

Week 7

Phase Diagrams and Critical Points

7.1 Virial Coefficients and Fugacity

2/21: • Relation between the interaction potential and the first virial coefficient (Equation 16.25).

- Statistical mechanics is important because it gives us the relation

$$B_{2V}(T) = -2\pi N_A \int_0^\infty \left(e^{-u(r)/k_B T} - 1 \right) r^2 dr$$

- We can derive this with our knowledge of statistical mechanics, but PGS will not go through this.
- Now recall the Lennard-Jones potential

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

- Note that the minimum is at $(2^{1/6}\sigma, -\epsilon)$.
- The limiting case of the Lennard-Jones potential is hard sphere repulsion (the repulsion as you approach a hard sphere, which is zero up until you're at the surface and then infinite repulsion). Thus, with no intermolecular attraction, $a = 0$, so in this case,

$$\begin{aligned} B_{2V}(T) &= -2\pi N_A \int_0^\sigma (-1) r^2 dr \\ &= \frac{2\pi N_A \sigma^3}{3} \\ &= b - \frac{0}{RT} \end{aligned}$$

- Now consider a potential that is van der Waals (c/r^6) up until a point and then hard sphere. In this case,

$$\begin{aligned} B_{2V}(T) &= \frac{2\pi N_A \sigma^3}{3} - 2\pi N_A \int_\sigma^\infty \left(e^{-c/r^6 k_B T} - 1 \right) r^2 dr \\ &= \frac{2\pi N_A \sigma^3}{3} - 2\pi N_A \int_\sigma^\infty \left(-\frac{c}{r^6 k_B T} \right) r^2 dr \\ &= b + \frac{2\pi N_A c}{k_B T} \cdot -\frac{1}{3\sigma^3} \end{aligned}$$

where we have used $e^x = 1 + x + \dots$ to get from the first line to the second.

■ Therefore,

$$a = \frac{2\pi N_A^2}{3} \frac{c}{\sigma^2}$$

- Derivation of the relation between $B_{2V}(T)$ and the interaction potential $u(r)$.
 - Consider a system of independent, indistinguishable particles.
 - The total Hamiltonian for the system has a kinetic energy part and an interaction part.

$$\hat{H}(p_i, r_i) = \sum_i \frac{\hat{p}_i^2}{2m} + \sum_{i < j} \hat{u}(r_i, r_j)$$

- The kinetic part (which ignores intermolecular interactions) will lead to the ideal gas partition function. The nonideal part of the partition function will come from the interaction potentials. Mathematically,

$$\begin{aligned} Q &= \frac{1}{N!} \int e^{-\beta E(p_i, r_i)} d^3p_i d^3r_i \\ &= \frac{1}{N!} \int \exp \left\{ -\beta \left[\sum_i \frac{p_i^2}{2m} + \sum_{i < j} u(r_i, r_j) \right] \right\} d^3p_i d^3r_i \\ &= \frac{1}{N!} \left(\int \exp \left[-\beta \sum_i \frac{p_i^2}{2m} \right] d^3p_i \right) \left(\int \exp \left[-\beta \sum_{i < j} u(r_i, r_j) \right] d^3r_i \right) \\ &= \underbrace{\frac{V^N}{N!} \left(\int \exp \left[-\beta \sum_i \frac{p_i^2}{2m} \right] d^3p_i \right)}_{Q_{\text{ideal}}} \cdot \underbrace{\frac{1}{V^N} \left(\int \exp \left[-\beta \sum_{i < j} u(r_i, r_j) \right] d^3r_i \right)}_{Q_u} \end{aligned}$$

- Define

$$f_{ij} = e^{-u(r_i, r_j)/k_B T} - 1$$

- Now note that the interaction between molecules is pretty small, and in fact $f_{ij} \rightarrow 0$ as $|r_i - r_j| \rightarrow \infty$.
- Thus,

$$\begin{aligned} Q_u &= \frac{1}{V^N} \int \exp \left[-\beta \sum_{i < j} u(r_i, r_j) \right] d^3r_i \\ &= \frac{1}{V^N} \int \prod_{i < j} (f_{ij} + 1) d^3r_i \end{aligned}$$

- We can do a **cluster expansion** on this small f_{ij} :

$$\prod_{i < j} (f_{ij} + 1) = 1 + \sum_{i < j} f_{ij} + \sum_{i < j} \sum_{k < \ell} f_{ij} f_{k\ell}$$

- In particular, $\sum_{i < j}$ is the sum of pairwise interactions while $f_{ij} \cdot f_{k\ell}$ are binary interactions, $f_{ij} f_{k\ell} f_{mn}$ are tertiary interactions, and so on and so forth.

- But at low density, the dominant term is the pairwise interaction so we have

$$\begin{aligned} Q_u &= \frac{1}{V^N} \int \left(1 + \sum_{i < j} f_{ij} \right) d^3 r_i \\ &= \frac{1}{V^N} \left(V^N + \frac{N(N-1)}{2} V^{N-2} \int f_{12} d^3 r_1 d^3 r_2 \right) \\ &= 1 + \frac{N(N-1)}{2V} \int (e^{-\beta u(r)} - 1) d^3 r \end{aligned}$$

- It follows that

$$Q = Q_{\text{id}} \left[1 + \frac{N(N-1)}{2V} \int (e^{-\beta u(r)} - 1) d^3 r \right]$$

