

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.

7.2 Office Hours (PGS)

- 2/25:
- Plotting the coexistence curve and determining the Maxwell equal area contraction line mathematically.
 - You can do these things with Mathematica and numerical approximations.
 - PGS does not know of an easy way to do this by hand. It looks like I would have to go all the way through the cubic formula and integrals.
 - I'm getting confused on treating the van der Waals equation as a cubic in \bar{V} , because its graph doesn't ever cross the x -axis, and, in fact, the equation is asymptotic to both the x - and y -axes. So what are its roots, and exactly what properties of it as a cubic are preserved?
 - It is cubic because it is cubic in \bar{V} (and solving for \bar{V} given P, T requires solving a cubic), not because it looks like the plot of a cubic function.
 - Why do intermolecular interactions behave the same way as intramolecular bonding interactions? B/c we used the Lennard-Jones potential for bond distance initially, and now we've applied it to two molecules interacting through their polarity?
 - The Lennard-Jones potential only applies to spherically symmetric distributions (e.g., not H_2O at short distances).
 - Not molecules of strong dipole or charge transfer either.
 - Thus perfect for **rare** (or inert) gases.
 - r^{-6} works well for any solids that are not charged.
 - What is the σ in the hard sphere potential? Isn't it the radius of the hard sphere? Because McQuarrie and Simon (1997) says it's the diameter multiple times.
 - If the molecule centered at the origin is a hard sphere of radius $\sigma/2$ and the molecule approaching the hard sphere centered at the origin is also a hard sphere of radius $\sigma/2$, then they won't interact until their centers are a distance σ apart.
 - Why can we use the ideal gas law to relate B_{iV} and B_{iP} ?
 - PSet 3, Question 2.
 - Use the two state model from class. Use a partition function with two states for N particles.
 - Curie's law probably isn't gonna be valid in this regime.
 - You need the heat capacity at 4 kelvin via the Debye model. You'll need the Debye temperature from the internet.

7.3 Chapter 16: The Properties of Gases

From McQuarrie and Simon (1997).

- Since the results of the Lennard-Jones potential can't be evaluated analytically, we often use other approximations that can be.
- Hard-sphere potential:** The potential of a hard sphere of radius σ . *Given by*

$$u(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases}$$

- This is the simplest representative potential.
- Despite its simplicity, it does account for the finite size of molecules, which turns out to be the dominant feature in determining the structure of liquids and solids.

- It does not account for intermolecular attractions, but since such attractions lessen as temperature increases, it is a good model for that condition.
- Under the hard-sphere potential,

$$\begin{aligned} B_{2V}(T) &= -2\pi N_A \int_0^\infty \left(e^{-u(r)/k_B T} - 1 \right) r^2 dr \\ &= -2\pi N_A \left[\int_0^\sigma (0 - 1) r^2 dr + \int_\sigma^\infty (1 - 1) r^2 dr \right] \\ &= \frac{2\pi\sigma^3 N_A}{3} \end{aligned}$$

- Thus, $B_{2V}(T)$ is equal to $1/2$ the volume of N_A hard spheres of radius σ .
- Although this formula for the second virial coefficient is not temperature dependent, it is indeed a good approximation at high temperatures, just the same way the potential is.
- **Square-well potential:** The potential of a hard-sphere of radius σ that is attractive at a consistent level from its surface up until a finite distance away. *Given by*

$$u(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon & \sigma < r < \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}$$

- ε is the depth of the well and $(\lambda - 1)\sigma$ is its width.
 - Under the square-well potential,
- $$\begin{aligned} B_{2V}(T) &= -2\pi N_A \left[\int_0^\sigma (0 - 1) r^2 dr + \int_\sigma^{\lambda\sigma} (e^{\varepsilon/k_B T} - 1) r^2 dr + \int_{\lambda\sigma}^\infty (1 - 1) r^2 dr \right] \\ &= -2\pi N_A \left[-\frac{\sigma^3}{3} + \frac{\sigma^3}{3} (\lambda^3 - 1)(e^{\varepsilon/k_B T} - 1) + 0 \right] \\ &= \frac{2\pi\sigma^3 N_A}{3} [1 - (\lambda^3 - 1)(e^{\varepsilon/k_B T} - 1)] \end{aligned}$$
- The agreement of the square-well potential with experimental data is very good, but it does have 3 adjustable parameters.
 - Relating the second virial coefficient to the van der Waals constants.
 - With the help of the expansion $1/(1 - x) = 1 + x + x^2 + \dots$, we have that

$$\begin{aligned} P &= \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \\ &= \frac{RT}{\bar{V}} \frac{1}{1 - b/\bar{V}} - \frac{a}{\bar{V}^2} \\ &= \frac{RT}{\bar{V}} \left[1 + \frac{b}{\bar{V}} + \frac{b^2}{\bar{V}^2} + \dots \right] - \frac{a}{\bar{V}^2} \\ &= \frac{RT}{\bar{V}} + (RTb - a) \frac{1}{\bar{V}^2} + \frac{RTb^2}{\bar{V}^3} + \dots \end{aligned}$$

- It follows that

$$Z = \frac{P\bar{V}}{RT} = 1 + \left(b - \frac{a}{RT} \right) \frac{1}{\bar{V}} + \frac{b^2}{\bar{V}^2} + \dots$$

- Thus,

$$B_{2V}(T) = b - \frac{a}{RT}$$

for the van der Waals equation.

