Lecture 11
Models of Imperfect Gases cont.

- We are now in a position to calculate the 2\textsuperscript{nd} virial coefficient (we will \textit{not} treat higher order virials at this time).

- Although we will ultimately be using the Lennard-Jones or 12-6 potential introduced in the last few lectures, we cannot analytically integrate $B_2(T)$ for this case.

- It is therefore instructive to use some other approximate forms of this potential

11.1 Hard-Sphere Potential

- This potential would be encountered for “Billiard-Ball” type interactions, where the particles are infinitely hard and there is no way of “squeezing” them together,

- This is a common potential used by theorists and it is the only potential for which the 1\textsuperscript{st} seven virial coefficients have been calculated

- The potential is given as,

$$U(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma \end{cases}$$  \hspace{1cm} (11.1)

which looks like,

Therefore, using Eq. 10.11, the second virial coefficient becomes,

$$B_2(T) = 2\pi \int_0^{\infty} \left[1 - e^{-\beta U(r)}\right] r^2 dr$$

$$= 2\pi \int_0^{\sigma} r^2 dr = \frac{2\pi\sigma^3}{3}$$  \hspace{1cm} (11.2)

which is 4 times the volume of a sphere and is also independent of temperature.
11.2 **Square-Well Potential**

- The square-well potential is the discretized version of the harmonic oscillator potential (which is parabolic) and is a reasonable model for describing the region near the bottom of the LJ potential,

- The potential may be described mathematically as a step function,

\[
U(r) = \begin{cases} 
\infty & r < \sigma \\
-\epsilon & \sigma < r < \lambda\sigma \\
0 & r > \lambda\sigma 
\end{cases}
\]  

(11.3)

where \( \lambda \) gives the range of the attractive well → usually taken to be between 1.5 and 2. This potential looks like,
• Substituting this potential into Eq. 10.11, we have

\[
B_2(T) = 2\pi \left\{ \int_0^{\sigma} [1 - e^{-\beta U(r)}] r^2 dr + \int_{\sigma}^{\lambda \sigma} [1 - e^{-\beta U(r)}] r^2 dr \right\}
\]

\[
= 2\pi \left\{ \frac{\sigma^3}{3} + \left( \frac{1 - e^{\beta \epsilon}}{3} \right) [\lambda \sigma)^3 - \sigma^3] \right\}
\]

\[
= \frac{2\pi \sigma^3}{3} [1 + (\lambda^3 - 1) (1 - e^{\beta \epsilon})]
\]

\[
= b_0 [1 + (\lambda^3 - 1) (1 - e^{\beta \epsilon})] \quad (11.4)
\]

\[
(11.5)
\]

where \(b_0 = (2\pi \sigma^3)/3\) is the hard-sphere second virial coefficient.

### 11.3 van der Waals Equation

• Keeping the hard-wall component of our previous approximation, we now consider a further refinement of the model:

• First, recognize under normal conditions \(kT >> U_0\), where \(-U_0\) is the minimum of the potential \(U(r) \rightarrow\) for e.g., for the LJ potential, \(U_0 = \epsilon\).

• Then, for values of \(r\) greater than the hard-wall limit, \(r = \sigma = 2r_0\), we can Taylor expand the integrand in 10.11, \(1 - e^{-\beta U(r)}\), which to leading order gives us \(U(r)/kT\).

• To summarize we have,

\[
[1 - e^{-\beta U(r)}] = \begin{cases} 
\frac{1}{U(r)} & r < 2r_0 \\
\frac{1}{kT} & r > 2r_0 
\end{cases}
\]

(11.6)

The “van der Waals” potential has the following form,
Using Eq. 11.10 above, the second virial coefficient can be evaluated as,

\[ B_2(T) = 2\pi \left\{ \int_0^{2r_0} r^2 dr + \int_{2r_0}^{\infty} \frac{U(r)}{kT} r^2 dr \right\} \]

\[ \equiv b - a \frac{kT}{kT} \]

where,

\[ a \equiv -2\pi \int_{2r_0}^{\infty} \frac{U(r)}{kT} r^2 dr \]

and

\[ b \equiv 4 \left( \frac{4\pi r_0^3}{3} \right) \equiv 4v_0 \equiv b_0 \]

which is again just our hard-sphere second virial coefficient.

If we now substitute the van der Waals second virial coefficient back into our virial expansion, Eq. 9.26, then we obtain the following,

\[ \frac{P}{kT} = \rho \left[ 1 + B_2(T)\rho \right] = \rho \left[ 1 + \rho \left( b - \frac{a}{kT} \right) \right] \]

\[ \frac{P}{kT} + \frac{\rho^2 a}{kT} = \rho \left( 1 + \rho b \right) \]

But in the dilute limit, \( \rho b \) will be small, hence,

\[ 1 + \rho b = (1 - \rho b)^{-1} \]

and therefore we arrive at van der Waals equation,

\[ (P + \rho^2 a) (1 - \rho b) = \rho kT \]  

where, \( a \) accounts for the long-range weakly attractive forces between molecules and \( b \) is just 4 times the single molecule volume.

Note that this derivation is only valid at low densities where \( \rho b << 1 \).

Interestingly, though, van der Waals equation is a good description of condensation phenomena where \( \rho b \) is not small.

However, experiments on substances near their critical point do not agree with van der Waals equation (which implicitly neglects higher order terms, or clusters, and thus this is not surprising).
11.4 Alternative formulation of the van der Waals model

- We are now in a reasonably good position to further explore phase transitions in more detail, now that we have accounted for molecular interactions in an approximate fashion.

- The van der Waals model is actually a type of mean-field theory, which approximates the specific interactions between a particular molecule and the other molecules in the system by treating the molecule as moving in an “effective” field created by all the other molecules in the system.

- In the present context, we can think of an effective potential, $U_{\text{eff}}(r)$, due to all the other molecules in the system and, hence, the partition function factorizes, since all molecules experience the same effective field (you can think of this as being analogous to a gravitational field that all molecules would feel independent of their specific intermolecular interactions). Hence,

$$Z = \frac{1}{N!} \left[ \int \int e^{-\frac{\beta p^2}{2m} + U_{\text{eff}}(r)} \frac{dp}{h^3} \right]^N$$  \hspace{1cm} (11.11)

- The integral over the momentum just gives us our quantum volume contribution and the above equation becomes,

$$Z = \frac{1}{N!} \left( \frac{2\pi m kT}{h^2} \right)^{\frac{3}{2}N} \left[ \int e^{-\beta U_{\text{eff}}(r)} dr \right]^N$$

- The integral extends over the full volume of the box, but as we noted in the previous section, there are going to be regions in the box where molecules will bump into each other and the potential will become infinite there. Let us represent the total excluded volume due to these repulsive regions as, $V_x$ ($x \equiv$ excluded).

- If we make a further approximation and consider that $U_{\text{eff}}$ does not change appreciably over the regions of interest, that is in the volume $V - V_x$, then we may replace $U_{\text{eff}}$ by a constant average value, $\langle U_{\text{eff}} \rangle$, and our partition function becomes,

$$Z = \frac{1}{N!} \left( \frac{2\pi m kT}{h^2} \right)^{\frac{3}{2}N} \left( V - V_x \right) e^{-\beta \langle U_{\text{eff}} \rangle}$$  \hspace{1cm} (11.12)

- Now, in general, for a system of $N$ molecules, there will be a total of $\frac{1}{2}N(N - 1)$ pair interactions which, for large $N$, is $\approx \frac{1}{2}N^2$. If the mean pair potential energy is denoted as $\langle u \rangle$, then the total mean potential energy is approximated as $\frac{1}{2}N^2 \langle u \rangle$.

- For our mean field treatment here, we have taken the total mean potential energy of the molecules as $N \langle U_{\text{eff}} \rangle$. Thus, self-consistency requires that,
How do we determine $\langle u \rangle$?

- We can take our van der Waals potential energy function, $U(r)$ in Eq. 11.10 to be of the form,

$$u(r) = \begin{cases} 
\infty & r < \sigma \\
-u_0 \left( \frac{\sigma}{r} \right)^s & r > \sigma 
\end{cases} \quad (11.13)$$

- To obtain an average, we need to define a probability distribution. What we really want to know is, given a molecule $k$, what is the probability of finding another molecule $j$ at some distance between $r$ and $r + dr$ from molecule $k$ (with $r > \sigma$)?

- For an isotropic system, with no external fields present or gradients, all locations are equally likely. Therefore, the probability of $j$ being at a distance $r$ and $r + dr$ is just $(4\pi r^2 dr) / V$, hence,

$$\langle u \rangle = \frac{1}{V} \int_{\sigma}^{R} u(r) 4\pi r^2 dr$$

$$= -\frac{4\pi u_0}{V} \int_{\sigma}^{R} \left( \frac{\sigma}{r} \right)^s r^2 dr$$

$$= -\frac{4\pi u_0}{V} \lim_{R \to \infty} [R^{3-s} - \sigma^{3-s}]$$

$$= -\frac{2a}{V} \quad (11.14)$$

where,

$$a \equiv \frac{2\pi}{3} \sigma^3 \left( \frac{3}{s - 3} \right) u_0. \quad (11.15)$$

which is a specific case of 11.8.

