State Variables, Zeroth and First laws

1.1 Microstates & Macrostates

- The state of a classical system is defined by giving the position and velocity of each of the constituent particles. In thermodynamics this is referred to as a 'microstate' in which all the microscopic parameters are defined.

- In this hierarchical world, however, we are often interested in the 'state' of a system on a 'macro' scale, defined by state variables – the pressure, temperature and volume of a gas for example. A macro state is a state of the system defined by state variables – but there are myriads of microstates that have these headline state variables.

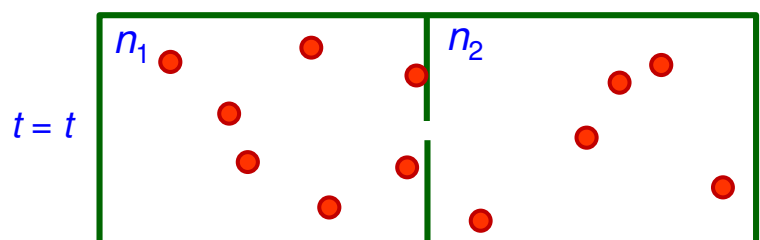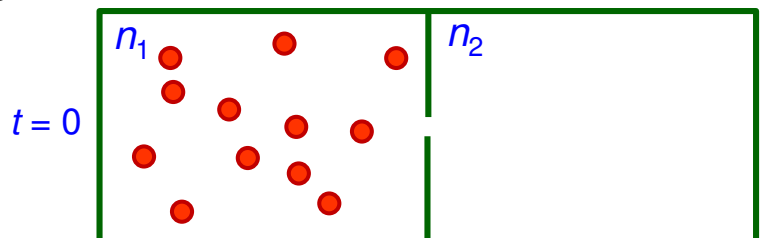*e.g.* particles in a partitioned box: define macrostate by n_1, n_2

- Start in an 'unusual' macrostate
$$n_1 = n , n_2 = 0$$

- After a while distribution settles down with $n_1 \approx n_2$

- The state variable n_1 has a well defined average value $n_1 = n/2$

- The fluctuations in n_1 depend on n and how long you measure for.

The use of state variables and time scales

- The use of state variables relies of the system sampling enough microstates on the timescale of interest so that when you measure/think about *e.g.* pressure a meaningful average can be established.

- The time scales of natural processes vary over many orders of magnitude.

  A quark-gluon plasma (produced, for example, by colliding Pb nuclei at the LHC) comes to thermal equilibrium on a timescale of about 1fm/c (3×10^{-24}s). Molecules in air collide at about 7GHz – so in 10^{-9}s some sort of local equilibrium is established. Systems involving electrons thermalize a few orders of magnitude faster. At the other end of the spectrum? The question is how long can you wait. A few million years for some geological process?? (10^{14}s). On the astronomical scale clusters of galaxies 'relax' on a time scale of 1 Gy (3×10^{16}s)

  The chance of you actually hitting a time scale on which something is changing at a rate so as to make state variables completely useless is slim: we are always approximating anyway in science.

- In general the internal processes are either faster than your time scale, in which case averaging over microstates to get state variables is fine (eg assuming a uniform mixture of O_2 and H_2 and no need to describe composition variations in space), or much slower (*e.g.* the rate at which O_2 and H_2 produce H_2O is so slow at room temperature that we can take the amount of water in the box as fixed,)

- Actually, you only need the system to be **locally** at equilibrium. Because a gas thermalizes so fast, an explosion or a shock wave can be described by locally varying but well defined temperature, pressure, density and composition.

'Multiparticle systems'

How many particles do you need?

- A gas of N atoms in thermal equilibrium with the walls of its container will typically show a fractional variation in its energy of the order of $0.8/\sqrt{N}$ – so **for 100 atoms we expect an 8% r.m.s. fluctuation in energy**.

- For N atoms in a box, the standard deviation of the no of gas molecules located in one half of a box is $0.5\sqrt{N}$ and so the fraction r.m.s. deviation of the number of molecules on one side of the box is $1/\sqrt{N}$.

- **The chance that N molecules of gas all are located in one half of a container is** $1/2^N$**..** $\approx 10^{-30}$ **for 100 atoms**. Suppose you had a 10cm cube: it takes air molecules about 10^{-4}s to get half way across this box – giving a 'new' configuration about 10^4 times a second. It would take 300 million times the projected age of the universe to get through 10^{30} configurations.

- We are often effectively averaging over the contributions of N atoms – so the fractional time variations in state variables scale as $1/\sqrt{N}$.

- **At normal temperature and pressure (NTP= 20° C, 101 325Pa) there are 2.5×10^{22} molecules in a litre of gas**. Meaning all state variables are pretty well defined.

  'Enough particles' is when the r.m.s. fluctuations in state variables are small enough for your current purposes.

Physics is the art of approximation

- One realises, with some disappointment, that the world is too complex to describe exactly: one needs approximations.

- A particular problem can be handled approximated to various levels.

- It thus becomes important in any context to know how accurately you want 'the answer' and that depends on what you intend to do with the answer.

- **Do you wish for a phenomenological, preferably analytical model**, that you can play with mentally or algebraically which models the 'essential' (= what you are interested in now) behaviour of a system and sheds light on 'how things work', **or do you want an computer to spend zillions of hours of CPU time working out a number as accurate as we can** – in which case that is all you get ('42') which has no general use, but gives the particular value in a particular circumstance as good as it can be found, if that is what you want… (Often it would be quicker and more accurate just to measure it if you are that fussy.)

- A key part of being able to approximate is to know the magnitudes of various 'phenomena' and constants to about 1 significant figure. For example, the separation of atoms in a metal is about 2.5 Å (1 Ångström=1×10^{-10}m), and an atom with room temperature thermal energy takes about 1ps to travel this distance. The mean free path of molecules in air at room temperature and pressure is 70nm etc etc.

29

Some definitions

- We distinguish between

    Homogenous systems (e.g. coffee + sugar) with a single phase.

