Lecture 24 - Van der Waals Phase Behavior

The van der Waals fluid is capable of two-phase (liquid and vapor) behavior. The attractive interactions allow for condensation. Let's examine the phase behavior in depth. There are three important parts of the phase diagram:

i) the coexistence curve (binodal)

ii) the limit of stability (spinodal)

iii) the critical point.

We can get all of these if we have the free energy. We got this last time. The free energy is

$$\frac{A}{Nk_BT} = \ln\left(\frac{N\lambda^3}{V-Nb}\right) - \frac{aN}{Vk_BT} - 1$$ compare to Sackur-Tetrode

A. coexistence curve

The binodals can be found using the equilibrium conditions

$\mu_l = \mu_g$ chemical equilibrium μ_i: chemical potential of phase i

$P_l = P_g$ mechanical equilibrium P_i: pressure of phase i

We can get both of these from derivatives of the Helmholtz free energy:

$$P = \left(\frac{\partial A}{\partial V}\right)_{T,N}$$ we found this last time

$$P = \frac{Nk_BT}{V-Nb} - \frac{aN^2}{V^2} \Rightarrow \boxed{P = \frac{k_BT}{v-b} - \frac{a}{v^2}} \qquad v = \frac{V}{N}$$

Let's derive μ now.

$$\mu = \left(\frac{\partial A}{\partial N_i}\right)_{P,T} = \frac{\partial}{\partial N}\left[Nk_BT\ln\left(\frac{N\lambda^3}{V-Nb}\right) - \frac{aN^2}{V} - Nk_BT\right]$$

$$\mu = \frac{\partial}{\partial N}\left[N k_B T \ln N + N k_B T \ln \lambda^3 - N k_B T \ln(V - Nb) - \frac{aN^2}{V} - N k_B T\right]$$

$$= k_B T \ln N + \frac{N k_B T}{N} + k_B T \ln \lambda^3 - k_B T \ln(V - Nb) - \frac{N k_B T}{V - Nb} \cdot (-b)$$

$$- \frac{2aN}{V} - k_B T$$

$$= k_B T \ln\left(\frac{N\lambda^3}{V - Nb}\right) + \frac{Nb k_B T}{V - Nb} - \frac{2aN}{V} \qquad v = V/N$$

$$= k_B T \ln\left(\frac{\lambda^3}{v - b}\right) + \frac{b k_B T}{v - b} - \frac{2a}{v} \qquad \beta = (k_B T)^{-1}$$

$$\boxed{\beta\mu = \ln\left(\frac{\lambda^3}{v - b}\right) + \frac{b}{v - b} - \frac{2\beta a}{v}}$$

With these two equations, we can now set

1) $P(v_l) = P(v_g)$
2) $\beta\mu(v_l) = \beta\mu(v_g)$

v_g : gas molar volume
v_l : liquid " "

$$\boxed{\begin{aligned} &1)\ \frac{k_B T}{v_l - b} - \frac{a}{v_l^2} = \frac{k_B T}{v_g - b} - \frac{a}{v_g^2} \\ &2)\ -\ln(v_l - b) + \frac{b}{v_l - b} - \frac{2\beta a}{v_l} = -\ln(v_g - b) + \frac{b}{v_g - b} - \frac{2\beta a}{v_g} \end{aligned}}$$

These can now be solved given parameters a, b and a temperature T for the coexisting molar volumes v_g & v_l.

B. Spinodal Curve

The spinodal occurs at the inflection point, i.e., the limit of stability, $\partial^2 A / \partial v^2 = 0$. Recall that,

$$P = \frac{\partial A}{\partial v} \Rightarrow \frac{\partial^2 A}{\partial v^2} = \frac{\partial P}{\partial v} \Rightarrow \frac{\partial P}{\partial v} = 0$$

Let's compute the spinodal.

$$\frac{\partial P}{\partial v} = \frac{\partial}{\partial v}\left[\frac{k_B T}{v-b} - \frac{a}{v^2}\right] = \frac{-k_B T}{(v-b)^2} + \frac{2a}{v^3} = 0$$

We need to eliminate T to find $v_{spinodal}$.

$$\frac{k_B T}{(v-b)^2} = \frac{2a}{v^3} \Rightarrow \boxed{k_B T = \frac{2a}{v^3}(v-b)^2}$$ Spinodal temperature

Plug into P to find the P-v relation

$$P = \frac{k_B T}{v-b} - \frac{a}{v^2} = \frac{2a}{v^3}(v-b)^2 \cdot \frac{1}{(v-b)} - \frac{a}{v^2}$$

$$\boxed{P = \frac{2a(v-b)}{v^3} - \frac{a}{v^2}}$$

can solve for points in P-v plane given a, b.

