Lecture 23 – The van der Waals Fluid

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.

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.

A. 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:

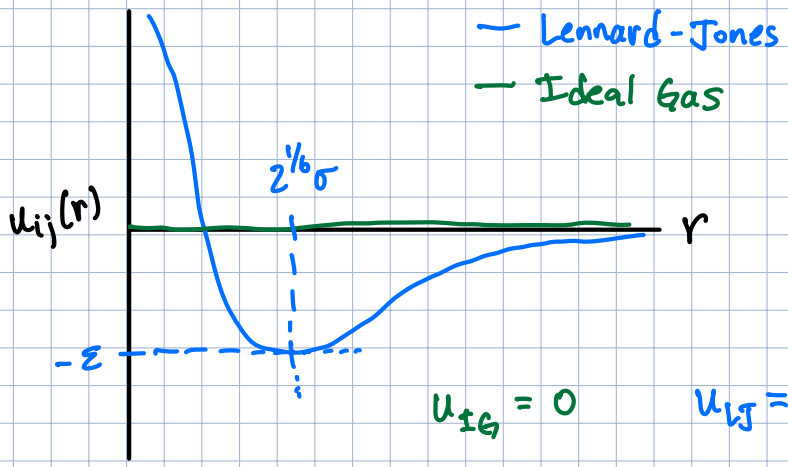
$$\frac{1}{2} \sum_{i}^{3N} \sum_{j}^{3N} u_{ij}(r)$$

p_i: momentum

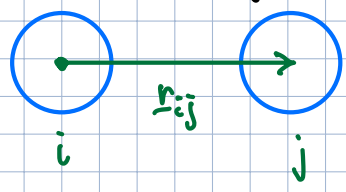
m: particle mass

u_{ij}: pair potential

Let's remember what the pair potential is



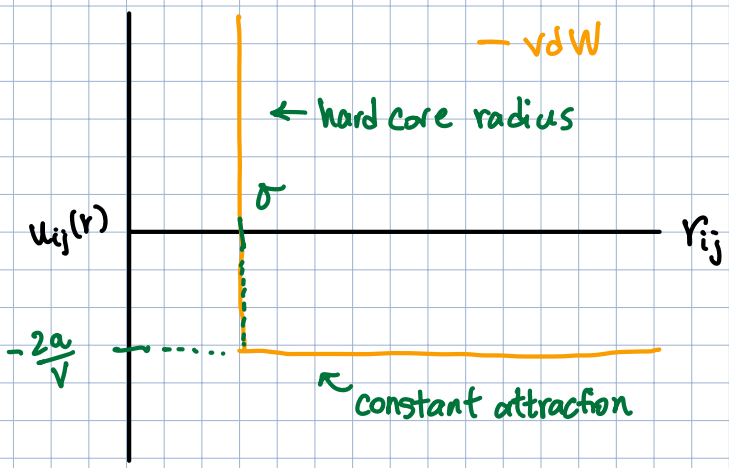
$u(r) = u_{ij}(|\underline{r}_j - \underline{r}_i|)$



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

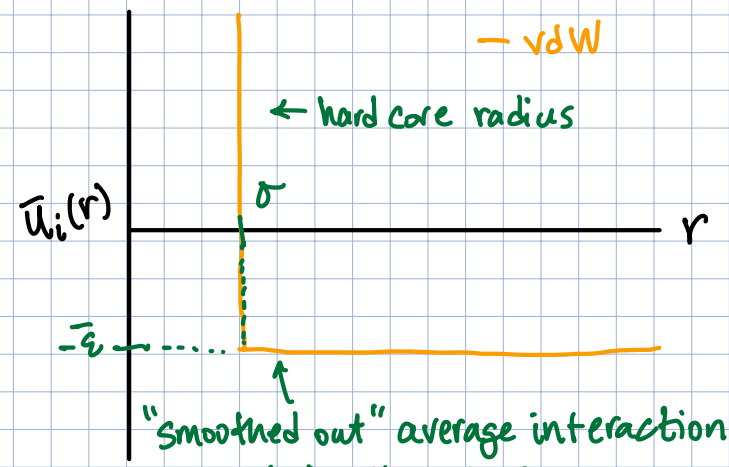
$u_{IG} = 0$ $\quad u_{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$

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



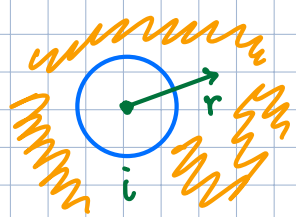
$$u_{vdW}(r_{ij}) = \begin{cases} \infty & r \le \sigma \\ -2a/v & r > \sigma \end{cases}$$

for double counting — attractive interaction per volume per particle



mean-field potential

$$\bar{u}_i(r) = \frac{1}{2}\sum_{j=1}^{N} u_{ij}(r)$$



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

$\bar{\varepsilon} = \frac{aN}{V}$ mean field attraction

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.