    In-homogenous systems (e.g. water + ice, which contains two different phases)

- We distinguish between 2 types of thermodynamic variables:

    'Extensive' variables are proportional to how much of a particular phase you have – if you double the system size (by adding an identical amount of 'identical system stuff') the value of an extensive variable doubles. *e.g.* volume, mass, internal energy.

    'Intensive' variables are those that are not proportional to the systems 'size' such as temperature and pressure.

Note: any extensive variable can be turned into an intensive one by dividing it by another extensive variable – *e.g.* the number of moles of material present, *e.g.* molar volume: $\bar{V} = V/n$

30

1.2 State variables and the laws of thermodynamics

- So far we have been considering the ramifications of what one might consider to be the **fundamental trick** (approximation) of thermodynamics:

  'A state composed of many particles which is in internal flux and can establish some sort of internal equilibrium may be characterised by state variables'.

- There are 4 established laws (labelled conveniently 0 to 3 – the zeroth law was an afterthought) and their first function is to establish some non-obvious state variables:

  0th law establishes temperature

  1st law establishes energy

  2nd law establishes entropy as a differential

  3rd law establishes an origin, a zero, for entropy

The laws of thermodynamics: the rules

- **State variables alone are useless,** one needs a way of relating them, and **there are four basic notions** which together prove **remarkably powerful**:

I Conservation of particles: 'too obvious' for a law, but it is a vital rule when it applies. (This is violated by things like photons which can be created and annihilated at will, but their creation is part of energy transfer and as such it is not an independent constraint on the system.)

II Conservation of energy – the first law: $dU = đQ + đW$, of limited use as it stands because the derivatives of Q and W are path dependent (*i.e.* not dependent only on changes to the state of the system, but also on how you move from one state to another) – but with our new state variables we can rewrite it as $dU = TdS − pdV$ and then 'do physics' by generating links between state variables just using algebra from this 'master equation'.

III A key corollary of **I**, **II** and the valid use of state variables is 'the fundamental principle' of thermodynamics that '*The state variables of a system in internal flux are defined by specifying its volume, contents and energy and any constraints on the internal fluctuations.*'

IV But not everything is 'allowed' ('disallowed'=overwhelmingly unlikely)**: the second law** basically says that *for multi-particle systems there are irreversible processes*: Heat flows from hot to cold, a gas expands into a vacuum – and even if you try and push back with a pump or a heat pump, then globally something else will have changed irreversibly. This concept can be quantified by the state function, '***entropy***', which rises for an irreversible process and is derived from the second law.

The laws of thermodynamics are (sort of) empirical laws

- **Historically they originated as experimental/empirical laws** – Count Rumford bored cannons with a blunt tool and showed the production of heat was limited only by how long and hard you drilled and not by the amount of metal removed, and Joule made meticulous measurements of warming water by mechanical work. **The second law and the concept of entropy was derived from a 'thought experiment'** - a consideration by Carnot of his idealised 'reversible' heat engine, coupled with Carnot's realisation that heat had to flow from hot to cold in order for work to be produced.

- The real 'proof' of the laws, however, comes from statistical considerations of quantum mechanical states, (and hence classical mechanics states).

- It could be argued that the greatest triumph (law?) of early thermodynamics is its contribution to the realisation that matter is made of particles - the rest follows from this + classical and/or quantum mechanics.

- Thermodynamics also gives very clear proof of the failure of classical mechanics – all you have to do is measure a heat capacity…

1.3 Zeroth law of thermodynamics

- Consider two isolated systems:
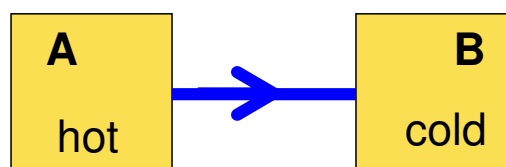
    When A and B are brought in thermal contact (*i.e.* made so heat can flow between them), heat will flow until it stops (!)

- For a particular pair of systems in thermal contact, we define the one from which heat flows as 'hot', and the one to which heat flows as 'cold'.

- If two systems are in thermal contact and no heat flows between them then these systems are defined to be in **thermal equilibrium.**

- If in addition particles can flow (e.g. through a porous membrane), and/or 'volume' can 'flow' (*i.e.* if there have a moveable wall between them) – and this flow also stops we would say the systems are in thermodynamic equilibrium.

Zeroth Law of Thermodynamics

- Now consider three systems: **A** and **B** and **C**.
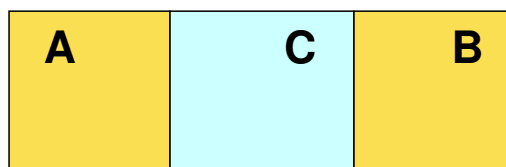
- 0th law:

> If system A is in thermal equilibrium with system C, and if system C is separately in thermal equilibrium with system B, then system A and B will also be in thermal equilibrium.

- The 0th law is empirical – *i.e.* based on observation.

- Therefore **there must be something about a system that is due to the state it is in which will determine whether heat flows from it to another** – and if we find a way of quantifying this, we will have a state variable which we call temperature. *i.e.* the 0th law proves that **temperature is a state variable**.

- If two systems are in thermal equilibrium then they have the same temperature. Notice that the 0th law **DOES NOT SAY ANYTHING ABOUT THE DIRECTION OF HEAT FLOW when they are not in thermal equilibrium** (that is the realm of the 2nd law).

How to measure temperature

- We need some quantity that changes as you heat/cool the material if we are to measure temperature,

    e.g. the volume change in mercury, resistivity in metals, or color change in liquid crystals, …

- But we also **need reference or fixed points** in order establish a temperature scale– melting/boiling points of pure water at atmospheric pressure are possible ones (if you neglect the fact that these temperatures are pressure dependent).

