Lecture 3

Note that NSF grad fellowship apps are in the office and due 9 November!!!

Outline:

Degrees of Freedom from chap 1
Equations of State
  • Ideal gas eq.
  • Virial eq
  • Van der Waals
  • Others
Critical behavior
  law of corresponding states

• Degrees of freedom
  o always total must be 3*N. DOF are not lost or gained by bonds
  o always 3 translational DOF total for molecule
  o either 2 or 3 rotational DOF depending on shape
  o remainder are vibrational

OK, now we will begin discussion of intermolecular interactions with simplest possible case – gasses with little or no interaction

Equations of State

An equation of state describes a pure gas using 4 variables: P, V, T, and n. What Eq. of state do you know already? PV=nRT. We will start by constructing this. Always keep in mind that we are searching for molecular explanations for bulk physical properties

Pressure, how to describe? Collisions of molecules with walls of container
Boyle’s law: (published 1662 by Robert Boyle) PV = constant or P = const * 1/V what shape do we expect? hyperbola

Show P vs. V isotherms (Noggle 1.9) (emphasize that they are only valid at low pressure and high temperature – ideal gas conditions)

Molecular explanation for inverse proportionality between P and V? Same # of molecules moving in bigger space means fewer collisions with wall.
**Charles’s Law:** $V = \text{constant} \times T$ or $\frac{V}{T} = \text{constant}$

(experiments done by Charles in 1787, published by Gay-Lussac in 1802) (Charles was second guy to make baloon flight, in 1783, first to use $\text{H}_2$. Guy-Lussac held balloon altitude record - over 4 miles - for 50 years)

show $V$ vs. $T$ graphs (MT 2.1) note that Kelvin is just a temp scale that forces $x$-intercept to be zero.

**Molecular explanation for direct proportionality?** Higher velocity collisions force larger volume (if pressure outside walls remains constant).

**Avogadro’s principle?** $V = \text{constant} \times n$ (at constant $T$ and $P$) or $\frac{V}{n} = \text{constant}$. (early 1800s)

Said another way, the molar volumes of all gases are about the same (22.4 L/mol at STP)

**STP:** 273.15 K and 101325 Pascals (1 atm, 760 torr, 1.01325 bar)

**Molecular explanation?** In ideal gas situation, molecules cannot distinguish each other, all that matters is total # of non-interacting particles.

We can now try to put these 3 experimental observations together (as done by Emil Clapeyron in 1834)

Combine $PV = \text{const}$ $\frac{V}{T} = \text{const}$ $\frac{V}{n} = \text{const}$

Only single consistent expression: $PV/nT = \text{const}$ or $PV = nRT$

Since we know 1 mol at STP occupies 22.4 L...

$$(1 \text{ atm})(22.4 \text{ L}) / (1 \text{ mol})(273.15 \text{ K}) = R = 0.08206 \text{ L atm / mol K}$$

**Real Gases**

Of course, molecules do interact causing ideal gas law to break down. **If we look at $U$ vs. $R$ what do we get?** (Not Morse, but Lennard-Jones) Illustrates different regions of interaction.

- $R$ large $\rightarrow$ approx no interaction
- $R$ medium $\rightarrow$ attractive
- $R$ small $\rightarrow$ repulsive

The Compressibility factor is an indicator of these intermolecular interactions $Z = \frac{PV}{RT}$

$
\vec{V}$ is $\frac{V}{n} = V_m$ is the molar volume.

**What should $Z$ be for an ideal gas?** One

- $Z = 1$ implies? ideal
- $Z < 1$ implies? less difficult to compress than ideal – attractive dominate
- $Z > 1$ implies? more difficult to compress than ideal – repulsive dominate
What should \( Z \) vs. \( P \) look like?

Relate figure to three regions of \( U(r) \) vs. \( r \) plot and of three possibilities for \( Z \).

So, the rest of today we will try to develop some more realistic equations of state.

