of the ratio \( (V_s/b) \) with the following empirical relation [9] is examined:

\[
\left( \frac{V_c}{V_s} \right) = \left( \frac{\rho_s}{\rho_c} \right) = 3.07
\]  

(4)

This result which empirically relates the molar solid state volume \( V_s \) to the critical volume \( V_c \) is found to be true for most substances, irrespective of the nature of molecular packing in the solid state. The significance of this exciting empirical feature has been overlooked by most researchers.

It might be tempting to argue that the solid state density which depends on crystalline form could not be taken as a reference while speaking of EOS for fluids. But, it so happens that when a material is cooled below its critical point, condensation takes place and there is a tendency towards an orderly arrangement of the molecules similar to its solid structure due to cohesive forces acting on them. As discussed by Eyring and John [10], the structure of a liquid is close to that of the solid [4,10] and the liquid structure can be treated as an admixture of solid-like and gas-like degrees of freedom. In fact, for most liquids [4,10], the liquid density at the normal boiling point differs from its state density only by about 10%.

For most substances, the ratio \( (\rho_t/\rho_c) \) between liquid state density \( \rho_t \) at normal boiling point and the critical density is typically around 2.7. For example, \( \rho_t = 1.4 \text{ gm/cm}^3, \) 1.14 \text{ gm/cm}^3 and 0.81 \text{ gm/cm}^3 respectively for Argon, Oxygen and Nitrogen while \( \rho_c = 0.53 \text{ gm/cm}^3, \) 0.43 \text{ gm/cm}^3 and 0.31 \text{ gm/cm}^3, respectively. Consequently, \( \rho_t/\rho_c = 2.7, \) 2.6 and 2.6 for the above substances in order. When the 10% density rise at solidification [4,10] is considered, \( (\rho_s/\rho_c) \) will come close to 3.0 in accord with the empirical relation given by equation (4).
This interesting invariance of the density ratio ($\rho_s/\rho_c$) can also be deduced from van der Waals EOS given by equation (1) which can be rewritten in terms of the reduced variables $p_r = p/p_c$, $V_r = V/V_c$ and $T_r = T/T_c$ as [5],

$$P_r = \frac{8T_r}{(3V_r - 1)} - \frac{3}{V_r^2}$$

(5)

By demanding that $p_r$ tends to infinity at the onset of the liquid-solid transitions, the reduced volume in the solid state may be obtained by setting $(3V_r - 1) = 0$ in equation (5). This yields $3V_s/V_c = 1$ or $V_c = 3V_s$ in close accord with equation (4). Thus, there is some sort principle of corresponding states that relates $V_c$ and $V_s$ and this important feature is borne out by van der Waals EOS and some of its subsequent modifications [5]. The above novel prediction of $V_c/V_s = 3$, by equation (5) has some interesting consequences which are discussed below.

4. Shortcomings of Van der Waals EOS

As shown in Table I, the prediction of the van der Waals EOS that $V_c = 3b$ combined with the above novel prediction of $V_c = 3V_s$ would imply $V_s = b$. But, the value of $b$ defined by equation (2) is four times the hard-core volume of molecules in one mole of the gas. Hence the above value of $V_s = b$ resulting from the van der Waals EOS is quite unrealistic. Thus van der Waals EOS not only overpredicts the critical compressibility factor $Z_c$, but it more grossly overpredicts the solid state volume $V_s$. The latter shortcoming has not been emphasized in the past.

5. Clausius Equation of State

Clausius modified van der Waals equation by introducing an adjustable parameter $c$ in the attractive pressure term of equation (1) as follows:

$$p = \frac{RT}{(V - b)} - \frac{a}{(V + c)^2}$$

(6)

This EOS allows the exact calculation of $Z_c$ for any substance by a convenient choice of $c$. Imposing the conditions given by equation (3), the above EOS yields,

$$Z_c = \frac{3b + 2c}{8(b + c)}$$

(7)

and

$$V_c = 3b + 2c$$

(8)

For a typical choice of $c = 2b$, the above EOS will yield $Z_c = 0.29$ close to the experimental value [1,5,9] of $Z_c = 0.27$ observed in most substances. But, the resulting value of $V_c = 5b$ combined with equation (4) will yield $V_s \sim (5/3)b$ which is far away from the reality. Thus it is evident that correct prediction of the critical compressibility factor $Z_c$ does not mean correct prediction of the behaviour at higher densities or near the critical point. The above argument can be reinforced by the following two-constant EOS which involves a more appropriate [5] form of the attractive pressure term.
6. Dieterici Equation

