

Chapter 1, continued

1.4

Before we get started, let's register our 'Clickers and take a reading quiz...

... so hopefully you remembered what we talked about last lecture re: systems and what you read.

Speaking of your reading, a key concept (highlighted by the quiz) is the state of a system

The whole reason we care about defining a system is so that we can talk about its state and state variables

— let's look at our PowerPoint handout from last time:

So, we see a difference between path and state variables + between irreversible and reversible processes.

We also see that $\oint_{\text{cyclic process}} dU = 0$, as we'll see on p. 57, any state variable

Finally, we see the point of talking about state variables is because there are useful equations of state

↳ such as the ideal gas law: $PV = NRT$

↳ or the Van der Waals equation: $(P + a\frac{N^2}{V^2})(V - Nb) = NRT$

↳ Let's look at this on the next slide

1.5

→ To properly use the $pV = NRT$ equation we needed to know:

- units
- moles (how to obtain them from M.W. and mass) → or # of particles and Avogadro's #
- R, the gas constant

we also learned how $pV = NRT$ leads to nice graphs!

Now, what happens when we mix things up? (next slide)

→ So, each gas in a mixture behaves as if it's alone, but the total pressure is a sum of all gases

Now let's put away our PowerPoint handouts and move on.

→ Real gases are better described by the van der Waals eqn:

$$\left(p + \frac{a}{\bar{V}^2}\right) (\bar{V} - b) = RT$$

← this means V/N , or V_m in the book

$\frac{a}{\bar{V}^2}$ → attraction between atoms or molecules of a real gas

b → volume of atoms or molecules in a real gas

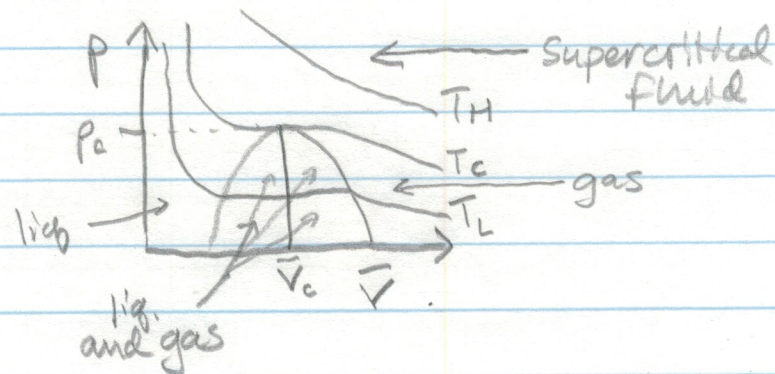
How wrong is $pV = NRT$? Just check Z , the compressibility:

$$Z = \frac{p\bar{V}}{RT} = \frac{\bar{V}_{\text{measured}}}{\bar{V}_{\text{ideal}}}$$

The shape of Z vs. pressure* is shown on p. 26

* Sections 1.5 + 1.6 are very tricky; to get the nice graph on page 26, we need to use reduced variables,

- ↳ First let's review the concept of phase (solid, liq., gas)
- ↳ reduced variables depend on the critical point:



→ for each substance P_c , T_c , and \bar{V}_c can be found

↳ once we have these, we create $P_r = \frac{P}{P_c}$, $T_r = \frac{T}{T_c}$, $\bar{V}_r = \frac{\bar{V}}{\bar{V}_c}$

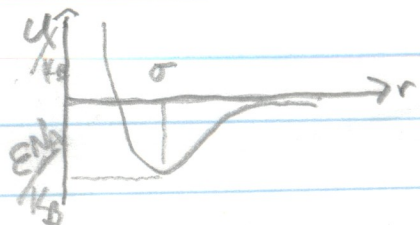
the "validity of the law of corresponding states" (p. 26) is the culmination of section 1.5 and transitions us to stat. mech.:

Statistical Mechanics 101: "Matter is made of particles"

↳ we hinted at this when we talked about attraction/volume of atoms and molecules.

↳ these are described by the Lennard-Jones "6-12" potential

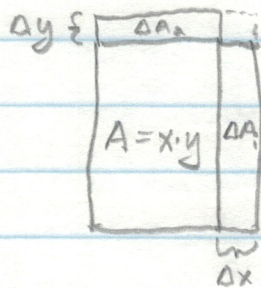
$$U_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$



Section 1.6 has some stat mech d'sguised as "kinetic theory"

→ But before we tackle this section, let's work on some math:

Partial derivatives (appendix 1.1), take area as an example:



if only x changes $\Delta A_1 = y \Delta x$

if only y changes $\Delta A_2 = x \Delta y$

if both change we need some math:

$$\Delta A = (x + \Delta x)(y + \Delta y) - x \cdot y = \overbrace{y \Delta x}^{\Delta A_1} + \overbrace{x \Delta y}^{\Delta A_2} + x \cdot y + \Delta x \Delta y - x \cdot y$$

$$= \Delta A_1 \cdot \frac{\Delta x}{\Delta x} + \Delta A_2 \cdot \frac{\Delta y}{\Delta y} + \Delta x \cdot \Delta y$$

as $\Delta x \rightarrow 0 + \Delta y \rightarrow 0$, $\Delta A \rightarrow dA$
and $\Delta x \cdot \Delta y$ is negligible

$$\text{So, } dA = \left(\frac{\partial A}{\partial x} \right)_y dx + \left(\frac{\partial A}{\partial y} \right)_x dy$$

↳ this is the form of many equations we'll see

There are also neat relations between partial derivatives: