

10.40 Thermodynamics
Problem Set 5

Fall 2003

Problem #3

We would like to make a few modifications to the van der Waals EOS and evaluate how the PVT behavior of a pure fluid might change.

- Expand the $RT/(V-b)$ term of the vdw EOS as a polynomial power series in b/V
- If we truncate the expansion after the $(b/V)^2$ term, how does the compressibility change as a function of density from very low density ($\rho = 0$) to high density ($\rho = 1/b$)?
- Is it possible for a fluid obeying this modified EOS to reach a Zeno condition where $Z = 1$? If so, where does this occur?
- Assuming that the Zeno condition is met for this pure material, estimate the fugacity coefficient (ϕ_i) at this point. How do you interpret your estimate?

Solution:

(a)

$$\text{van der Waals EOS: } P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\text{Rewriting the first term: } \frac{RT}{V-b} = \frac{RT/V}{1-b/V}$$

Expand using the following series expansion: $(1-x)^{-1} = 1 + x + x^2 + x^3 + x^4 + \dots$ for $x^2 < 1$

Since b is an exclusion volume, $(b/V)^2 < 1$.

$$\text{Applying the expansion: } \frac{RT/V}{1-b/V} = \frac{RT}{V} \left(1 + \left(\frac{b}{V}\right) + \left(\frac{b}{V}\right)^2 + \left(\frac{b}{V}\right)^3 + \dots \right)$$

$$\frac{RT/V}{1-b/V} = RT(\rho + b\rho^2 + b^2\rho^3 + \dots)$$

(b)

After truncation:

$$P = \frac{RT}{V} \left(1 + \left(\frac{b}{V} \right) + \left(\frac{b}{V} \right)^2 \right) - \frac{a}{V^2} = \frac{RT}{V} + \frac{RT}{V^2} \left(b + \frac{b^2}{V} - \frac{a}{RT} \right)$$

$$Z = \frac{PV}{RT} = 1 + \frac{b}{V} + \left(\frac{b}{V} \right)^2 - \frac{a}{RTV} \quad (1)$$

$$Z = 1 + b\rho + b^2\rho^2 - \frac{a}{RT}\rho$$

$$\rho \rightarrow 0, \quad Z = 1$$

$$\rho \rightarrow 1/b, \quad Z = 3 - \frac{a}{bRT}$$

For the $\rho = 1/b$ case, it should strike us as odd that we get an arbitrary number, 3, in our result. Looking at our arithmetic, we realize that the value of 3 comes from us truncating after $(b/V)^2$. If we had left more terms in the truncation, we would have had a larger constant in the solution. If we had left infinite terms, we would have a constant equal to infinite. The reason for this is that at $\rho = 1/b$, the series expansion that we used is no longer valid since $b/V = 1$. We conclude that

$$\text{As } V \rightarrow b, \quad \frac{RT}{V-b} \rightarrow \infty$$

In the VdW EOS, b represents the exclusion volume of the molecules and describes the repulsive forces between molecules. If $V=b$, then the molecules would be in intimate contact with no space between them. This can be interpreted as meaning that an infinite pressure is needed to bring these molecules into such a condensed state.

(c)

As shown in part (b), it is possible for a fluid that is obeying the truncated EOS to reach $Z=1$ condition.

The trivial case for $Z=1$ is $\rho \rightarrow 0$

The second case is:

$$Z = 1 + b\rho + b^2\rho^2 - \frac{a}{RT}\rho = 1$$

$$b + b^2\rho = \frac{a}{RT} \quad (2)$$

This represents the point at which the attractive forces (described by a) are perfectly balanced by the repulsive forces (described by b) between the molecules.

(d)

We are interested in the second case for $Z=1$ (equation (1)).