In 1899, Dieterici proposed the following EOS [1,3,5] as a significant refinement over the van der Waals EOS:

\[
p = \frac{RT}{(V - b)} \exp \left( -\frac{a}{RTV} \right)
\]  

(9)

If this equation is viewed in the context of the perturbed hard-sphere model [5,8], which considers a liquid as a hard-sphere gas moving in a uniform background provided by the attractive force between the molecules, then the effect of the attractive potential of this internal force field would be to reduce the density of the hard-sphere gas by the Boltzmann factor [4]

\[
\exp(-E_p/k_BT).
\]

Here, \(E_p\) is the potential energy of a molecule in the attractive force field and \(k_B\) is the Boltzmann constant. On empirical basis, Dieterici assumed [1] \(E_p\) to vary as \(V^{-1}\). In this respect, Dieterici equation has a sound physical basis on a par with the modern approach envisaged by the perturbed hard-sphere model [8], but for the crude hard-sphere term \(RT/(V - b)\) arising from the hard-core repulsion potential [1-5].

Table I illustrates that the critical compressibility \(Z_c = 0.271\) predicted by equation (9) remarkably agrees with the experimental value of \(Z_c\) for most fluids [1,5,9]. However, with \(V_c = 2b\) and \(V_c = 3V_s\) predicted by equation (4), \(V_s\) becomes equal to \((2/3)b\) which is also unrealistic. This unrealistic prediction clearly indicates the need for refining the hard-sphere pressure term of the Dieterici equation in order to match the outcome of more accurate machine calculations [5,8].

7. Guggenhein Equation

In 1965, Guggenheim [2,5] suggested a modified hard-sphere pressure term \(RT/V(1 - y)^4\) in lieu of the corresponding term \(RT/V(1 - 4y)\) of equation (1) with \(y = b/4V\) and proposed the following EOS:

\[
p = \frac{RT}{V(1 - b/4V)^4} - \frac{a}{V^2}
\]  

(10)

As discussed in a recent review [5], this new hard-sphere pressure term compares well with the results of machine calculations employing molecular dynamics and Monte-Carlo procedure [5,6,8]. However as seen in Table I, the critical compressibility factor \(Z_c = 0.36\) predicted by equation (10) is about 30% higher than the experimental value of \(Z_c = 0.27\) for most substances [1,9]. It can be readily seen that most other improved versions of van der Waals EOS suggested by Redlich-Kwong, Carnaham-Starling, Sevast’ Yanov etc [5] also would suffer from such shortcomings, by virtue of the van der Waals type of attractive term \((-a/V^2)\).

8. New Equation of State

In 1994, a new EOS [7] has been proposed by replacing the hard-sphere pressure term of the Dieterici equation by that of Guggenhein equation to obtain the following combination:

\[
p = \frac{RT}{V(1 - b/4V)^4} \exp \left( -\frac{a}{RTV} \right)
\]  

(11)

As seen in Table I, this EOS predicts \(V_c = 0.75b\) which when combined with its prediction of \(V_c = 3V_s\) would yield \(V_s = 0.25b\) in sensible agreement with real situations for most cases. Also,
\( Z_c = 0.252 \) predicted by this simple analytical EOS agrees within 10\% with the experimental values of \( Z_c = 0.27 \) for most substances [1,5,9]. In fact, the critical pressure \( p_c \) predicted by this new EOS has been found to be in accord with the predictions of more sophisticated approaches [7] for some nuclear fuels. This marks the importance of Dieterici type of attractive term [5]. Moreover, there is scope for improving this EOS, without affecting the above predictions, by replacing the cohesion factor \( a \) by \( a_0 T^{-1/2} \) as done by Redlich and Kwong [5].

9. Conclusions

Thus, the invariance of the ratio between the density at the solid state and the critical point of substances leads to a new criterion for assessing various EOS. Though Guggenheim form of hardsphere term is rather less accurate than Sevast’ Yanov form [5], the former yields analytical solution for \( V_c \) in terms of \( b \) and works so well with Dieterici form of attractive pressure term that the new EOS given by equation (11) simultaneously predicts \( Z_c \) and \( (V_s/b) \) with better accuracy than most other EOS [1–6]. In addition, for better prediction of vapour pressures at various temperatures, the new EOS can be readily modified by incorporating a temperature dependent cohesion factor term \( a_0 T^{-1/2} \) instead of \( a \) in equation (11), as was done by Redlich and Kwong [5].

References