Lecture 4 - Pure Component Phase Behavior

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Lecture 4: Pure Component Phase Behavior

Up until now, we have simply established the mathematical and theoretical tools for connecting the properties of molecules to their bulk (e.g., thermodynamic) properties and behavior. In this lecture, we will turn our attention to pure components and try and learn something about pure component phase behavior. We will first work on understanding non-ideal gases, then we will also consider liquids and solids.

I. Non-Ideal Gases

A. The van der Waals Fluid

We will first look at the most simple model of a non-ideal gas, the van der Waals fluid. This model is analytically solvable and its P-V-T equation of state is the well-known van der Waals equation of state.

Recall the steps we need to go through to compute an equation of state (or any other thermodynamic property.

1) Determine the Hamiltonian
2) Compute the partition function
3) Use the thermodynamic connection formula and classical thermodynamic relations to compute the quantity of interest.

Step 1: Determine the Hamiltonian

Recall that we said for N particles interacting with a pairwise potential, the Hamiltonian is given as

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{i<j}^{3N}\sum^{3N} u_{ij}(r)$$

this sum can also be written as:

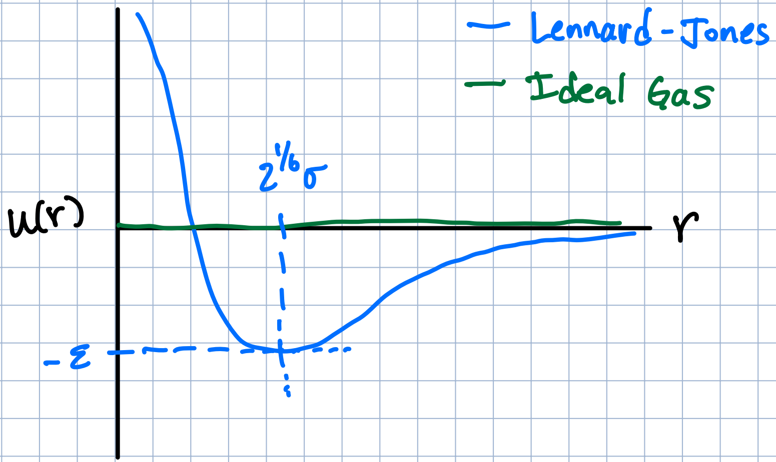
$$\frac{1}{2}\sum_{i}^{3N}\sum_{j}^{3N} u_{ij}(r)$$

p_i: momentum

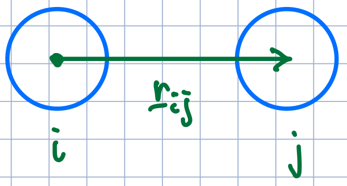
m: particle mass

u_{ij}: pair potential

Let's remember what the pair potential is



$$u(r) = u_{ij}(|\underline{r}_j - \underline{r}_i|)$$

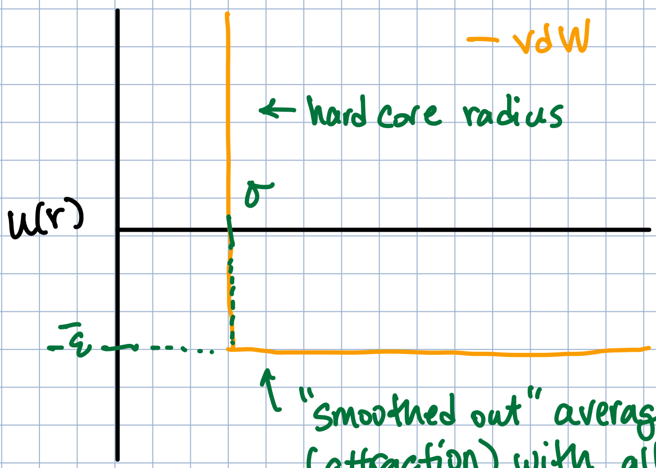


$$r = |\underline{r}_{ij}| = |\underline{r}_j - \underline{r}_i|$$

$$u_{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$u_{IG} = 0$$

For a van der Waals fluid, we define the following potential



$$\bar{u}_{vdW}(r) = \begin{cases} \infty & r \leq \sigma \\ -\bar{\varepsilon} & r > \sigma \end{cases}$$

$$\bar{\varepsilon} = a\frac{N}{V}$$

→ density

avg. interaction per particle

↑ "smoothed out" average interaction (attraction) with all other particles

The vdW potential is an "average" potential. This is a "mean field" approximation. Each particle feels general attraction from everyone, but the particle-particle distance fluctuations don't matter for $u(r>\sigma)$.