From equation 9-143 (text) for a pure material,

$$RT \ln \phi_i = RT \ln \frac{f_i}{P} = - \int_{\infty}^V \left[\left(\frac{\partial P}{\partial N} \right)_{T,V} - \frac{RT}{V} \right] dV - RT \underbrace{\ln Z}_{=0} \quad (3)$$

Calculating the partial derivative from the truncated vdw EOS

$$P = \frac{NRT}{V} + \frac{RTbN^2}{V^2} + \frac{RTb^2N^3}{V^3} - \frac{aN^2}{V^2} \quad (4)$$

$$\left(\frac{\partial P}{\partial N} \right)_{T,V} = \frac{RT}{V} + \frac{2RTbN}{V^2} + \frac{3RTb^2N^2}{V^3} - \frac{2aN}{V^2}$$

Plugging equation (4) into equation (3) yields,

$$RT \ln \phi_i = - \int_{\infty}^V \left[\frac{RT}{V} + \frac{2RTbN}{V^2} + \frac{3RTb^2N^2}{V^3} - \frac{2aN}{V^2} - \frac{RT}{V} \right] dV$$

$$RT \ln \phi_i = - \left[-\frac{2RTbN}{V} - \frac{3}{2} \frac{RTb^2N^2}{V^2} + \frac{2aN}{V} \right]_{\infty}^V$$

At $V = \infty$, all terms go to zero

$$\text{At } V, a = RT \left(b + \frac{b^2N}{V} \right)$$

$$\ln \phi_i = \frac{2bN}{V} + \frac{3}{2} \frac{b^2N^2}{V^2} - \frac{2bN}{V} - \frac{2b^2N^2}{V^2}$$

$$\ln \phi_i = -\frac{1}{2} \frac{b^2N^2}{V^2} = -\frac{1}{2} \frac{b^2}{V^2}$$

Alternate method: departure function

From equation 9-113 (text),

$$RT \ln \phi_i = RT \ln \frac{f_i}{P} = G_i - G_i^0$$

From section 8.5 (text)

$$\begin{aligned}
 G - G^0 &= (H - H^0) - T(S - S^0) \\
 G - G^0 &= (A - A^0) + PV - RT + T(S - S^0) - T(S - S^0) \\
 G - G^0 &= (A - A^0) + PV - RT
 \end{aligned} \tag{5}$$

We would like to calculate the Gibbs Free Energy departure function by using the Helmholtz Free Energy departure function since the Helmholtz Free Energy departure function is a function of temperature and volume.

Start by calculating the Helmholtz Free Energy departure function.

$$A - A^0 = -\int_{\infty}^V \left(P - \frac{RT}{V} \right) dV + RT \ln \frac{V^0}{V} \tag{6}$$

Plug equation (1) into (6).

$$A - A^0 = -\int_{\infty}^V \left(\frac{RT}{V} + b \frac{RT}{V^2} + b^2 \frac{RT}{V^3} - \frac{a}{V^2} - \frac{RT}{V} \right) dV + RT \ln \frac{V^0}{V}$$

$$A - A^0 = \left[b \frac{RT}{V} + \frac{b^2}{2} \frac{RT}{V^2} - \frac{a}{V} \right]_{\infty}^V + RT \ln \frac{V^0}{V}$$

$$\text{At } V, a = RT \left(b + \frac{b^2}{V} \right)$$

$$A - A^0 = b \frac{RT}{V} + \frac{b^2}{2} \frac{RT}{V^2} - b \frac{RT}{V} - b^2 \frac{RT}{V^2} + RT \ln \frac{V^0}{V}$$

$$A - A^0 = -\frac{b^2}{2} \frac{RT}{V^2} + RT \ln \frac{V^0}{V}$$

Plug the expression for the departure function for the Helmholtz Free Energy into equation (5).

$$G - G^0 = -\frac{b^2 RT}{2V^2} + RT \ln \frac{V^0}{V} + PV - RT$$

$$V^0 = \frac{RT}{P} \Rightarrow RT \ln \frac{V^0}{V} = RT \ln \frac{RT}{PV} = -RT \underbrace{\ln Z}_{=0} = 0$$

and $PV = RT$ since $Z=1$

$$\ln \phi_i = G - G^0 = -\frac{b^2 RT}{2V^2} + \underbrace{RT \ln \frac{V^0}{V}}_{=0} + \underbrace{PV - RT}_{=0}$$

$$\ln \phi_i = -\frac{1}{2} \frac{b^2}{V^2}$$

The departure function method yields the same result as starting from equation 9-113 (text).

This result illustrates that although $Z = 1$, the pure fluid does *not* behave ideally at all points along the Zeno line. In fact, the more condensed the fluid (the smaller the value of V), the greater the departure from ideality.