- The 'quantity that varies with temperature' is then used to interpolate between the fixed points

- Since Galileo's time many different reference systems have been developed…
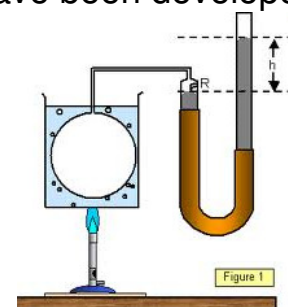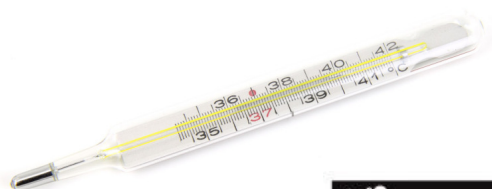
🔴 And then we also need to assign values to these reference points, and define a functional form to connect these reference points (e.g. Celsius, Farenheit, Rømer, Reumir, …)
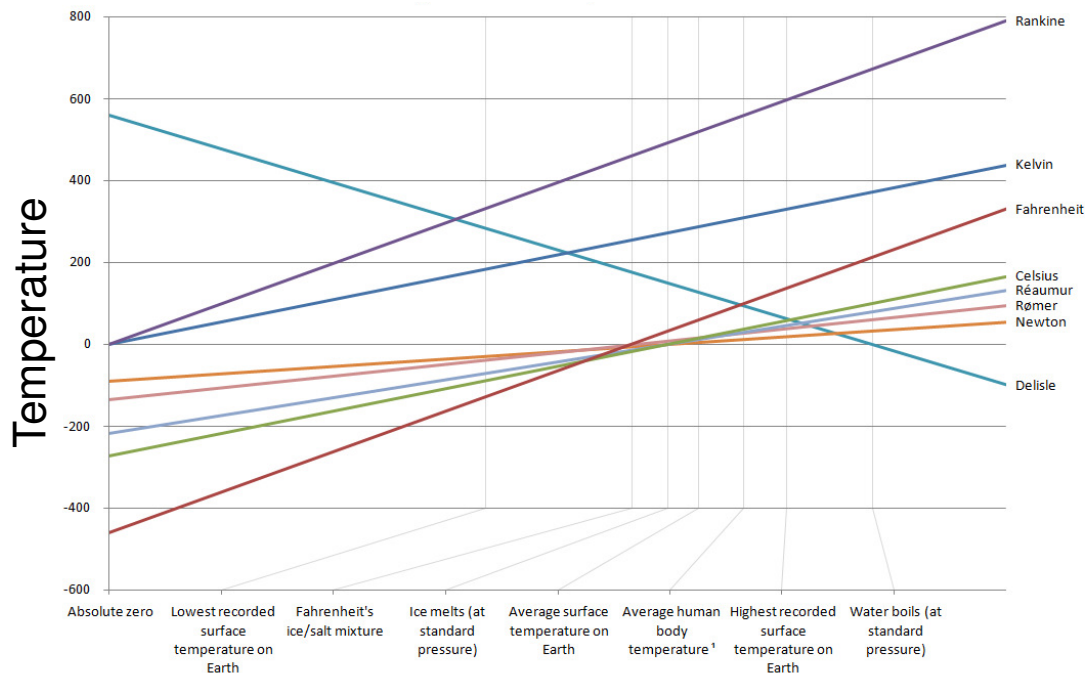
http://en.wikipedia.org/wiki/Conversion_of_units_of_temperature

37

Temperature scales: ideal gas temperature (I)

🔴 A system that gives us a well defined temperature scale and the absolute zero temperature is the **ideal gas thermometer**.

🔴 It is based on **Boyle's law**. (1662: first law written in mathematical form):

$$\lim_{p \to 0}(pV) = \text{constant} = f(T)$$

and **Charles' law** (1780, unpublished work), as formulated by Dalton (October 1801 and confirmed by Gay-Lussac in January 1802) who showed that for all 'gases and vapours of liquids' that he measured, the fractional change in volume (at constant pressure) between two fixed temperature points (e.g. mpt and bpt of water) was the same, *i.e.* the ratio:

$$\frac{V_{100°C} - V_{0°C}}{V_{0°C}}$$

is the same for all gasses provided the pressure is 'low' and one is not near the liquefaction temperature of the gas

38

Temperature scales: ideal gas temperature (II)

- Combing Boyle's and Charles' laws, and using limiting values of pV as the pressure tends to zero, **we can set up a well defined, material independent, temperature scale, which defines a change in temperature as being proportional to change in the limiting value of pV**.

  The Celsius temperature (which takes the boiling (100°C) and melting (0°C) point of water as reference points) would then be:

$$T_{Celsius} = 100 \frac{(pV)_T - (pV)_{mpt}}{(pV)_{bpt} - (pV)_{mpt}}$$

Ideal gas temperature scale: Absolute zero

- Since all gasses obey Charles and Boyles law, then extrapolating graphs of the low pressure limiting value of pV one finds they will all reach $f(T)=pV=0$ at the same temperature -273.15°C – so one could use this point as a reference point – giving the 'absolute temperature' scale:

Use concept of absolute zero for a 'fixed point'

$f(T)$

Gas B

Gas A

- 273.15   0   100 T [°C]
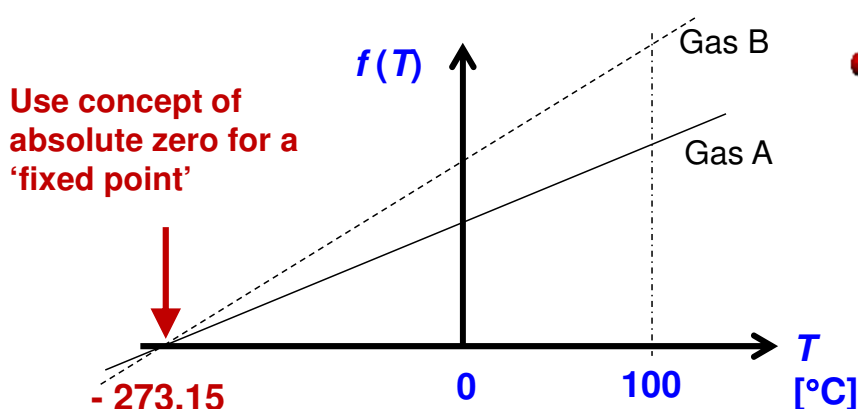
- Absolute temperature is then:

$$T(K) = T(°C) + 273.15$$

- Note: this DOES NOT mean that 0K is the lowest temperature – it merely defines a very useful '0K' reference point. All gases are liquefied before this point anyway – one has to extrapolate the graphs.