Step 2: Find Q

In the second step we have to do the hard work of solving for the partition function, Q.

$$Q = \int_{\Gamma} e^{-\beta H(\underline{x})} \frac{1}{h^{3N} N!} d\underline{x} \qquad \underline{x} = \{\underline{q}, \underline{p}\} = \{q_1, q_2, \ldots, q_{3N}, p_1, p_2, \ldots, p_{3N}\}$$

Canonical Ensemble

$$Q = \frac{1}{h^{3N} N!} \int\int \cdots \int \exp\left(-\beta\left[\underbrace{\sum_i \frac{p_i^2}{2m}}_{\text{only depends on } \underline{p}} + \frac{1}{2} \underbrace{\sum_i \sum_j u_{ij}(r)}_{\text{only depends on } \underline{q}}\right]\right) d\underline{q}\, d\underline{p}$$

$$Q = \frac{1}{h^{3N} N!} \underbrace{\int \exp\left(-\beta \sum_{i=1}^{3N} \frac{p_i^2}{2m}\right) d\underline{p}}_{\text{we did the kinetic energy integral for the ideal gas}} \underbrace{\int \exp\left(-\frac{1}{2}\beta \sum_{i=1}^{N} \sum_{j=1}^{N} u_{ij}(r)\right) d\underline{q}}_{\text{We will call this } Z(N,V,T) \text{ the configurational partition function.}}$$

Remember:

$$\int \exp\left(-\beta \sum_{i=1}^{3N} \frac{p_i^2}{2m}\right) d\underline{p} = \prod_{i=1}^{3N} \int_{-\infty}^{\infty} \exp\left(\frac{-\beta p_i^2}{2m}\right) dp_i$$

$$= \left[\int_{-\infty}^{\infty} \exp\left(\frac{-\beta p_i^2}{2m}\right) dp_i\right]^{3N}$$

$$= \left(\frac{2\pi m}{\beta}\right)^{3N/2} = (2\pi m k_B T)^{3N/2}$$

$$Q = \frac{1}{h^{3N} N!} (2\pi m k_B T)^{3N/2} \; z(N,V,T) \qquad \lambda_{th} = \frac{h}{(2\pi m k_B T)^{1/2}}$$

$$= \frac{1}{N! \, \lambda_{th}^{3N}} \; z(N,V,T)$$

Note: sometimes one defines a normalized configurational partition function.

$$\tilde{z} = \frac{1}{V^N} \int \exp\left(-\frac{1}{2} \beta \sum_i \sum_j u_{ij}(r)\right) d\underline{q}$$

This gives

$$Q = \underbrace{\frac{V^N}{N! \, \lambda_{th}^{3N}}}_{Q_{IG}\text{: ideal gas partition function}} \; \tilde{z}(N,V,T)$$

Non-ideal "correction"

Now, we need to solve the integral z.

$$z = \int_{V^N} \exp\left(-\frac{1}{2} \beta \sum_{i=1}^{N} \sum_{j=1}^{N} u_{ij}(r)\right) d\underline{q}$$

The ½ is to stop double counting.

$$\bar{u}_i(r) = \frac{1}{2} \sum_{j=1}^{N} u_{ij}(r) = \sum_{j=1}^{N} \begin{cases} \infty & \text{if } r \leq \sigma \\ -\frac{a}{V} & \text{if } r > \sigma \end{cases}$$

absorb the $\frac{1}{2}$ into a

$$= \begin{cases} \infty & \text{if } r \leq \sigma \\ -\frac{aN}{V} & \text{if } r > \sigma \end{cases} = \begin{cases} \infty & \text{if } r \leq \sigma \\ -\bar{\varepsilon} & \text{if } r > \sigma \end{cases} = \bar{u}_{vdW}(r)$$

$$z = \int_{V^N} \exp\left(-\beta \sum_{i=1}^{N} \bar{u}_i(r)\right) d\underline{q}$$

$$\exp(-\beta u_1 - \beta u_2 \ldots - \beta \bar{u}_N) = \exp(-\beta u_1) \exp(-\beta u_2) \ldots \exp(-\beta \bar{u}_N)$$

There are N independent volume integrals here.

$$Z = \int_{V^N} \prod_{i=1}^{N} \left[e^{-\beta \bar{u}_i(\underline{r})} \right] d\underline{q} \quad \leftarrow \quad \underline{q} = \{q_1, q_2, \ldots, q_{3N}\}$$

$$= \prod_{i=1}^{N} \left[\int_V e^{-\beta \bar{u}_i(r)} \, d\underline{q} \right] \quad \leftarrow \quad \underline{q} = \{q_1, q_2, q_3\}$$

$$= \Big[\underbrace{\int_V e^{-\beta \bar{u}(r)} \, d\underline{q}}_{z_1 = z(1,V,T)} \Big]^N$$

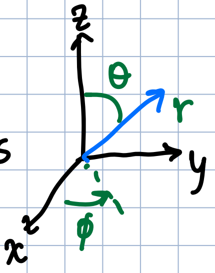
I dropped the i because they are all the same.

$z_1 = z(1,V,T)$: 1 particle configuration partition function

Now, we need to do some multivariable calculus to evaluate our 3D integral.

$$z_1 = \int_V e^{-\beta \bar{u}} \, d\underline{q} = \int_0^R \int_0^{2\pi} \int_0^{\pi} e^{-\beta \bar{u}} \, r^2 \sin\theta \, d\theta \, d\phi \, dr$$

spherical coordinates



$\theta \in [0, \pi]$

$\phi \in [0, 2\pi]$

$r \in [0, R]$

"Box" volume

$V = \frac{4}{3}\pi R^3$

$$z_1 = \underbrace{\int_0^{\pi} \sin\theta \, d\theta}_{-\cos\theta \big|_0^{\pi} = -(-1)+1 = 2} \; \underbrace{\int_0^{2\pi} d\phi}_{\to 2\pi} \int_0^R r^2 e^{-\beta \bar{u}(r)} \, dr = 4\pi \int_0^R r^2 e^{-\beta \bar{u}(r)} \, dr$$

$$= 4\pi \left[\int_0^{\sigma} r^2 e^{-\beta \bar{u}(r)} \, dr + \int_{\sigma}^{R} r^2 e^{-\beta \bar{u}(r)} \, dr \right]$$

$\bar{u} = \infty$, $e^{-\beta \cdot \infty} \to 0$

$\bar{u} = -\varepsilon$

$$z_1 = 4\pi \int_\sigma^R r^2 \underset{\nwarrow \text{constant}}{e^{\beta\bar{\varepsilon}}}\, dr = 4\pi e^{\beta\bar{\varepsilon}} \underbrace{\int_\sigma^R r^2\, dr}_{\frac{r^3}{3}\Big|_\sigma^R = \frac{R^3}{3} - \frac{\sigma^3}{3}}$$

$$z_1 = \Bigg(\underbrace{\frac{4\pi R^3}{3}}_{\text{box volume}, V} - \underbrace{\frac{4\pi\sigma^3}{3}}_{\text{excluded volume}, b}\Bigg) e^{\beta\bar{\varepsilon}}$$

let $Nb = v \Rightarrow \underset{\nearrow}{b} = \frac{1}{N} v$

excluded volume per neighbor particle.

$$z_1 = (V - Nb)\, e^{\beta\bar{\varepsilon}}$$

Now, we can plug this into our equation for z and Q

$$z = \left[(V - Nb)\, e^{\beta\bar{\varepsilon}}\right]^N$$

$$\boxed{Q = \frac{1}{N!\,\lambda_{th}^{3N}} \left[(V - Nb)\, e^{\beta\bar{\varepsilon}}\right]^N \qquad \bar{\varepsilon} = aN/V}$$

Compared to Q_{IG} we have a reduction in available volume that can be explored $(V-Nb)^N$ vs. V^N. We also have attractive interactions $e^{N\beta\bar{\varepsilon}}$.

<u>Step 3</u>: Connect to thermo and compute the E.o.s.

$$A = -k_B T \ln Q$$

$$= -k_B T \ln\left[\frac{1}{N!\,\lambda_{th}^{3N}} (V - Nb)^N e^{N\beta\bar{\varepsilon}}\right] \qquad \bar{\varepsilon} = \frac{aN}{V}$$

$$= k_B T \ln N! + k_B T \ln \lambda_{th}^{3N} - k_B T \ln (V - Nb)^N - k_B T \cdot N\beta\bar{\varepsilon}$$

$$\beta A = N \ln N - N + 3N \ln \lambda_{th} - N \ln (V - Nb) - \beta a N^2/V \quad \ast$$

Now compute the pressure

$$dA = -S\,dT - p\,dV$$

$$p = -\frac{\partial A}{\partial V}$$

$$p = -k_BT\frac{\partial}{\partial V}\left[N\cancel{\ln N}-N + 3N\cancel{\ln}\,\lambda_{th} - N\ln(V-Nb) - \frac{\beta a N^2}{V}\right]$$

$$= -k_BT\left[-N\frac{1}{V-Nb} + \frac{\beta a N^2}{V^2}\right]$$

$$\boxed{p = \frac{Nk_BT}{V-Nb} - \frac{aN^2}{V^2}}$$

Van der Waals Equation of State

B. vdW Phase Behavior and corresponding states

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 above. 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

(i). 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:

$$P = \left(\frac{\partial F}{\partial V}\right)_{T,N}$$ we already found this above

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

$$\mu = \left(\frac{\partial F}{\partial N_i}\right)_{P,T}$$

Let's derive μ now.

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

$$= \frac{\partial}{\partial N}\Big[Nk_BT\ln N + Nk_BT\ln\lambda^3 - Nk_BT\ln(V-Nb) - \frac{aN^2}{V} - Nk_BT\Big]$$

$$= k_BT\ln N + \cancel{\frac{Nk_BT}{N}} + k_BT\ln\lambda^3 - k_BT\ln(V-Nb) - \frac{Nk_BT}{V-Nb}\cdot(-b) - \frac{2aN}{V} - \cancel{k_BT}$$

$$\mu = k_BT \ln\left(\frac{N\lambda^3}{V-Nb}\right) + \frac{Nbk_BT}{V-Nb} - \frac{2aN}{V} \qquad \text{let } v = \frac{V}{N}$$

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

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

With these two equations, we can now set

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

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

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

(ii) Spinodal

The spinodal occurs at the inflection point

$$\frac{\partial P}{\partial v} = 0$$

This corresponds to $\frac{\partial^2 A}{\partial v^2} = 0$, the limit of stability. Lets compute it.

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

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

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

Plug into P to find the P - v relation

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

$$\boxed{P = \frac{2a(v-b)}{v^3} - \frac{a}{v^2}}$$ can solve for points in P - v plane given a, b.

(iii) 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.

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

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

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

$$\frac{\partial^2 P}{\partial v^2} = \frac{2}{(v-b)^{\overset{1}{\cancel{3}}}} \frac{2a}{v^3} \cancel{(v-b)}^2 - \frac{6a}{v^4} = 0$$

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

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

$$\Rightarrow 1 - \frac{b}{v} = \frac{2}{3} \Rightarrow \frac{b}{v} = \frac{1}{3} \quad \boxed{v_c = 3b}$$ critical volume

Plug back into kT to find T_c

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

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

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

Finally, we can get P_c

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

$$\frac{8}{54} = \frac{4}{27}$$

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

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

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

See Python plot of vdW phase diagram.

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 (universal?!) 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 $P(v,T)$:

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

$$\left.\begin{aligned} \tilde{P} &= P/P_c = \frac{P\,27b^2}{a} \\ \tilde{T} &= T/T_c = T\,\frac{27b k_B}{8a} \\ \tilde{v} &= v/v_c = \frac{v}{3b} \end{aligned}\right\} \text{substitute and simplify}$$

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

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

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

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 Guggenheim 1945, fig. 2).