- Relating the van der Waals constants to the Lennard-Jones parameters.

- Consider the following intermolecular potential, which is a hybrid of the hard-sphere and Lennard-Jones potentials.

$$u(r) = \begin{cases} \infty & r < \sigma \\ -\frac{c_6}{r^6} & r > \sigma \end{cases}$$

- We can now calculate $B_{2V}(T)$ in terms of $u(r)$ with the help of the approximation $e^x = 1 + x$ (applicable since the argument of the exponent function will be very small).

$$\begin{aligned} B_{2V}(T) &= -2\pi N_A \left[\int_0^\sigma (0 - 1)r^2 dr + \int_\sigma^\infty (e^{c_6/k_B T r^6} - 1)r^2 dr \right] \\ &= \frac{2\pi\sigma^3 N_A}{3} - \frac{2\pi N_A c_6}{k_B T} \int_\sigma^\infty \frac{1}{r^6} \cdot r^2 dr \\ &= \frac{2\pi\sigma^3 N_A}{3} - \frac{2\pi N_A c_6}{k_B T} \left[-\frac{1}{3r^3} \right]_\sigma^\infty \\ &= \frac{2\pi\sigma^3 N_A}{3} - \frac{2\pi N_A c_6}{3k_B T \sigma^3} \end{aligned}$$

- It follows by comparison with the result from the previous section that

$$a = \frac{2\pi N_A^2 c_6}{3\sigma^3} \qquad b = \frac{2\pi\sigma^3 N_A}{3}$$

- Physical interpretations: $a \propto c_6$ and b is one-half the volume of the molecules.

- In a similar fashion, we can relate $B_{2V}(T)$ to the Redlich-Kwong constants and Peng-Robinson functions.

$$B_{2V}(T) = B - \frac{A}{RT^{3/2}} \qquad B_{2V}(T) = \beta - \frac{\alpha}{RT}$$

7.4 Chapter 22: Helmholtz and Gibbs Energies

From McQuarrie and Simon (1997).

- Generalizing the equation $\bar{G} = G^\circ + RT \ln Q$ to the case of a real gas.

- We begin by substituting the virial expansion in terms of pressure into the equation $(\partial \bar{G} / \partial P)_T = \bar{V}$.

$$\begin{aligned} \left(\frac{\partial \bar{G}}{\partial P} \right)_T &= \bar{V} \\ &= \frac{RT}{P} [1 + B_{2P}(T)P + B_{3P}(T)P^2 + \dots] \\ \int_{P^{\text{id}}}^P d\bar{G} &= RT \int_{P^{\text{id}}}^P \frac{dP'}{P'} + RT B_{2P}(T) \int_{P^{\text{id}}}^P dP' + RT B_{3P}(T) \int_{P^{\text{id}}}^P P' dP' \\ \bar{G}(T, P) &= \bar{G}(T, P^{\text{id}}) + RT \ln \frac{P}{P^{\text{id}}} + RT B_{2P}(T)P + RT B_{3P}(T) \frac{P^2}{2} + \dots \end{aligned}$$

- Note that we neglect P_{id} in every term except the first because it is so close to zero.

- Substituting $\bar{G}(T, P^{\text{id}}) = G^{\circ}(T) + RT \ln P^{\text{id}}/P^{\circ}$ and combining the first two terms yields

$$\bar{G}(T, P) = G^{\circ}(T) + RT \ln \frac{P}{P^{\circ}} + RTB_{2P}(T)P + RTB_{3P}(T)\frac{P^2}{2} + \dots$$

- The above equation is exact, but complicated and different for each gas (depending on the virial coefficients).
- It will be more convenient to, especially for calculations involving chemical equilibria, to define the **fugacity**.
- **Fugacity**: A state function of P and T describing the nonideality of the energy of a system. *Denoted by f . Given by*

$$\bar{G}(T, P) = G^{\circ}(T) + RT \ln \frac{f(P, T)}{f^{\circ}}$$

- Fugacity must have the property that $f(P, T) \rightarrow P$ as $P \rightarrow 0$, so that the above equation can reduce to $\bar{G} = G^{\circ} + RT \ln P/P^{\circ}$.
- By setting the above equal to the virial expansion, we learn that

$$\frac{f(P, T)}{f^{\circ}} = \frac{P}{P^{\circ}} \exp[B_{2P}(T)P + B_{3P}(T)P^2 + \dots]$$

- “The standard state of the real gas... is taken to be the corresponding ideal gas at one bar” (McQuarrie & Simon, 1997, p. 906).
 - Mathematically, $f^{\circ} = P^{\circ}$.
 - Note that we can also derive this from the virial expansion expression for $f(P, T)/f^{\circ}$ since all of the virial coefficients are equal to zero in the standard state.
- McQuarrie and Simon (1997) goes through the derivation of

$$\ln \frac{f}{P} = \int_0^P \left(\frac{\bar{V}}{RT} - \frac{1}{P'} \right) dP'$$

exactly as in class.

- The above equation allows us to calculate the ratio of the fugacity to the pressure of a gas at any pressure and temperature, given either P - V - T data or an equation of state.
- **Fugacity coefficient**: The following ratio. *Denoted by γ . Given by*

$$\gamma = \frac{f}{P}$$

- Also note the equation

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

and that we can use this equation with the reduced pressure.