States of matter, structure

Most familiar

- Gas

- Liquid

- Solid

- Plasma

And since it is CM1 course none others will be considered and we will also omit plasma

Perfect Gases – kinetic theory

We have been looking mostly at solids relating macroscopic and microscopic properties. Macroscopically, a gas has no fixed volume or shape. It has to be confined by walls to define its volume and shape and the molecules then bounce off the walls providing a force on the walls which we can measure in the form of **pressure.** In fact, a gas has only a very small number of macroscopic properties which we can simply list as **P**, **V**, **T**, the total number of molecules **N** or equivalently the total number of moles **n**. At the molecular level a given gas molecule has mass **m**, position **r(x,y,z)** and velocity **v** or equivalently momentum **p = m*v**. We will be trying to answer our usual Q: how can we relate M and μ properties. Now that we listed the properties this should be real easy!

Gas in Equilibrium – macroscopic bit

1. Boyle (c. 1660): $PV=const$ at $T=const$

2. Charles (1787), Gay-Lussac (1802): $V=V_0(1+\alpha T)$, m, $P=const$

3. $P=P_0(1+\beta T)$

4. $PV=RT$ (follows from above, R depends only the quantity of gas).

5. Avogadro: $R \approx 8.3\ J*K^{-1}*mol^{-1}$ for given quantity of gas

6. Dalton: $P=P_1+P_2+...+P_n$

Gas in Equilibrium – microscopic bit

Lets assume that there is no macroscopic flow of energy or momentum in the gas and its macroscopic density is uniform. Lets now see what is happening microscopically. Gas molecules would travel in a straight line (accord2Newt1stLaw) as there is no interaction between molecules except when they collide. The energy of gas will be defined by the kinetic energy of this motion (as there is no potential interaction, molecules are too far apart).

In fact we assume:

- All gas molecules are identical and of mass m

- Of zero size and do not collide with one another

- Exert no forces on one another

- Move randomly and collide with the walls of the container elastically

Gas in Equilibrium – microscopic bit

$$E = \sum_{i=1}^{N} \frac{1}{2} m v_i^2$$

Now, we shall consider average energy of this ensemble (as it is something we eventually may be able to connect to macroscopic properties).

$$\overline{E} \equiv \overline{\frac{1}{2} m v_i^2} = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{2} m v_i^2 \Rightarrow E = N \overline{E} = N \overline{\frac{1}{2} m v_i^2}$$

Lets look at the collision of molecules with the container walls

$$p = 2 m v_i$$

Now, p has direction, so need to split v into components. Moreover, lets split large container (with n molecules per m³) into small cubes side l and chose components $v_{l1} \perp v_{l2} \perp v_{l3} \parallel$ to the the sides of the cube ($v^2 = v_{l1}^2 + v_{l2}^2 + v_{l3}^2$)

Gas in Equilibrium – microscopic bit

$$p_{l1} = 2mv_{l1}$$ for single collision and will have to wait $2l/v_{l1}$ until next one on the same wall ($v_{l1}/2l$ coll per sec)

Remember, $P=F/A$, so we work towards P microscopically, $F= dp/dt$, and momentum transfer per molecule per sec (or force per molecule) is:

$$2mv_{l1}\left(\frac{v_{l1}}{2l}\right) = \frac{mv_{l1}^2}{l}$$ or 4all molecules in our cute cube $$\frac{m}{l}\sum v_{l1}^2$$

we have $N_l = n_l l^3$ molecules in our little volume, hence average speed is

$$\overline{v_{l1}^2} = \frac{\sum v_{l1}^2}{n_l l^3} \Rightarrow \frac{m}{l} n_l l^3 \overline{v_{l1}^2} = mn_l l^2 \overline{v_{l1}^2} = mn_l \overline{v_{l1}^2} l^2$$ momentum transfer per sec (or force)

Hence, microscopic pressure is simply $$P_l^\mu = F/l^2 = mn_l \overline{v_{l1}^2}$$

Now we need to bring it all up2macroscopic world

Gas in Equilibrium – microscopic2macroscopic bit

$$\overline{v_{l1}^2} = \overline{v_{l2}^2} = \overline{v_{l3}^2} = \frac{1}{3}v_l^2 \qquad \text{As there is no preferred direction}$$