- The fact that one cannot cool a system below 0K – *i.e.* that 0K is really is an **absolute** zero, derives from the 3rd law (all entropies go to same value – taken as zero – at 0K).

Triple point of water/Absolute Temperature Scale

● Experimentally precise melting and boiling points of water are not easy to achieve – the melting and boiling of water depend on pressure, so the ambient pressure must be precisely 1 atmosphere (defined as 101325Pa).

● **Ice, water and water vapour only co-exist at one temperature T_{tr} = 0.01ºC and pressure** (point A on phase diagram)

● Experimentally the triple point is relatively easy to achieve – simply pump water vapour out of a vessel containing pure water. Any air above the water is pumped away with the water vapour, air dissolved is stripped out as the water boils under the reduced pressure, and the latent heat lost means some of the water freezes..

Water Phase diagram

● So if you keep 1K and 1ºC as being the same interval then T_{tr} = **273.16K** and:

$$T_{Kelvin} = 273.16 \frac{(pV)_T}{(pV)_{triple\ pt}}$$

41
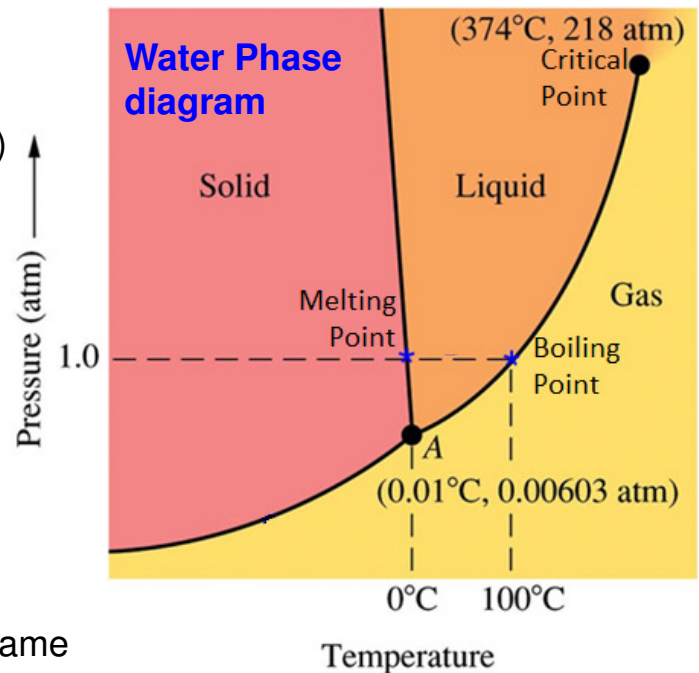
1.4 Ideal gas equation of state (I)

● Recall: **a change in temperature was defined as being proportional to the change in the product pV for a gas at low pressures**, provided the gas was well away from its liquification point. The combination of Charles' and Boyle's laws meant this gave **a material independent definition.**

● From the way we chose to define T, it follows that a graph of the limiting value of pV against T is a straight line, with the lines for all gases and all quantities of gases crossing the T axis at the same point and this point was chosen to be the zero of a scale called the absolute temperature scale.

● **Thus, for any gas**, at temperatures well away from the liquefaction point, **the limiting value of pV at low pressures is proportional to T,** and given V is an extensive quantity (depends on how much gas is there) and p and intensive, (does not), then Charles' and Boyles laws combined with our definition of absolute temperature give:

$$pV = cnT$$

where n is the amount of gas (number of moles) and we would expect c to be a material dependent constant.

42

Ideal gas equation of state (II): Avogadro's law

- In 1811 Avogadro hypothesized that equal volumes of gas at the same pressure and temperature contained equal numbers of molecules, which turned out to be true, as for Boyle's and Charles' laws, for low pressures and for gasses well away from their liquefaction point.

- This means all gases at low pressures have the same value for 'c', which is therefore know as the ideal gas constant, *R,* and we have the ideal gas equation of state:

$$pV = nRT$$

  (An '**equation of state**' links state variables for a particular material)

- This can also be written in terms of the number of molecules in a gas, *N*, and Boltzmann's constant k_B.

$$pV = Nk_BT$$

- The ideal gas equation is an experimental/empirical law (not least because it is used to define T) that relates state variables to each other and is referred to as an **equation of state**.

$pV = Nk_BT$: Why are there 3 independent variables?

- Rearranging the ideal gas law as $\qquad p = R\dfrac{nT}{V}$

  makes it clear that there are 3 independent variables – but why 3?

- *c.f.* 'fundamental principle of thermodynamics': if you **(1) set up a box of a certain size (2) put a certain numbers of particles of different types in it and (3) put in a certain amount of energy** then if it is in a state of internal flux after a while it will establish some sort of equilibrium state which can be uniquely characterised on the macroscopic scale by state variables. *i.e.* **if particles are conserved you need to specify three things (contents, V and energy).**

- In the ideal gas equation (1) the size of the box, *V*, and (2) the contents of the box (*i.e.* no of moles of particles, *n*) appear explicitly in the equation. For an ideal gas there is no interactions between particles so the internal energy per particle does not depend on the particle separation and hence volume (Joule's Law-see later) – hence the energy per particle is a function of T only, and T in the ideal gas equation becomes a proxy for the energy.

- The number of photons in a system is not, however, conserved, and is related to the energy, and we shall see later that the 'equation of state' for a box filled with photons has a different number of independent variables.

e.g. $$pV = nRT$$

● So, an **equation of state** is an equation that relates state variables *i.e.* it defines one state variable in term of others. *e.g.* the ideal gas equation can be written to give **p** as a function of **n**, **V** and **T**, *i.e.* we know $p(n, V, T)$.

● However $p(n, V, T)$ does not tell us everything there is to know about a system – for example it does not tell us the internal energy. An ideal monatomic gas stores energy only in the translational motion of the atoms, but a diatomic gas can store energy in the rotations/vibrations of the molecule – but they both obey the same equation of state at low pressures.

