3321

3 main topics of physical chemistry are

- quantum mechanics (3322)
- thermodynamics / statistical mechanics
- kinetics

Quantum → properties of atoms & molecules

eg. dipole moment
quadrapole moment
vibrational frequencies

Thermo → collective properties

eg. melting point
density

Stat. Mech → links these two : how the macroscopic quantities are connected to the microscopic properties.

This course: mainly thermodynamics → but we will make connections to micro. to enhance concepts

The textbook often makes the statistical mechanics link in the thermo. chapters because it does quantum mechanics first. We won't be able to do this because quantum is 3322 – next semester.

Chapter 16:

thermodynamic variables: state functions like

volume	V
pressure	P → see page 2a
temperature	T
number of moles	n
enthalpy	H ...

Equation of State: a relationship between the thermodynamic variables that allows us to predict the system properties as we change one or more of the state functions.

Simplest example: ideal gas equation of state

$$PV = nRT$$

or $P\left(\frac{V}{n}\right) = RT \Rightarrow P\bar{V} = RT$

↳ molar volume

Molecular picture: point particles which do not interact with each other, but they do see (bounce off) the walls of the container they are in.

difference between V and $\bar{V}$

↳ intensive - does not depend on system size

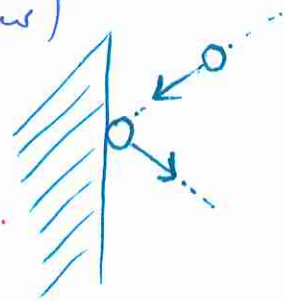
↳ extensive - directly proportional to system size

ex: V, M, E

P, T, ρ

Pressure: force per unit area exerted by gas (on container walls)

also the force per unit area exerted by the container on this gas (Newton's 3rd law)



units SI: force: $1\ N = 1\ kg\ m/s^2$

force to accelerate a 1 kg mass at $1\ m/s^2$.

area: m^2

$$\Rightarrow 1\ N/m^2 = 1\ \frac{kg}{m s^2} = 1\ Pa = 1\ \text{pascal}.$$

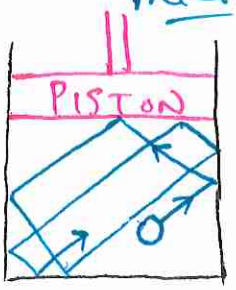
note: $1\ Pa \cdot m^3 = \frac{1\ kg\ m^3}{m s^2} = 1\ kg \frac{m^2}{s^2} = 1\ J$ (energy)

P V

other units: $1\ bar = 1 \times 10^5\ Pa$

$1\ atm = 1.01325\ bar$

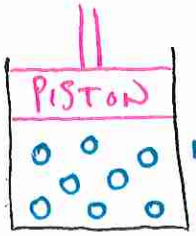
micro/macro connection:



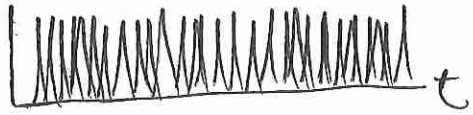
What does the piston feel?

most of the time → nothing

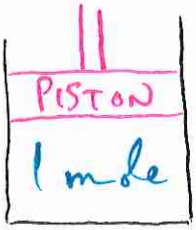
occasionally → collision



more atoms



force fluctuates over time



F constant to within exp. measurement

small system random unpredictable → large system deterministic predictable

Note that we are doing equilibrium thermodynamics in this course.
↳ no net change in the thermo. variables over time.

Real gases: show deviations from ideal behavior at high pressure.

Can measure this deviation by calculating $Z = \frac{P\bar{V}}{RT}$ experimentally. Z is called the "compressibility factor".

$Z = 1$ for an ideal gas.

Show Fig 16.3 and 16.4

Low T → attractive forces dominate

High T and/or high P → repulsive forces dominate

each gas has a different curve.