Thus $\qquad P_l^\mu = \frac{1}{3}mn_l\overline{v_l^2}$

and 4all groups of molecules in their cute cubes

$$P = \sum_l P_l^\mu = \frac{1}{3}\sum_l mn_l v_l^2 = \frac{2}{3}\sum_l \frac{1}{2}mn_l v_l^2 = \frac{2}{3}\frac{E}{V}$$

and thus *PV=2/3E,* we already defined

$$\overline{v^2} = \frac{1}{N}\sum_i v_i^2 \Rightarrow \frac{1}{nV}\sum_i v_i^2 \Rightarrow \frac{1}{n}\sum_l n_l v_l^2 \Rightarrow$$

$$P = \frac{1}{3}mn\overline{v^2} \Rightarrow PV = \frac{1}{3}mN\overline{v^2}$$

$$PV = \frac{1}{3}mN_A\overline{v^2} = RT \quad \text{for 1 mole, also definition of T}$$

Gas in Equilibrium – microscopic2macroscopic bit

$$\overline{E} \equiv \overline{\frac{1}{2}mv_i^2} = \frac{1}{N}\sum_{i=1}^{N}\frac{1}{2}mv_i^2 \Rightarrow E = N\overline{E} = N\overline{\frac{1}{2}mv_i^2}$$

$$RT = \frac{1}{3}mN_A\overline{v^2} \Rightarrow \overline{E} = \frac{3}{2}\frac{RT}{N_A} \equiv \frac{3}{2}k_B T$$

Gas in Equilibrium – macroscopic bit

1. PV=2/3E hence, *PV=const* at *T=const* (Boyle)

2. Charles (1787) Gay-Lussac (1802): $V=V_0(1+\alpha T)$, *m, P=const*

3. $P=P_0(1+\beta T)$

4. *PV=RT (follows from above, R depends only the quantity of gas).*

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The Van der Waals eq. of state

The equation of state we considered above describes any sufficiently dilute gas in which the molecules on average are further apart than the range of the interatomic potentials. However, if the gas is compressed so that the molecules are much closer together and are able to interact with each other continuously then the equation of state changes to reflect this. A gas in which the interatomic interactions are as important as the kinetic energy we will call a real gas as opposed to the ideal gas mentioned above. The problem with real gases I that the equation of state will now be different for each different interatomic potential! What people have done is to look for approximate equations of state to represent these real gases in which only a few additional parameters are introduced which can be used to fit the equation of state to measurements on specific gases. One very interesting attempt to do this is due to J. D. Van der Waals a Dutch physicist of the late 19th century who proposed an equation of state which is more complicated than the one we considered but which is surprisingly useful.

The Van der Waals eq. of state cntd.

It can be fitted to the noble gases like Neon, Argon and Krypton with good accuracy and it moreover takes account of two very general features of interatomic potentials, namely that there is (1) a strongly repulsive core at short interparticle distances and (2) a weakly attractive tail to the potentials at greater distances but which rapidly goes to zero as in the Lennard-Jones potential for example. As an added bonus the Van der Waals equation of state gives some insight into how a dense real gas turns into a liquid.

Let me simply state the form of the Van der Waals equation of state and later justify this form. It is again a relation between P, V and T but it has the form (for n moles of material)