If we have the above kind of complicated function, **what is the first way we should think about expressing it? What is our normal physics trick?** 

Expansion!

\[
Z = \frac{P \bar{V}}{RT} = 1 + B_2(T) \frac{1}{\bar{V}} + B_3(T) \frac{1}{\bar{V}^2} + \ldots
\]

This is called the virial expansion, or **virial equation of state**. It could also be in terms of \( P \). Of course, as \( \bar{V} \) gets big (or \( P \) small) we approach \( Z = 1 \), ideal behavior

**How might be figure out what the coefficients look like?**

Experiments to measure many combinations of \( P, V, \) and \( T \).

Read book, but it turns out that the second coefficient is primarily a measure of the attractive forces that lead to non-ideality – intermolecular interactions

The virial equation of state is a mathematical/empirical construction that works well and turns out (not uncommonly) to relate nicely to physical behavior. In contrast, the Van der Waals equation uses physical insight to account for non-ideal behavior.

\[
\left( P + \frac{a}{\bar{V}^2} \right) \left( \bar{V} - b \right) = RT \quad P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}
\]

**what are the two interactions we need to account for?** attraction and repulsion

where are those in the equation? \( a / \bar{V}^2 \) is attraction and \( b \) is repulsion:

\[
P_{\text{Ideal}} = P_{\text{Actual}} + \frac{a}{\bar{V}^2} \quad \bar{V}_{\text{Ideal}} = \bar{V}_{\text{Actual}} - b
\]

\[
P_{\text{Actual}} = P_{\text{Ideal}} - \frac{a}{\bar{V}^2} \quad \bar{V}_{\text{Actual}} = \bar{V}_{\text{Ideal}} + b
\]

Actual \( P \) is less than ideal (attraction) and actual \( V \) is greater than ideal (repulsion).

**Why is \( V^2 \) in the denominator rather than just \( V \)?** Attractive forces reduce both force and number of collisions.

There are many other equations of state. Two of the most common are the Redlich-Kwon and the Peng-Robinson. They are more accurate than vdW, but less physically intuitive. These are described in your book so we won’t go over them here.

In practice, the ideal gas law works pretty well for most gasses. However, the non-ideal attractive forces are what make condensed phases possible. So they are clearly important.
Critical behavior

The transition point where we can begin to distinguish liquid and gas is the critical point. Characterized by critical temp ($T_c$), pressure ($P_c$), volume ($V_c$), and density ($\rho_c$) below $T_c$ substances exist as both liquids and gases. Above $T_c$, only gases

$T_c$ for He = 5.3 K  $T_c$ for CO$_2$ = 304.2 K

On a hot day (> 88F) you can never make dry ice, regardless of pressure

Critical behavior is important because it is related to non-ideal properties of gases.

Show Noggle 1.9, 1.6 and MT 2.9

Ideal gas isotherms show smooth PVT behavior.

Non-ideal gases show complicated behavior with inflection points. Note cubic shape of PVT data – an equation of state must be cubic to describe both gases and liquids

At the critical point what can we say about the derivatives? Both first and second derivatives are zero. This gives us 2 equations. How convenient that vdW has 2 parameters!

van der Waals equation and derivatives:

$$P_c = \frac{RT_c}{V_c} - \frac{a}{V_c^2}$$

$$\frac{dP}{dV} = \frac{RT_c}{(V_c - b)^2} + 2\frac{a}{V_c^3} = 0$$

$$\frac{d^2P}{dV^2} = 2\frac{RT_c}{(V_c - b)^3} - 6\frac{a}{V_c^4} = 0$$

Putting these two equations together gives:

$$T_c = \frac{8a}{27bR}  \quad V_c = 3b  \quad P_c = \frac{a}{27b^2}$$

Note that the van der Waals $a$ and $b$ parameters are usually determined from the critical point.

This suggests the Law of Corresponding States: all gases behave the same if we consider reduced $P$, $V$, and $T$ (relative to the critical point). $T_r = T/T_c$ and so on.

So, H$_2$ at twice its critical $T$, $P$, and $V$ behaves the same as CH$_4$ at twice its $T$, $V$, and $P$. Book has some good plots on this.