How do we take the intermolecular interactions into account?

van der Waals equation of state

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

a → attractive component

b → repulsive (size) component

a, b different for each compound

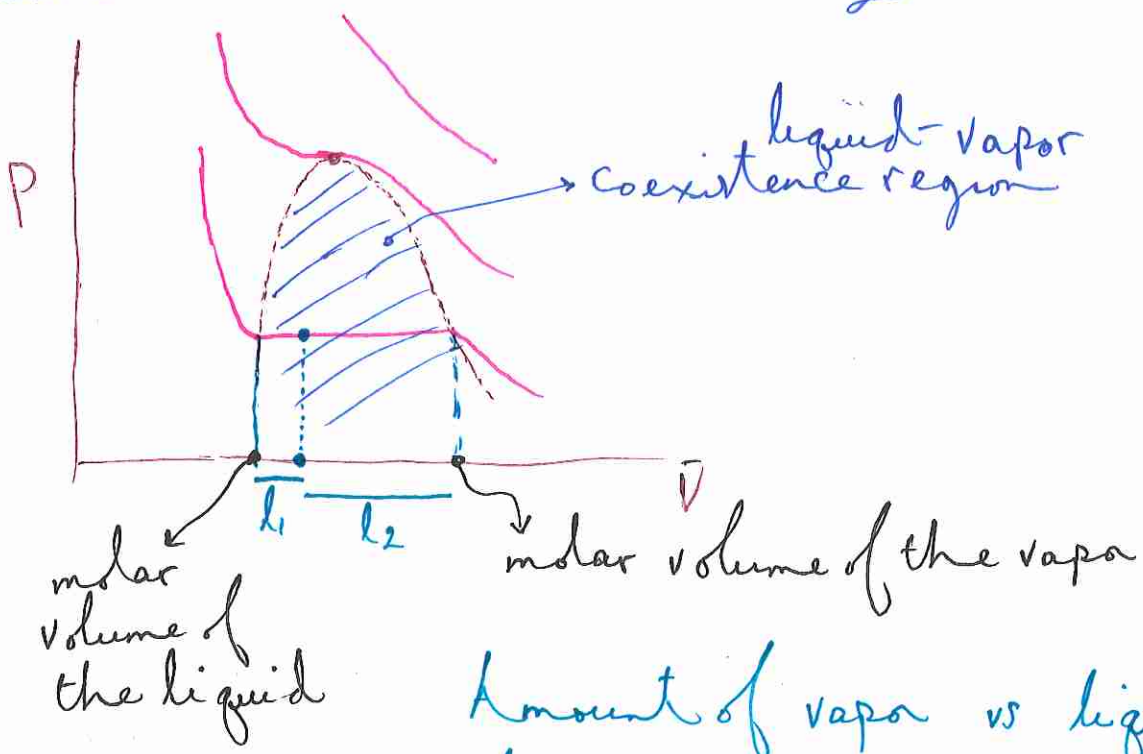
Interestingly, the van der Waals equation of state captures the vapor $\rightleftharpoons$ liquid phase ~~change~~ transition, which is obviously missing from the ideal gas model.

To see this we will look at P-V isotherms; namely how pressure varies with volume at constant T.

For an ideal gas these look like $PV = \text{constant}$

or $P = \dfrac{\text{constant}}{V}$.

For a real substance, these look like Fig 16.7



Amount of vapor vs liquid?

$$\frac{l_1}{l_1+l_2} = \text{vapor fraction}$$

$$\frac{l_2}{l_1+l_2} = \text{liquid fraction}$$

l = length of line segment.

There is a temperature, T_c, above which a gas cannot be liquified. The P_c and V_c corresponding to this represent the critical point on the phase diagram.

Above the critical point we have a "supercritical fluid". It can effuse through solids like a gas and dissolve materials like a liquid. → $T_c = 304\ K$; $P_c = 73\ atm$

Supercritical CO_2 is used to decaffeinate coffee. It is forced through green coffee beans and dissolves 97 - 99% of the caffeine present. Then the caffeine is recovered and used in soft drinks.

Now look at the vander Waals isotherms Fig 16.8, 16.9. They have some unphysical features but if we "fix" these with the Maxwell equal-area construction then we get something reasonable.