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

Where a and b are two constants that depend only on the type of gas we are dealing with. Looking at the same Eq. we can also see, that there seems to be $T>0$ at which $P=0$, meaning our molecules no longer exert any pressure on the walls of the container! Physically, this means that molecules are now bound together. Thus term n^2a/V^2 is associated with weak attraction force, which in fact will reduce the momentum transfer to the wall as molecules hit one as compared to the ideal gas.
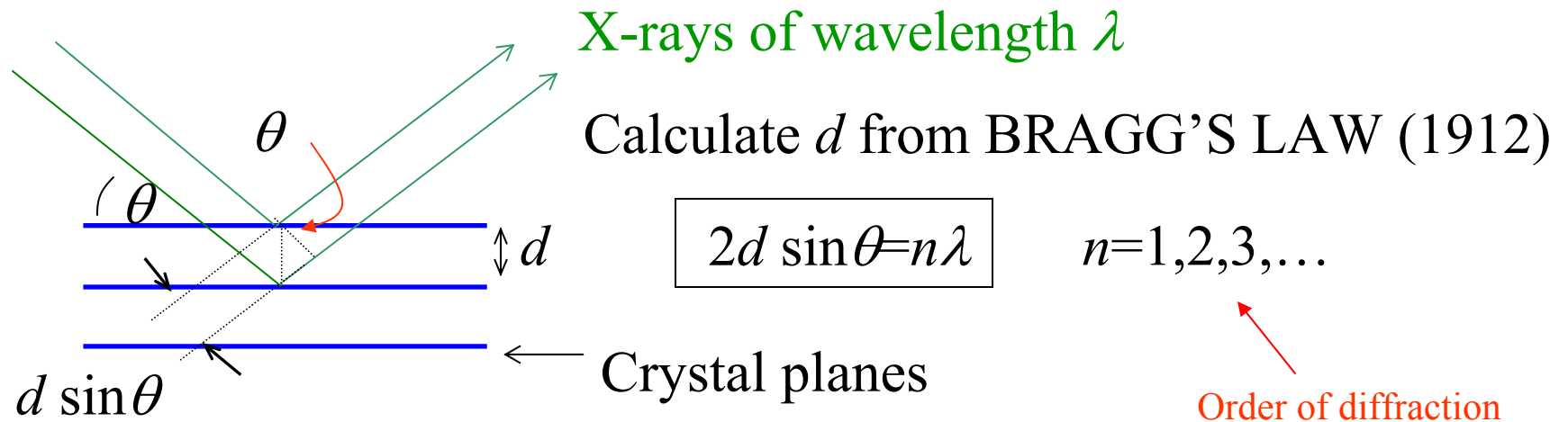
NB

1. Typical kinetic energy of a gas molecule at room T is ~0.04eV<<5eV of electron energies in molecules. Hence collisions can be considered as elastic!

2. Any kinetic theory (e.g. of ether) that relates pressure to the kinetic energy is bound to give PV≈2/3E. This is because P~F/A, and E/V~F*L/V~F/A
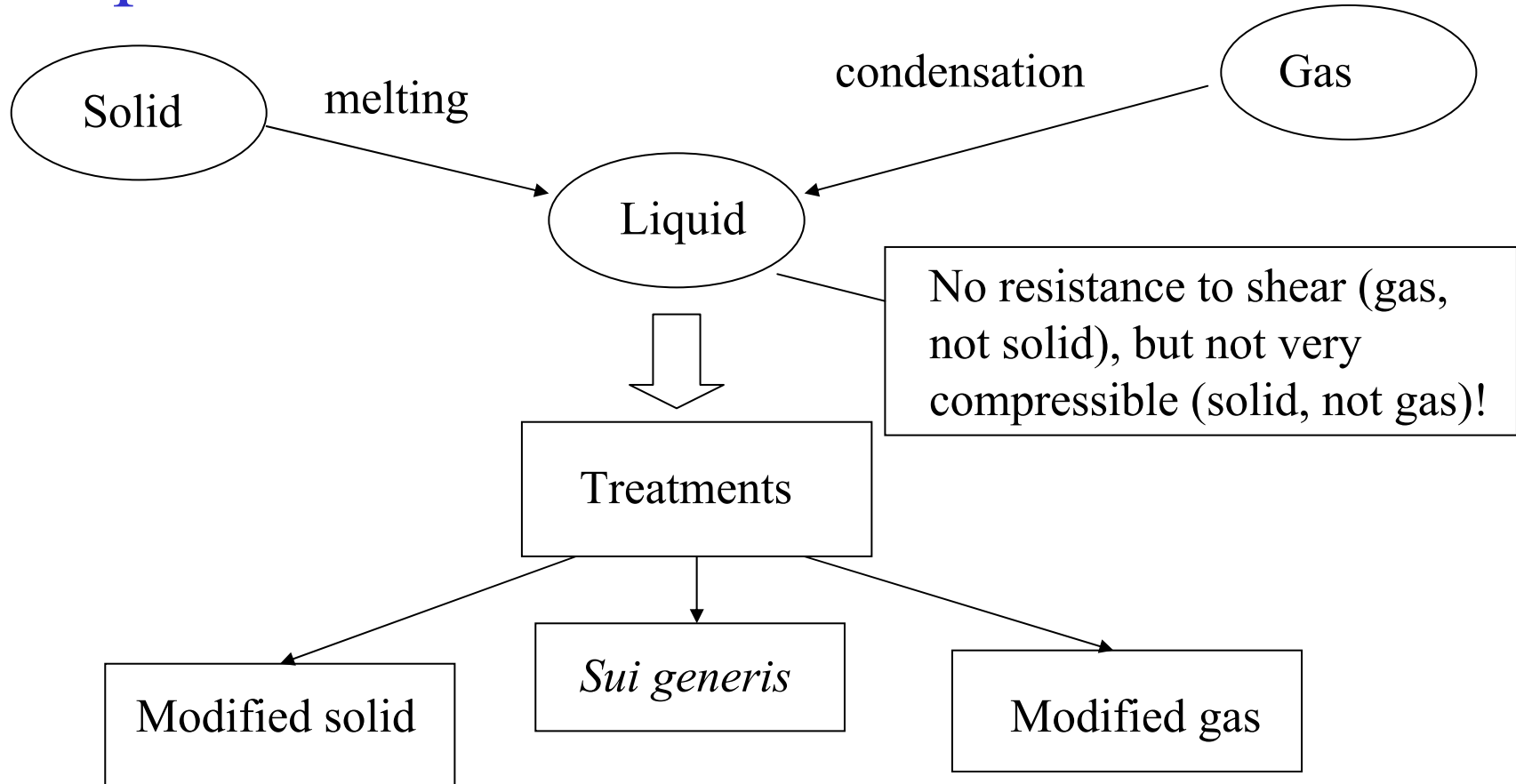
Solids

We want microscopic information – need radiation with wavelength comparable to the size of feature – atom, interatomic spacing (1-2Å). Hence – X-rays (Röntgen, 1895).

For solid crystals we use X-ray diffraction to get information about crystal plane spacing:

θ

θ

d

$d \sin\theta$

X-rays of wavelength λ

Calculate d from BRAGG'S LAW (1912)

$$2d \sin\theta = n\lambda$$

$n = 1, 2, 3, \ldots$

← Crystal planes

Order of diffraction

Liquids

Solid → **melting** → Liquid

Gas → **condensation** → Liquid

No resistance to shear (gas, not solid), but not very compressible (solid, not gas)!

Liquid ⟱ Treatments

Treatments →
- Modified solid
- *Sui generis*
- Modified gas

Modified gas

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

$$V_c = 3\overline{b} \Rightarrow V_c - \overline{b} > 0$$

but

$$V_c^L - \overline{b} < 0!$$

Now

$$\overline{a}\Big/V^2$$

$$\overline{a} = \frac{1}{3}N_A V_m \varepsilon$$

and can be very large (10^3-10^5 atm.) compared to P due to ε of liquid

Hence, modification of Van der Waals eq. is required!

Moreover, we have seen earlier that surface tension effectively means that a liquid can withstand negative pressure!

It turns out that liquids bare some resemblance to the solid phase. For example, the bulk coordination number for a close packed solid is 12 and is only slightly reduced to 10 in the liquid phase

Liquids act as a less ordered diffraction planes and so generate only a few diffraction lines with X-ray diffraction. Atoms in liquids do not occupy closely specified positions as the do in solids: they have more room for manoeuvre and are not particular about their neighbours

This is expressed by the RADIAL DISTRIBUTION FUNCTION, $P(r)$, e.g. $P(r)$ for liquid Hg