B. Find Q (Canonical Ensemble)

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

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

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

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

Remember

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

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

So,

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

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

Note: one can define 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

$$Q = \underbrace{\frac{V^N}{N!\,\lambda_{th}^{3N}}}_{Q_{IG}} \tilde{Z}(N,V,T)$$

$\tilde{Z}$: Non-ideal "correction"

Q_{IG}: ideal gas partition function

Now, we need to solve the integral Z.

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

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

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

$\exp(-\beta\bar{u}_1 - \beta\bar{u}_2 \dots -\beta\bar{u}_N) = \exp(-\beta\bar{u}_1)\exp(-\beta\bar{u}_2)\dots\exp(-\beta\bar{u}_N)$

There are N independent volume integrals here.

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

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

$$= \left[\int_V e^{-\beta\bar{u}(r)}\, d\underline{q}\right]^N$$

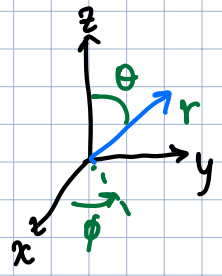
I dropped the i because they are all the same.

$Z_1 = Z(1,V,T)$: 1 particle configuration partition function

We need to do some multivariable calculus to evaluate the 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



$\theta \in [0, \pi]$ "Box" volume

$\phi \in [0, 2\pi]$ $V = \frac{4}{3}\pi R^3$

$r \in [0, R]$

$$z_1 = \int_0^{\pi} \sin\theta \, d\theta \int_0^{2\pi} d\phi \int_0^{R} r^2 e^{-\beta \bar{u}(r)} \, dr = 4\pi \int_0^{R} r^2 e^{-\beta \bar{u}(r)} \, dr$$

$-\cos\theta \Big|_0^{\pi} = -(-1) + 1 = 2$ → 2π

$$z_1 = 4\pi \left[\int_0^{\sigma} r^2 e^{-\beta \bar{u}(r)} \, dr + \int_{\sigma}^{R} r^2 e^{-\beta \bar{u}(r)} \, dr \right]$$

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

$$z_1 = 4\pi \int_{\sigma}^{R} r^2 e^{\beta \bar{\varepsilon}} \, dr = 4\pi e^{\beta \bar{\varepsilon}} \int_{\sigma}^{R} r^2 \, dr$$

$e^{\beta\bar{\varepsilon}}$: constant

$\int_{\sigma}^{R} r^2 dr$: $\frac{r^3}{3}\Big|_{\sigma}^{R} = \frac{R^3}{3} - \frac{\sigma^3}{3}$

$$z_1 = \left(\frac{4\pi R^3}{3} - \frac{4\pi \sigma^3}{3} \right) e^{\beta \bar{\varepsilon}}$$

$\frac{4\pi R^3}{3}$: box volume, V $\quad$ $\frac{4\pi\sigma^3}{3}$: excluded volume, b

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

b: 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

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

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

$$\bar{\varepsilon} = aN/V$$

$$Q = Q_{IG} \left(\frac{V - Nb}{V} \right)^N e^{N\beta\bar{\varepsilon}}$$

$\left(\frac{V - Nb}{V} \right) < 1$

Get IG when $a, b \to 0$.

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 $e^{N\beta\bar{\varepsilon}}$.

C. Connect to thermo and compute the E.o.s.

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

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

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

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

$$= N\left[\ln N - 1 + 3\ln\lambda_{th} - \ln(V-Nb) - \beta a N/V\right]$$

$$\boxed{\frac{\beta A}{N} = \ln\left(\frac{N\lambda^3}{V-Nb}\right) - \frac{\beta a N}{V} - 1}$$

Van der Waals Helmholtz Free Energy

Now compute the pressure

$$dA = -SdT - pdV + \mu dN$$

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

$$P = -k_B T \frac{\partial}{\partial V}\left[N\ln N - N + 3N\ln\lambda_{th} - N\ln(V-Nb) - \beta a\frac{N^2}{V}\right]$$

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

$$\boxed{P = \frac{N k_B T}{V-Nb} - \frac{aN^2}{V^2}}$$

Van der Waals PVT Equation of State

Compute the Heat Capacity

$$A = U - TS \quad \Rightarrow \quad U = A + TS$$

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

$$\lambda = h/(2\pi m k_B T)^{1/2}$$

$$\frac{\partial \lambda}{\partial T} = h\left[-\tfrac{1}{2}(2\pi m k_B T)^{-3/2}(2\pi m k_B)\right] = -\tfrac{1}{2}\left(\frac{h}{2\pi m k_B T}\right)^{1/2}\frac{2\pi m k_B}{2\pi m k_B T} = -\frac{\lambda}{2T}$$

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

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

$$\boxed{S = -N k_B \ln\left(\frac{N\lambda^3}{V-Nb}\right) + \frac{5}{2} N k_B}$$

$$U = A + TS$$

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

$$\boxed{U = \frac{3}{2} N k_B T - \frac{aN^2}{V}}$$

Ideal gas – attractive interactions

$$C_V = \frac{\partial U}{\partial T} = \frac{3}{2} N k_B$$

$$\boxed{C_V = \frac{3}{2} N k_B}$$

Same as ideal gas