The critical point is an inflection point so we can express this as

$$\left.\frac{\partial P}{\partial \bar{V}}\right)_T = 0 = \left.\frac{\partial^2 P}{\partial \bar{V}^2}\right)_T$$

From $\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$ we can write

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

We can immediately write

$$\left.\frac{\partial P}{\partial \bar{V}}\right)_T = -\frac{RT}{(\bar{V}-b)^2} + \frac{2a}{\bar{V}^3}$$

$$\left.\frac{\partial^2 P}{\partial \bar{V}^2}\right)_T = \frac{2RT}{(\bar{V}-b)^3} - \frac{6a}{\bar{V}^4}$$

which gives : $\dfrac{RT_c}{(\bar{V}_c-b)^2} = \dfrac{2a}{\bar{V}_c^3}$ and $\dfrac{RT_c}{(\bar{V}_c-b)^3} = \dfrac{3a}{\bar{V}_c^4}$

Eliminate T_c : $\dfrac{2a(\bar{V}_c-b)^2}{R\bar{V}_c^3} = \dfrac{3a(\bar{V}_c-b)^3}{R\bar{V}_c^4}$

or $\boxed{\bar{V}_c = 3b}$

Now $T_c = \dfrac{2a(3b-b)^2}{R(3b)^3} = \boxed{\dfrac{8a}{27bR} = T_c}$

Then $P_c = \dfrac{R}{2b}\cdot\dfrac{8a}{27bR} - \dfrac{a}{9b^2} = \dfrac{4a}{27b^2} - \dfrac{3a}{27b^2} = \boxed{\dfrac{a}{27b^2} = P_c}$

Now write the van der Waals equation of state using

$\bar{V}_c = 3b \Rightarrow b = \frac{1}{3}\bar{V}_c$ and $\dfrac{a}{27b^2} = P_c \Rightarrow a = 27P_c\cdot\frac{1}{9}\bar{V}_c^2 = 3P_c\bar{V}_c^2$

$$\left(P + \frac{3P_c\bar{V}_c^2}{\bar{V}^2}\right)\left(\bar{V} - \frac{1}{3}\bar{V}_c\right) = RT$$

We need one more result to proceed.

$$P_c\bar{V}_c = \frac{a}{27b^2}\cdot 3b \quad \text{and} \quad \frac{8a}{27bR} = T_c \Rightarrow a = \frac{27bRT_c}{8}$$

So $P_c\bar{V}_c = \dfrac{27bRT_c \cdot 3b}{8 \cdot 27b^2} = \dfrac{3}{8}RT_c$

Now divide through by $P_c\bar{V}_c$:

$$\left(\frac{P}{P_c} + \frac{3\bar{V}_c^{\,2}}{\bar{V}^2}\right)\left(\frac{\bar{V}}{\bar{V}_c} - \frac{1}{3}\right) = \frac{RT}{3/8\, RT_c} = \frac{8}{3}\frac{T}{T_c}$$

and define reduced quantities $P_R = \dfrac{P}{P_c}$; $\bar{V}_R = \dfrac{\bar{V}}{\bar{V}_c}$; $T_R = \dfrac{T}{T_c}$

to obtain
$$\left(P_R + \frac{3}{\bar{V}_R^{\,2}}\right)\left(\bar{V}_R - \frac{1}{3}\right) = \frac{8}{3}T_R$$

This is called the Law of Corresponding States.

It is very powerful and important from a conceptual standpoint.

We have moved away from an ideal gas description but have found another concept (reduced quantities relative to the critical point) which unifies the behavior of gases and allows us to think about real gases in a powerful manner.

See Fig 16.10 for real gases (van der Waals is approximate)

§16-5 : Virial EOS

A more systematic equation of state is given by

$$Z = \frac{P\bar{V}}{RT} = 1 + \frac{B_{2V}(T)}{\bar{V}} + \frac{B_{3V}(T)}{\bar{V}^2} + \dots$$

expansion in powers of $1/\bar{V}$

2nd virial coefficient

3rd virial coefficient

$B_{2V}(T)$ is negative at low T and is zero at the Boyle temperature, where the attractive and repulsive parts of the intermolecular interactions more or less cancel each other out.

[ther EOS possible, like Redlich-Kwong and Peng-Robinson. These can be useful for engineers].