- But now we need to extract an equation of state from the partition function. To do so, we use

$$\begin{aligned} P &= k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T} \\ &= k_B T \left(\frac{\partial \ln Q_{\text{id}}}{\partial V} \right)_{N,T} + k_B T \left(\frac{\partial \ln Q_u}{\partial V} \right)_{N,T} \end{aligned}$$

- We know that the first term above is equal to $Nk_B T/V$, but it takes a bit more work for the second one.
- We have that

$$\begin{aligned} \ln Q_u &= \ln \left(1 + \underbrace{\frac{N(N-1)}{2V}}_{\substack{\text{Approximately} \\ \text{the intermolecular} \\ \text{distance } 1/\rho^3}} \underbrace{\int (e^{-\beta u(r)} - 1) d^3 r}_{\substack{\text{Approximately} \\ \text{the molecular} \\ \text{volume } a^3}} \right) \\ &= \frac{N(N-1)}{2V} \int (e^{-\beta u(r)} - 1) d^3 r \end{aligned}$$

since the second term is a small number and the natural log of a small number plus 1 is approximately that small number.

- Thus,

$$\left(\frac{\partial \ln Q_u}{\partial V} \right)_{N,T} = -\frac{N(N-1)}{2V^2} \int (e^{-\beta u(r)} - 1) d^3 r$$

so

$$\begin{aligned} P &= \frac{Nk_B T}{V} - \frac{Nk_B T}{V} \frac{N-1}{2V} \int (e^{-\beta u(r)} - 1) d^3 r \\ &= \frac{RT}{\bar{V}} - \frac{RT}{\bar{V}} \frac{N-1}{2V} \int (e^{-\beta u(r)} - 1) d^3 r \end{aligned}$$

- Consequently,

$$Z = \frac{P\bar{V}}{RT} = 1 - \frac{N_A}{\bar{V}} \cdot \frac{1}{2} \int (e^{-\beta u(r)} - 1) d^3 r$$

- Therefore, by comparison with the virial expansion,

$$\begin{aligned} B_{2V}(T) &= -\frac{N_A}{2} \int (e^{-\beta u(r)} - 1) d^3 r \\ &= -\frac{N_A}{2} \int_0^\infty (e^{-\beta u(r)} - 1) 4\pi r^2 dr \\ &= -2\pi N_A \int_0^\infty (e^{-u(r)/k_B T} - 1) r^2 dr \end{aligned}$$

- Free energy as a function of (T, P) for a real gas. Definition of fugacity and fugacity coefficients.
 - We want to find $\Delta G(T, P)$.
 - We have that $d\bar{G} = -\bar{S}dT + \bar{V}dP$. It follows that

$$\left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}$$

- Thus,

$$\bar{G}(T, P) = \bar{G}(T, P_0) + \int_{P_0}^P \bar{V} dP$$

- In the ideal case,

$$\begin{aligned}\bar{G}_{\text{ideal}}(T, P) &= \bar{G}_{\text{ideal}}(T, P_0) + \int_{P_0}^P \frac{RT}{P} dP \\ &= \bar{G}_{\text{ideal}}(T, P_0) + RT \ln \frac{P}{P_0}\end{aligned}$$

- In the nonideal case, we define a fugacity f by

$$\bar{G}_{\text{ideal}}(T, P) = \bar{G}_{\text{ideal}}(T, P_0) + RT \ln \frac{f}{P_0}$$

- The second term in the above equation refers to the Gibbs free energy of an ideal gas at $P_0 = 1$ bar or $P_0 = 1$ atm. Note that even at $P_0 = 1$ atm, however, there is too much pressure for truly ideal behavior, so $f \neq P_0$.
- Imagine that $\Delta \bar{G}_1$ takes us from a real gas at (T, P) to an ideal gas at (T, P) . Then

$$\begin{aligned}\Delta \bar{G}_1 &= \bar{G}_{\text{ideal}}(T, P) - \bar{G}_{\text{real}}(T, P) \\ &= \left[\bar{G}_{\text{ideal}}(T, P_0) + RT \ln \frac{P}{P_0} \right] - \left[\bar{G}_{\text{ideal}}(T, P_0) + RT \ln \frac{f}{P_0} \right] \\ &= -RT \ln \frac{f}{P}\end{aligned}$$

- Now let $\Delta \bar{G}_2$ take us from a real gas at (T, P) to a real gas at T and $P \rightarrow 0$, which will be the same as an ideal gas at T and $P \rightarrow 0$. Then let $\Delta \bar{G}_3$ take us from this ideal gas at T and $P \rightarrow 0$ to an ideal gas at (T, P) . It follows that

$$\Delta \bar{G}_2 = - \int_{P \rightarrow 0}^P \bar{V} dP' \qquad \Delta \bar{G}_3 = \int_{P \rightarrow 0}^P \frac{RT}{P'} dP'$$

- Thus, since $\Delta \bar{G}_1 = \Delta \bar{G}_2 + \Delta \bar{G}_3$ (G is a state function),

$$-RT \ln \frac{f}{P} = \int_{P \rightarrow 0}^P \left(-\bar{V} + \frac{RT}{P'} \right) dP'$$

- We then define γ to be the **fugacity coefficient** by $\gamma = f/P$. It follows that

$$\ln \gamma = \int_0^P \frac{z - 1}{P'} dP'$$

- Fugacity coefficient expressed in terms of the compressibility deviation from unity.
 - At low temperature, $z < 1$, so $\gamma < 1$ and hence $f < P$.
 - At high pressure, $z > 1$ (excluded volume), so $\gamma > 1$ and hence $f > P$.
- Introduces phase diagrams and their notable properties.