

THE THERMODYNAMICS OF THE REAL FLUIDS- van der Waals equation of state SELF STUDY MODULE

Objective

The objective of this module is to remove the assumptions from the ideal gas law. Upon successful completion of this module, the student should be able to estimate either one of PVT for real fluids. In addition to the values of these variables, it is also possible to estimate the vapor-liquid equilibria for fluids that are at temperatures lower than the critical temperature.

Reading assignment

Read Chapter 6 Sandler's Thermodynamics, 4th edition.

The assumptions of the ideal gas law

The ideal gas law has the following assumptions:

1. The volume occupied by the molecules, in comparison to the total volume, is negligible
2. The molecules do not interact.

Using this starting point, Lord Kelvin discovered the absolute zero, by plotting PV (a measure of energy) of a gas as a function of T. This plot had two features. The first feature of the plot, was that it was a straight line with a slope equal for all the gases investigated. The slope is what we call R, the universal gas constant. Universal indicates that the constant is valid for all of the gases under the conditions that they behave ideally. The second feature was the intercept of the Temperature axis. This temperature signified the condition where net energy is zero.

The van der Waals Equation of State

Let us now remove the assumptions of the ideal gas law one by one:

1. There is a finite volume that the molecules occupy. In fact, this is even more important when we move close to the liquid state. Let's call this volume b , such that the volume of voids that is calculated by the ideal gas law becomes $(V - b)$ and the new equation of state is $P(V - b) = RT$
2. We will also remove the second assumption by adding a term that represents the molecular interactions. For the discussion we will conduct here, the interaction parameter we chose will be $\frac{a}{V^2}$, this parameter will correct the local pressures sensed by the molecules, for the attractive interactions.

As a result, our new equation of state took the following form:

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

This is the van der Waals equation of state. It will be the basis of our discussions. The van der Waals (vdW) equation of state (EOS) is a cubic polynomial in terms of V . There is a group of equations of state called cubic equations due to the fact that in all of these equations, the highest power of V is three, but the function does not have to be a polynomial. Now, in the Figure below, you see a plot of two isotherms emanating from VDW EOS. One of the isotherms (orange colored) is at the critical temperature, and the other one (blue) is at a temperature lower than the critical temperature, such that the vapor and liquid coexistence can be experienced.

The cubic equation of state exhibits three extrema: a maximum, a minimum, and a saddle point at which the concave curve and convex curve meet. These extrema are represented by the following mathematical equalities at the critical point.

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 = -\frac{RT}{(V-b)^2} + 2\frac{a}{V^3}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2RT}{(V-b)^3} - 6\frac{a}{V^4} = 0$$

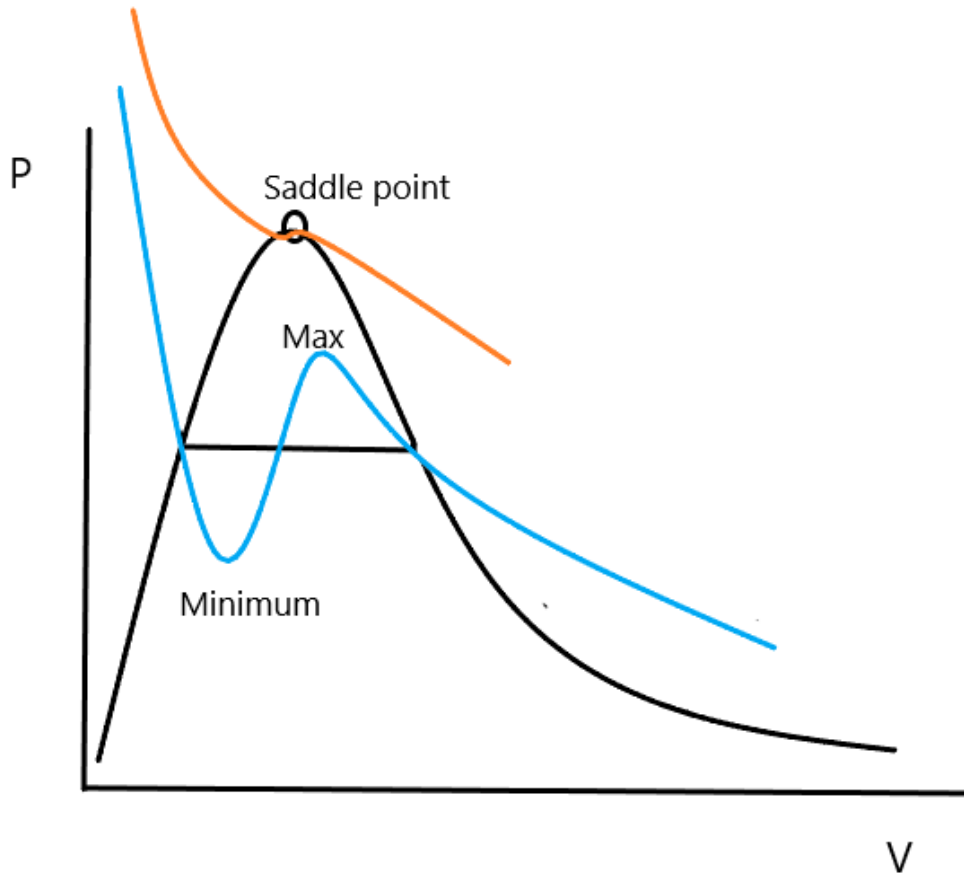
These two identities give us a set of equations that we can calculate and b

$$a = \frac{9V_c RT_c}{8}$$

$$b = \frac{V_c}{3}$$

Substitute these values to vdW to obtain the critical pressure.

$$P_c = \frac{a}{27b^2}$$



As seen, there is a horizontal line connecting the vapor equilibrium curve with that of the liquid equilibrium curve. The locus of this curve was decided such that the area remaining above the curve and below are equal.

We have removed the ideal gas assumptions from the equation of state. Now we will do the same for the internal energy.

Calculate

1. Using the van der Waals equation of state, plot $T=400$ K isotherm for water. Determine the equilibrium pressure at this temperature using the Maxwell rule of equal area construction.
2. Compare the critical point of different fluids.
 - a. Using the van der Waals equation of state, plot the isotherm at the critical temperature for the following fluids. You can use MATHCAD, MATLAB or EXCEL to generate your plots.
 - i. Water,
 - ii. Ethylene
 - iii. Carbon dioxide
 - b. Now, normalize your isotherms generated in part a. Normalize your temperature by using the reduced functions. $T_R = \frac{T}{T_C}$; $P_R = \frac{P}{P_C}$. How do the isotherms for different fluids look like? Can you generalize a conclusion?
3. Estimate the specific volume of liquid water and water vapor at the following temperatures using van der Waals equation of state. Compare your estimations with the values reported in the steam table.
4. Estimate the equilibrium pressure of methane at 120 K. Compare the estimation with the value you read from Figure 3.3-2, Sandler (4th edition) .

Evaluate yourself

Check if you have answers to the following questions:

1. Why do we need these four different forms of energy, i.e., U, H, G and A?
2. What is the difference between internal energy and enthalpy?
3. What is the difference between Helmholtz free energy and Gibbs Free Energy?

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4. Why Helmholtz Free Energy and Gibbs Free Energy are called free energies? What makes them free? Is there a bound energy?
5. Why is entropy an independent variable in the thermodynamic landscape?