C. Critical point

The critical point occurs at the maximum of the limit of stability,

$$\frac{\partial}{\partial v}\left(\frac{\partial P}{\partial v}\right) = 0 \Rightarrow \frac{\partial^2 P}{\partial v^2} = 0$$

Let's find the critical point.

$$\frac{\partial P}{\partial v} = \frac{-k_B T}{(v-b)^2} + \frac{2a}{v^3}$$

$$\frac{\partial^2 P}{\partial v^2} = \frac{2 k_B T}{(v-b)^3} - \frac{6a}{v^4} = 0$$

we can use $k_B T = \frac{2a}{v^3}(v-b)^2$ because the critical point must lie on the spinodal

$$\frac{\partial^2 P}{\partial v^2} = \frac{2}{(v-b)^3} \frac{2a}{v^3}(v-b)^2 - \frac{6a}{v^4} = 0$$

$$= \frac{4a}{(v-b)v^3} - \frac{6a}{v^4} = 0$$

$$\frac{\partial^2 P}{\partial v^2} = \frac{2}{(v-b)} - \frac{3}{v} = 0 \Rightarrow \frac{v-b}{v} = \frac{2}{3} \Rightarrow 1 - \frac{b}{v} = \frac{2}{3} \Rightarrow \frac{b}{v} = \frac{1}{3}$$

$$\boxed{v_c = 3b}$$ critical volume

Plug back into kT to find T_c

$$kT = \frac{2a}{v^3}(v-b)^2$$

$$kT_c = \frac{2a}{(3b)^3}(3b-b)^2 = \frac{2a}{27b^3} 4b^2 = \frac{8a}{27b}$$

$$\boxed{kT_c = \frac{8a}{27b}}$$ critical temperature

Finally, we can get P_c

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

$$P_c = \frac{8a/27b}{3b-b} - \frac{a}{(3b)^2} = \frac{8a}{(27b)(2b)} - \frac{a}{9b^2} \qquad \frac{8}{54} = \frac{4}{27}$$

$$= \frac{4a}{27b^2} - \frac{a}{9b^2} = \frac{4a-3a}{27b^2} = \frac{a}{27b^2}$$

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

See Python plot of vdW phase diagram

D. Corresponding States

We now have a phase diagram based on only two molecular parameters: a & b (mean-field attraction and repulsion). This suggests our phase diagram might be general to many different fluids! Conveniently, the critical point (P_c, T_c, V_c) was described by a and b only. Perhaps we could non-dimensionalize by the critical point to "scale out" all of our molecular uniqueness to get a universal curve!

Let's non-dimensionalize $P(v,T)$:

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

$$\tilde{T} = T/T_c = T\frac{27 b k_B}{8a}$$

$$\tilde{v} = v/v_c = \frac{v}{3b}$$

} substitute and simplify

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

$$\tilde{P}\cdot\frac{a}{27b^2} = \frac{\tilde{T}\frac{8a}{27b}}{3b\tilde{v}-b} - \frac{a}{(3b\tilde{v})^2} \Rightarrow \frac{a}{b^2}\cdot\frac{\tilde{P}}{27} = \frac{a}{b^2}\frac{8\tilde{T}}{27(3\tilde{v}-1)} - \frac{a}{b^2}\frac{1}{9\tilde{v}^2}$$

$$\boxed{\tilde{P} = \frac{8\tilde{T}}{3\tilde{v}-1} - \frac{3}{\tilde{v}^2}}$$

An identical procedure can be done for A and μ to get coexistence curves and spinodals.

Unfortunately, the data (see plot by Johnston 2014) does not agree very well with the prediction by van der Waals. Even for the monoatomic fluids the fit is quite poor. However, 1) this is a very simple mean-field theory. This is still pretty impressive. 2) The idea of a universal curve where molecular details (captured by the critical point) are scaled out actually works quite well! The vdW model is just not great. This idea is called "corresponding states!" (show Eugenheim 1945, fig. 2).