● As we will see later there are some functions, '***thermodynamic potentials***', (**U(S,V)**, **H(S,p)**, **G(T,p)**, **F(T,V)**) from which 'all relevant thermodynamic quantities' of a system (= ones in the 'master equation') can be deduced, provided you express the potentials in their 'natural variables'.

● Classical thermodynamics gives us a standard set of relationships between thermodynamic variables, but to use these you also need a system dependent equation of state, which ideally would give one of the thermodynamic potentials as a function of its natural variables: in practice these are measured and published as tables from which one can interpolate.

Internal energy of ideal gases and temperature (I)

● **Classical thermodynamics cannot give you the internal energy** – you need to measure, for example, a heat capacity, so we will have to use some simple statistical thermodynamics to derive the internal energy of a monatomic ideal gas and see how it relates to the temperature.

● Consider **N** gas atoms, mass **m**, in a box of volume V moving with speeds u_x towards one of the walls and velocity (u_y, u_z) parallel to a piece of wall of area **A** – and consider an elastic collision with the wall.
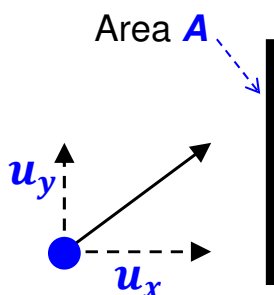
Impulse when atom hits wall = $2mu_x$

Average force on wall = average impulse x collision rate

Area **A**

u_y

u_x

We have N/V atoms per unit volume, of which half will be moving towards the wall. In 1 second atoms a distance u_x away from the wall that are moving towards the wall will hit it, so the no of collisions per second is half of the atoms in a volume Au_x and:

Collision rate $= \frac{1}{2} Au_x N/V$

Internal energy of ideal gases and temperature (II)

Area **A**

u_y

u_x
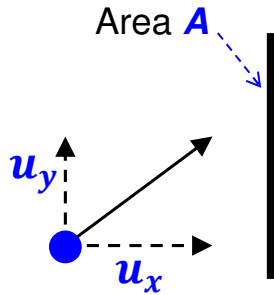
Average force on wall $= mu_x^2 A \dfrac{N}{V}$

Pressure on wall, $p = mu_x^2 \dfrac{N}{V}$

But we need an average value: $p = m\overline{u_x^2} \dfrac{N}{V}$

Since $u_x^2 + u_y^2 + u_z^2 = u^2$, on average: $\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} = \dfrac{1}{3}\overline{u^2}$

So we have $pV = \dfrac{1}{3}Nm\overline{u^2} = nRT = Nk_BT$

(*n* is the number of moles of gas and $k_B = R/N_{\text{Avogadro}}$ is the Boltzmann constant)

For a monatomic gas, the internal energy is stored as translational kinetic energy, so the internal energy is: $U = \dfrac{1}{2}Nm\overline{u^2} = \dfrac{3}{2}nRT = \dfrac{3}{2}Nk_BT$

The mean translational KE per atom/molecule is: $\dfrac{1}{2}m\overline{u^2} = \dfrac{3}{2}k_BT$ *i.e.* **the KE is proportional to temperature as defined by the ideal gas thermometer**.

For molecular gases, energy can be stored in rotations and vibrations as well so U is higher, and since these modes are only excited at elevated temperatures (a QM effect) , the heat capacities will be temperature dependent. 47

1.5 First law of thermodynamics: the concept of energy

- Concept of energy enters physics as the 'capacity to do work', either by virtue of a body's position (P.E.) or its motion (K.E).

- A fundamental result is the expression for kinetic energy – derived by integrating Newton's second law (an empirical, vector law) with respect to space.

$$\mathbf{F} = m\mathbf{a} = m\frac{d\mathbf{v}}{dt}$$

Drop in P. E. = work done = $\displaystyle\int \mathbf{F}.\,d\mathbf{x} = m\int_{\mathbf{v_1}}^{\mathbf{v_2}} \frac{d\mathbf{v}}{dt}.\,d\mathbf{x} = m\int_{\mathbf{v_1}}^{\mathbf{v_2}} d\mathbf{v}.\frac{d\mathbf{x}}{dt}$

$= m\int_{\mathbf{v_1}}^{\mathbf{v_2}} \mathbf{v}.\,d\mathbf{v} = \dfrac{1}{2}mv^2 - \dfrac{1}{2}mv^2 =$ **gain in K.E.**

- But mechanical (K.E. + P.E.) is lost from any real system.

- Joule (1843) and others realised that this 'lost' mechanical energy appears as heat – and formulated the first law based on this, which may be stated as:

1st law: Energy is conserved if heat is taken into account.

47

Consequences of the first law : U as a state variable

- The first law shows that energy is stored as heat in a body - you put a certain amount of energy as heat into a body, and then if you return the body to its initial state, you can recover the energy you put in

- The fact that energy is conserved means the amount of energy you can get out of a body is independent of how you do it *i.e.* **we can define a state variable (U) that is the energy stored in the body.**

- If you don't change the amount of material in a body there are two ways you can change the internal energy of a body – by doing work on it, or by transferring heat to it hence :

$$\mathrm{d}U = đQ + đW$$

Heat transferred TO body   **Work done ON body**

State variables v. path dependent variables

- State variables only depend on the current state of the system and are not affected by how the system arrived at this state.

- Other variables like **mechanical work done** or **heat transfer** as a system moves from one state to another **depend on the path taken between states** and so are not changes in state variables, and are denoted with a 'crossed d' ($đQ$) in the infinitesimal.

- Since state variables only depend on the current state of the system and are not affected by how the system arrived at this state, we note that state variables have no memory – any trace of their history has been lost in the thermalisation process – *i.e.* the processes whereby local equilibrium is established.

- It is an **empirical** statement.

- Based on Joule's experiments (ca. 1840) that showed the equivalence of work and heat.

- (Superseded older "caloric" theory whereby heat was regarded as a conserved fluid.)

J.P. Joule

Joule's paddle wheel apparatus

51

http://www.rmutphysics.com/charud/virtualexperiment/labphysics2/caloriemeter/joule.htm

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Comments on the first law (II): $dU = đQ + đW$

- It was quickly understood (by some – not Joule!, and in general not the physicists ☹) that **heat is in fact mechanical energy (P.E. and K.E.) stored in the internal motions/positions of the constituent particles in matter**, and indeed the first law gave a lot of support to the theory that matter was composed of atoms. It then becomes clear that **conservation of energy was actually nothing more than the integral of force and Newton 2 with respect to space**. Interestingly **conservation of momentum enters physics as the integral of force and Newton 3 with respect to time**.

- **U** is a state variable, so for any change, d**U** is an exact derivative, but **the work done, đq, and heat transferred, đw, depend on the path taken, so are inexact derivatives** (designated with a crossed d - đ) and are not derivatives of a state variable

- The first law would be much more useful if written in purely in terms of state variables – but one needs to first 'discover' entropy in order to do this. **Once transformed a state variable equation it becomes the 'master equation' of thermodynamics** - one equation that encompasses all the laws of thermodynamics, and essentially from which the rest of classical thermodynamics is derived.

52

An example of work : Mechanical work on a gas
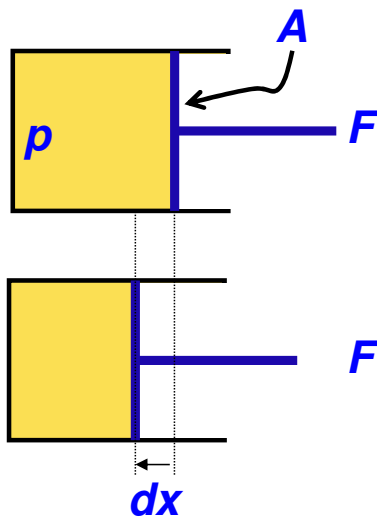
- Force on piston: **F = pA**

- Move piston in by **dx** – and it does work on the gas:

$$Fdx = pAdx$$

- Now: $Adx = dV$

$$\Rightarrow \quad \boxed{đw = -pdV}$$

- Note negative sign: positive work done is done **on** the gas when the gas is compressed (d*V* negative).

- **đ** indicates that this is not an exact differential (because **w** is not a function of state and **đw** is path dependent).

- NOTE: equating $đw = -pdV$ is only meaningful if the pressure on the piston is the same as in the gas: it requires the pressure to be in equilibrium - *i.e.* we have restricted the of motion of piston (= specified a path) to being slow enough for this to be true.

53

Other forms of work

- Note: **đ*W* = - *p*d*V*** applies to any compressible system under hydrostatic pressure.

- **Work is done on a system whenever it responds ('moves') to the change in some external constraint ('force')**

- Analogue expressions for other forms of work:

Extension of a wire in tension	$đW = Fdx$
Increase in area, **A**, with surface tension γ	$đW = \gamma dA$
Electrostatic energy in a dielectric	$đW = -PdE$
Electrochemical work	$đW = -VdQ$

conjugate pairs of intensive and extensive variables introduced earlier

- '*pV*' work in thermodynamics is taken, via **đ*W* = - *p*d*V***, as a representative of any work term – so if you have another sort of work, translate the formulae from *p* and *V* to the variables related to the work that is actually being done.

54

1.6 Applications : Heat Capacities

- **Heat Capacity** = heat needed to cause unit increase in temperature in a system.

- Specific heat (capacity) is often used (heat capacity per unit mass, SI units **J K⁻¹ kg⁻¹**) or molar heat capacity (heat capacity per mole, units **J K⁻¹ mol⁻¹**). Symbol: c_p or c_v at constant pressure or volume.
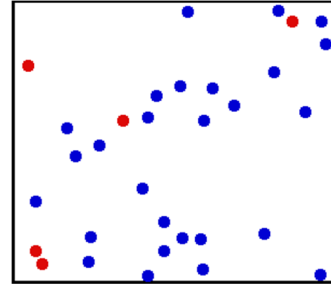
$$dU = đQ - pdV \implies đQ = dU + pdV$$

- At constant V, all heat will go into increasing the internal energy.

- At constant p extra heat is must be supplied to give the energy needed to perform work on surroundings. As the gas expands it has to push back its surroundings – and in doing so does work on them.

Heat Capacity @ Constant Volume

- Heat capacity at constant volume relates directly to changes in internal energy.

    Since $dU = đQ + đW$

    If $đW = pdV = 0$ then $dU = đQ$

    and $C_v = \left(\dfrac{dQ}{dT}\right)_v = \left(\dfrac{\partial U}{\partial T}\right)_v$

    (Note $đQ$ is not an exact derivative – i.e. Q is not function of state that one can take a partial derivative of, so 'straight' 'd's are used in the path dependent derivative expression for C_v in terms of dQ/dT)

- Monoatomic ideal gas: $U = \dfrac{3}{2}nRT \Rightarrow C_{v,m} = \dfrac{3}{2}R$

    ($C_{v,m}$ is heat capacity at constant volume per mole.)

- Diatomic ideal gas (typically 2 rotations excited, see later):

$$U = \dfrac{5}{2}nRT \Rightarrow C_{v,m} = \dfrac{5}{2}R$$

(we will see later that stat. thermo. gives principle of equipartition of energy: ½$k_B T$ per 'quadratic' (e.g. ½ mv²) degree of freedom for classical systems)

Heat Capacity @ Constant Pressure

● By definition the heat capacity at constant pressure is:
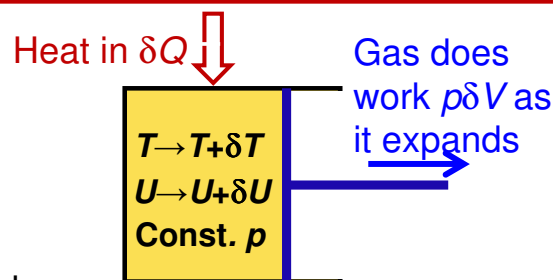
$$C_p = \left(\frac{dQ}{dT}\right)_p$$

Heat in δQ

$T \rightarrow T+\delta T$
$U \rightarrow U+\delta U$
Const. p

Gas does work $p\delta V$ as it expands

● But how does C_p relate to C_v? Start with the first law:

$$đQ = dU - đW = dU + pdV$$

Change in internal energy

Energy required to push back surroundings as system expands

● We need an expression for dU. We already have $C_v = \left(\frac{\partial U}{\partial T}\right)_V$, which suggests we should consider U as a function of T and V – which is clearly a reasonable proposition.

(Note $U(T,V)$ is not expressed in its 'natural variables' and as such we would not be able to get complete information from it (we cannot get p – see the question sheet), but it suffices for the current problem.)

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

C_v

57

Heat Capacity @ Constant Pressure

● Substituting expression for dU into $đQ = dU + pdV$ gives:

$$đQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + pdV$$

● Then create a partial derivative from the infinitesimal $đQ$ by dividing by dT and specifying a path with constant p

(Technically what you actually do is back off from the limit and convert $đQ$ *etc* back to δQ *etc*, convert the = to ≈, then divide by δT, specify a path of constant p, then go back to the limit $\delta Q \rightarrow 0$ and create the partial derivatives, at which point the ≈ becomes = again.)

Extra heat needed if the internal energy changes with volume

Extra heat needed to give energy converted to work as the gas expands and pushes back its surroundings

$$C_p = \left(\frac{dQ}{dT}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right)_p + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$$

C_v 1

$$= C_v + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

You need to learn to 'read' the equations – interpreting what each term 'means'

58

Heat Capacities (continued)

- In general
$$C_p = C_v + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

- In the specific case of an ideal gas where there are no intermolecular forces there is no potential energy contribution to the internal energy which is therefore independent of volume, we have:

$$U = U(N, T) \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_T = 0$$

Also, for 1 mole $\quad pV = RT$

$\Rightarrow$ for 1 mole $\quad \left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p} \quad \Rightarrow \boxed{C_{p,m} = C_{v,m} + R}$

(Heat capacity per mole)

Does the maths have to be that bad?

- Thermodynamics involves a lot of equations with partial derivatives, and one has to work out how cope. There are some key points:

  - You have got to work out how to handle this sort of problem.

  - Don't make it more complicated than it needs to be.

  - Keep reminding yourself where it is going – *i.e.* 'what's the plan'.

  - Write down clearly what you know/are given, and what you don't know / what you are trying to find out – it helps to see where you (might) be going.

  - Learn to ask yourself questions – and learn what questions to ask. 'Have I seen anything similar before? – if so what was it and how can I adapt it', 'Do I know any equation that has these symbols in it?'. 'Why don't I like this problem? Why can I not do it? What is the sticking point? What would I like it to look like? How can I change/rewrite the problem so if does not look so bad?'

  - Problem solving is a very active activity! Don't just stare at it, do something.

  - You need to know what you know – codify your knowledge, write and learn single page summaries of subjects.

So, more compactly: Ideal gas C_p and C_v

● For an ideal gas, use asap the fact that for an ideal gas the internal energy is stored only as KE - *i.e.* it is independent of volume:

Consider $U(T, V)$,   = 0

$$đQ = dU + pdV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + pdV$$

$$= C_v dT + pdV$$

$$C_{p,m} = \left(\frac{dQ}{dT}\right)_p = C_{v,m}\left(\frac{\partial T}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p = C_{v,m} + R$$

1.7 Applications: Ideal Gas Expansions

● Expansion is a ***process***, not a ***state***, so in thermodynamics you need to specify how it is done – what 'path'.

● E.g. ***Isothermal expansion***: ***T*** = const. $\Rightarrow$ ***pV*** = const.

● Consider gas expanded slowly against a piston – the gas does work on the piston, so would cool, but heat is allowed to flow in from the surroundings to keep the gas at constant temperature

Gas does work $p\delta V$ as it expands
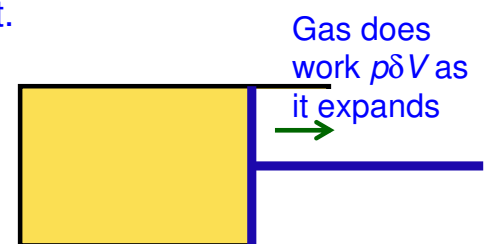
● For an ideal gas, U is purely kinetic energy so is independent of volume - so $U = U(N, T)$ $\Rightarrow$

$$\Delta U = 0 \quad \Rightarrow \quad đQ = dU - đW = pdV = \frac{RT}{V}dV$$

$$\Rightarrow \quad \Delta Q = \int_{V_0}^{V_1} pdV = \int_{V_0}^{V_1} \frac{RT}{V}dV = RT\ln\left(\frac{V_1}{V_0}\right)$$

i.e. need to put heat in when the gas expands to provide the energy that is converted to the work required to push back the surroundings (or the piston if its done in a cylinder) and to keep ***U*** constant.

Ideal Gas Expansions

- **Isotherms** are hyperbolae on a **p–V** diagram.

- Sometimes called an "Indicator diagram" – any state of a fixed contents system is represented by a point in the **p – V** plane.

$$P = \frac{nRT}{V}$$

Isotherms are hyperbolas
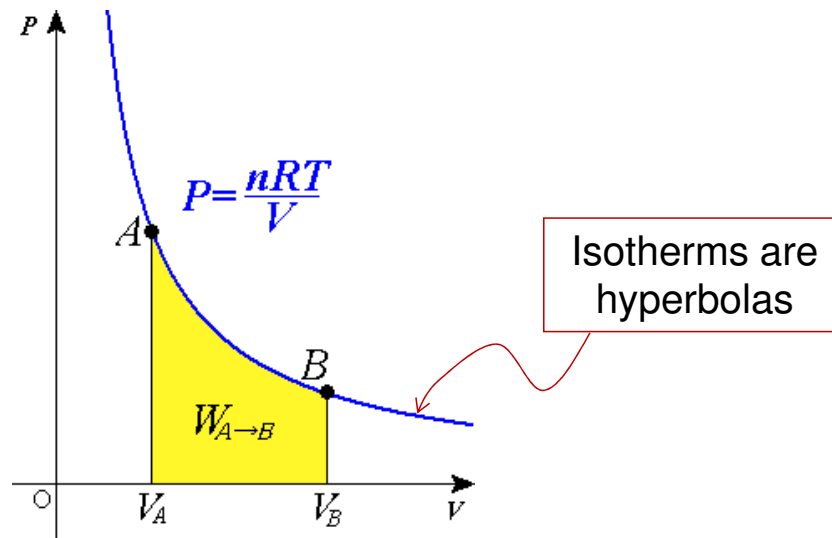
- During an isothermal expansion of an ideal gas, the internal energy stays the same, so heat must be supplied equal to the work done – which is equal to the area (shaded yellow) under a p v. V graph ($W_{A \rightarrow B}$)

Reversibility

- A subtle but important concept.