$P(r)$

Proportional to number of neighbours at distance r

2

1

r

dr

3 Å   5.5 Å
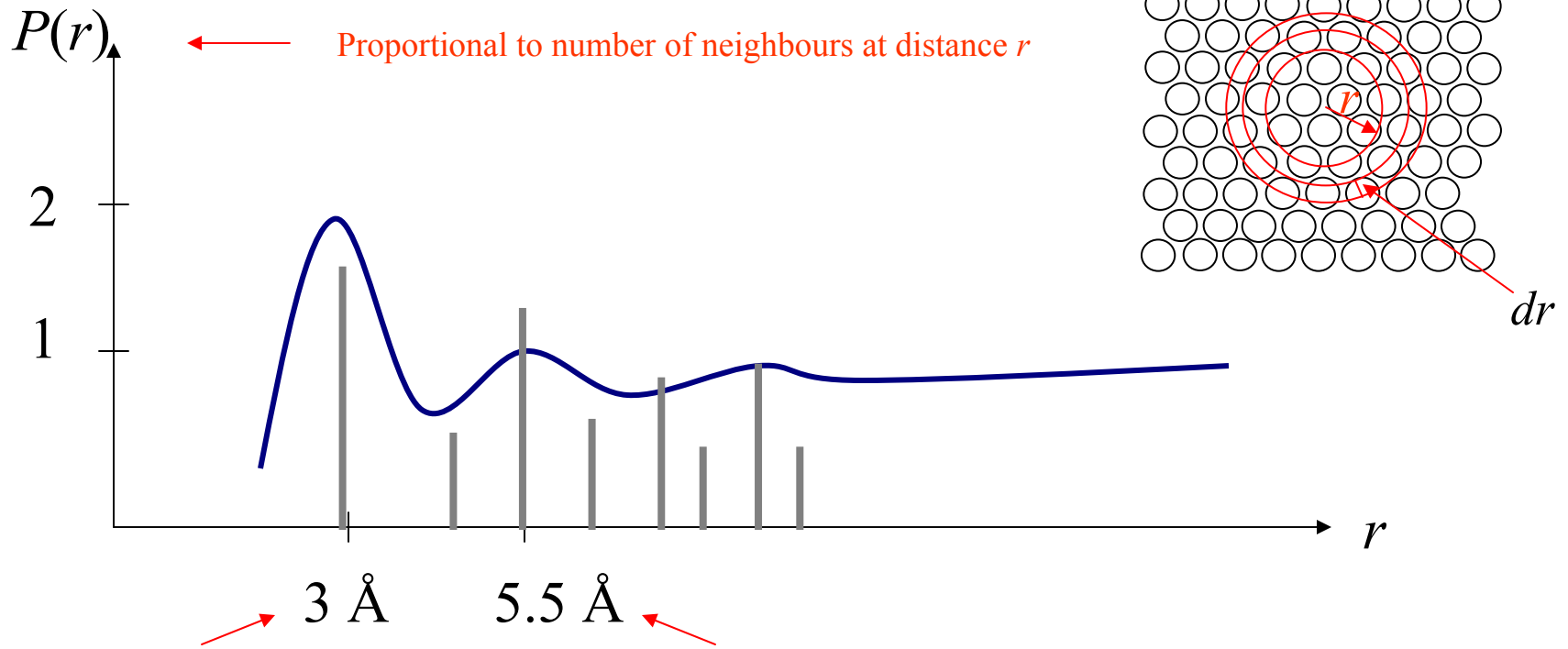
First nearest neighbour distance in solid   Second nearest neighbour distance in solid

$$P(r) = \frac{\text{Number of atoms in a shell of volume } 4\pi r^2 dr}{4\pi r^2 n_{av} dr}$$

Here n_{av} = average number of particles per unit volume

This is a NORMALISED definition of $P(r)$

Thus, RDF is a measure of the average density as a function of distance from some arbitrary origin.

EXERCISE: Real liquids experience a viscous resistance to flow
The force per m^2 to overcome the viscous resistance is by definition:

$$F = \eta \frac{du}{dz}$$

where η is the viscosity and du/dz is the velocity gradient between two neighbouring planes. Fluids that obey this relationship are known as NEWTONIAN fluids. Can you develop a simple model that relates viscosity to interatomic forces?

Hence, modified solid

Solids expand by 5-15% on melting. Hence, concept of *free volume.* Clearly, some extra volume comes from increase of distance between molecules or atoms. But this can also be achieved by taking a solid with 8 or 12 neighbours and subtracting 1 or 2. This will introduce a degree of topological disorder, but will still bare relation to the original solid. Moreover, x-ray diffraction studies suggest that interatomic distance only changes by 1% in Ar on melting, but volume increase suggests that distance change must be about 5%.This justifies the view of melting as creation of "holes" in the structure which otherwise closely resembles the one of solid. This observations led to "hole-theory" of liquids.

sui generis

1. Randomly packed structure with local symmetry (but lower than in solid, e.g. five fold, one can still divide 360 by 5). Essentially gives a snapshot (10^{-15}s) of the liquid and thus a static model.

2. Molecular dynamics approach. A dynamic model and hence transport properties can be evaluated. Starts off from placing molecules (treated as hard spheres that collide elastically) in a box and lets them move with equal speeds in random directions and their subsequent movements are determined by Newton's laws of motion. The total energy is determined by initial velocities and remains constant determining the temperature of the system. The behaviour of the system depends on the velocity and packing of the particles