Therefore, $\langle U_{\text{eff}} \rangle$ becomes,

$$\langle U_{\text{eff}} \rangle = -a \frac{N}{V} \quad (11.16)$$

We still must evaluate the excluded volume per molecule, $V_x$. Focus on a given molecule $k$, then the volume that is inaccessible to another molecule $j$ due to the presence of $k$ is just the volume of a sphere of radius $\sigma$ (see figure below).
• Since there are \( \approx \frac{1}{2} N^2 \) pairs of molecules, the total excluded volume is,

\[
V_{\text{tot}} = \frac{1}{2} N^2 \left( \frac{4\pi}{3} \sigma^3 \right)
\]

But, to be consistent, this expression must be equal to, \( NV_x \), if \( V_x \) is the total excluded volume per molecule. This implies that,

\[
V_x = bN
\]

where,

\[
b = \frac{2\pi}{3} \sigma^3 = 4 \left[ \frac{4\pi}{3} \left( \frac{\sigma}{2} \right)^3 \right]
\]

which is the same \( b \) that we calculated above.

Substituting these results into the partition function, Eq. 11.12, we may calculate the mean pressure according to,

\[
P = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} = \frac{1}{\beta} \frac{\partial}{\partial V} \left[ N \ln (V - V_x) - N\beta \langle U_{\text{eff}} \rangle \right]
\]

\[
= kTN \frac{V}{V - bN} - a \frac{N^2}{V^2}
\]

Upon rearrangement, we arrive at van der Waals equation again,

\[
\left( P + a \frac{N^2}{V^2} \right) (V - bN) = NkT
\]

• Although we have made a number of rough approximations here, this treatment did not assume that the gas is of low density. Thus, it is reasonably valid to use this equation to describe a liquid and we may thus consider gas-liquid phase transitions.
11.5 Phase Transitions with the van der Waals model

- With a more realistic model for our system, the van der Waals model, we may now revisit the topic of phase transitions. We begin by plotting out a set of curves of mean pressure $P$ versus the molar volume $v$, for different values of $T$, as dictated by Eq. 11.20.

![Pressure-volume isotherms](image)

- This figure is similar to the one we analyzed earlier in the course, but now we have explicitly included the details of the PV curves within the coexistence region. Notice that these curves have both positive and negative curvature. To study this further, we need to perform stability analysis of the Gibbs free energy against volume fluctuations.

11.5.1 Stability analysis for volume fluctuations

Imagine that we have isolated a small region $S$ in our system, such that the rest of the system acts as a reservoir $R$ at some constant temperature $T_0$ and pressure $P_0$. Then the condition for thermodynamic equilibrium is that the Gibbs free energy achieves a minimum,

$$ G_0 \equiv \bar{E} - T_0 S + P_0 V = G_{\text{min}} \quad (11.21) $$

- Consider now small variations in the volume and examine how this affects the stability of our system.

- Perform an expansion of $G_0$ about $V = V_{\text{min}}$, the volume corresponding to the minimum in $G$,

$$ \Delta G_0 \equiv G_0(V + \Delta V) - G_{\text{min}} = \left( \frac{\partial G_0}{\partial V} \right)_{V_{\text{min}}} \Delta V + \frac{1}{2} \left( \frac{\partial^2 G_0}{\partial V^2} \right)_{V_{\text{min}}} (\Delta V)^2 + \cdots \quad (11.22) $$
LECTURE 11. MODELS OF IMPERFECT GASES CONT.

- But by definition, the minimum of $G_0$ is,
  \[
  \left( \frac{\partial G_0}{\partial V} \right)_{V_{\text{min}}} = 0 \tag{11.23}
  \]

  From ?? we also have,
  \[
  \left( \frac{\partial G_0}{\partial V} \right)_{T_0} = \left( \frac{\partial \bar{E}}{\partial V} \right)_{T_0} - T_0 \left( \frac{\partial S}{\partial V} \right)_{T_0} + P_0
  \]

- But from the first law of thermodynamics, we may write
  \[
  \left( \frac{\partial \bar{E}}{\partial V} \right)_{T} = T \left( \frac{\partial S}{\partial V} \right)_{T} - \bar{P}
  \tag{11.24}
  \]

  Therefore we obtain,
  \[
  \left( \frac{\partial G_0}{\partial V} \right)_{T_0} = T_0 \left( \frac{\partial S}{\partial V} \right)_{T_0} - \bar{P} - T_0 \left( \frac{\partial S}{\partial V} \right)_{T_0} + P_0
  \]

  and, hence,
  \[
  \left( \frac{\partial G_0}{\partial V} \right)_{T_0} = -P + P_0 \tag{11.25}
  \]

- Comparing to Eq. 11.23, we obtain the obvious result that at equilibrium,
  \[
  \bar{P} = P_0, \tag{11.26}
  \]

  which means that the pressure of the subsystem $S$ must be equal to that of the reservoir $R$.

- Actually,11.23 defines the extremum of $G$, the condition that $G$ is a minimum is that $\Delta G_0 \geq 0$ which from Eq. 11.22 implies that the second derivative of $G_0$ is positive. From 11.25 this means that,
  \[
  \left( \frac{\partial^2 G_0}{\partial V^2} \right)_{T_0} = - \left( \frac{\partial \bar{P}}{\partial V} \right)_{T_0} \geq 0 \tag{11.27}
  \]

  This important equation defines the condition for **mechanical stability**, namely that $\left( \frac{\partial \bar{P}}{\partial V} \right)_{T_0} \leq 0$. The above stability condition is consistent with “Le Châtelier’s principle”:

  ♣

  If a system is in stable equilibrium, then any spontaneous change of its parameters must bring about processes which tend to restore the system to equilibrium.

In the present context, if there is an *increase* in the volume of the subsystem $S$, then the pressure $\bar{P}$ of $S$ must *decrease* below that of its surroundings to ensure that the net force on $S$ by $R$ is in a direction such that it tends to reduce its volume back to its former value.
11.6 van der Waal loops and Maxwell constructions

Let’s look in detail at one of the PV isotherms in the previous figure, what do we notice.

- For \( P < P_1 \), the slope is negative, as required for mechanical stability, and the magnitude of the slope is small \( \rightarrow \) large compressibility. This is characteristic of the gas phase.

- For \( P > P_2 \), the slope is still negative, but is much steeper \( \rightarrow \) low compressibility. This corresponds to the liquid phase.

What happens in the intermediate regime, for \( P_2 < P < P_1 \), where there are three possible values of the volume.

- Notice that between \( v_1 \) and \( v_2 \), \( \partial P/\partial v \leq 0 \) and, hence, values of the volume in this region are not permitted.

- This still leaves two possible values of the volume, which requires us to make a choice based on the relative stability of the system at these two volumes. This implies that we should look at the corresponding gibbs free energy, which in differential form is,

\[
dG = d(E - TS + PV) = -SdT + VdP = Nd\mu
\]

Therefore, at constant temperature we have,

\[
dg = vdP = d\mu
\]  
(11.28)

where we have the molar Gibbs free energy, \( g = G/N \) and molar volume, \( v = V/N \).

- If we now integrate \( g \) along the isotherm traced out in the above figure we have,

\[
\int_1^2 dg = g(2) - g(1) = int_1^2 vdP
\]  
(11.29)
where 1 and 2 are arbitrary beginning and ending points, respectively.

The corresponding curve that is obtained in the gP phase diagram is as follows,

- The portion of the curve consisting of the points ABXC are associated with the gas phase (large volumes).
- The portion of the curve consisting of the points EXFG are associated with the liquid phase (small volumes).
- The van der Waals “loop” is associated with the portion of the curve XCDE, where along CDE the system is unstable.
- Comparing the points B (gas phase) and E (liquid phase), we see that since the free energy is lower for the gas phase, this is the more stable one.
- Similarly, looking at the points C (gas phase) and F (liquid phase), we see that the free energy is lower at F and, hence, the liquid phase is more stable.
- At the point X, the free energies for the gas and liquid phase are equal, \( g(X) = g(Y) \), and the two phases can coexist. From 11.29, this implies that,

\[
\int_{Y}^{C} vdP = 0
\]
\[
\int_{Y}^{C} vdP + \int_{C}^{D} vdP + \int_{D}^{E} vdP + \int_{E}^{X} vdP = 0
\]
\[
\left( \int_{Y}^{C} vdP - \int_{D}^{C} vdP \right) + \left( -\int_{E}^{D} vdP + \int_{E}^{X} vdP \right) = 0
\]
\[
\text{area}(DCY) = \text{area}(XED) \quad (11.30)
\]
- Thus the two shaded regions depicted in the PV isotherm above must have equal area, hence the name “equal-area or Maxwell construction”.

\[ g \]
\[ P \]
\[ A \]
\[ B \]
\[ X \]
\[ C \]
\[ D \]
\[ E \]
\[ F \]
\[ G \]
\[ P_1 \]
\[ P_X \]
\[ P_2 \]

\( T = \text{constant} \)
• Referring to the first figure in this section, consisting of a number of PV isotherms, one observes that for $T < T_c$, the removal of the van der Waals loops leaves a single “tie-line” connecting the points on the coexistence curve.

• These "tie-lines" are defined by the equation $(\partial P/\partial v)_T = 0$ and are known as spinodals.

• States between the coexistence curve and the spinodal are metastable single-phase states.