- A process is **reversible** if it proceeds by infinitesimal steps from one state of equilibrium to another. The process can be reversed by means of an infinitesimal change in some property of the system.

- Example: heat transfer between two objects '**A**' and '**B**'

  If both **A** and **B** are at the same temperature no heat flows.

  If T_A increases infinitesimally, heat will flow from **A** to **B** . This change can be reversed by decreasing T_A infinitesimally. Both objects can be returned to their original state.

  By contrast if T_A is higher (hot) than T_B (cold), heat flows from **A** to **B** , but there is no infinitesimal changes to either T_A or T_B that can reverse this. Heat flow from hot to cold is not a reversible process.

  (If you are worried about the 'infinitesimally small case', we can 'do the job properly' and show that the irreversible problem really does go away in the limit of infinitesimally small temperature changes once we have mastered the concept of entropy)

- The 'isothermal' expansion we considered was reversible: the piston moved slowly enough for heat to flow in and keep the temperature constant.

Reversible Adiabatic Expansion

- 'Adiabatic' so $dQ = 0 \Rightarrow dU = -pdV$

- Ideal gas (using 1 mole):

$$dU = C_V dT = \frac{C_V}{R}(pdV + Vdp) = -pdV$$

Ideal gas: U indep. of V, so $dU = C_v dT$ for any path

(Using: $pV = RT \Rightarrow pdV + Vdp = RdT$)

$$C_V(pdV + Vdp) + pRdV = 0$$

$$C_V Vdp + (C_V + R)pdV = 0$$

$$\Rightarrow \quad C_V Vdp + C_p pdV = 0$$

$$\Rightarrow \quad C_V \frac{dp}{p} + C_p \frac{dV}{V} = 0 \qquad \Rightarrow \quad \boxed{\frac{dp}{p} + \gamma\frac{dV}{V} = 0}$$

With $\gamma = C_p/C_V$

65

Adiabatic Expansion Equations

- Integrating $\dfrac{dp}{p} + \gamma\dfrac{dV}{V} = 0$ we have:

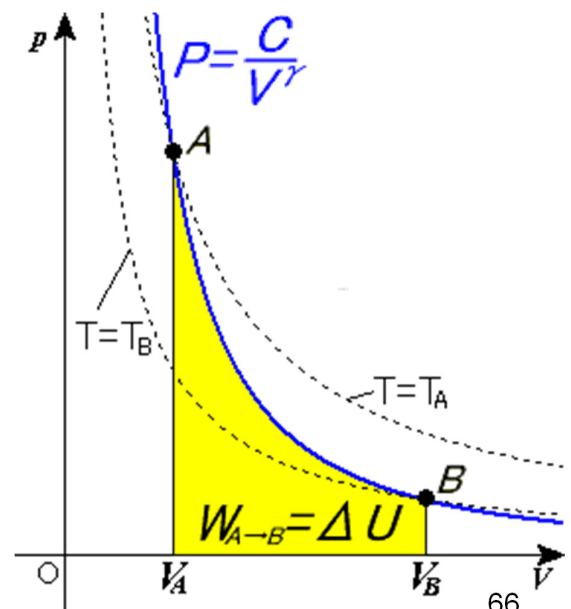$$\ln p + \gamma \ln V = \text{const.} \qquad \Rightarrow \qquad \boxed{pV^\gamma = \text{const.}}$$

- Using $pV = RT$, we can derive two further relations:

$$TV^{\gamma-1} = \text{const.}$$

$$T^\gamma p^{1-\gamma} = \text{const.}$$

- For a **monatomic gas** molar heat capacities are: $C_v=3/2R$, $C_p=5/2R$ so γ=1.67, for a **diatomic** (vibrations not excited) $C_v=5/2R$, $C_p=7/2R$, γ=1.4
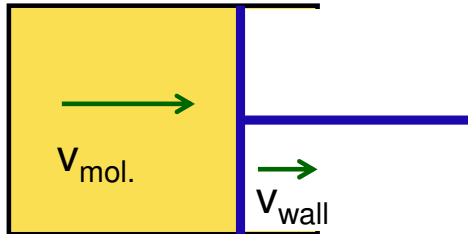

66

Reversible Gas Expansion: how is heat converted to work?

- If a gas molecule hits a surface moving away from it the magnitude of its perpendicular velocity component is always reduced if the collision is elastic.

Before collision with wall
(closing speed= V_{mol}-V_{wall})

After: molecule recoils with reduced speed (in frame of wall the closing speed is reversed)

$V_{mol.}$

V_{wall}

$V_{mol.}$-$2V_{wall}$

V_{wall}
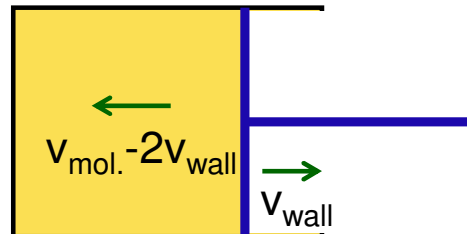
- Each time a molecule hits the moving wall its velocity is, on average, reduced, and the gas cools. For isothermal expansion, heat must flow in from walls to compensate, so the expansion must be very slow for this to happen reversibly (negligible temperature gradients).

- For an ideal gas, where there are no collisions between molecules, the molecule then flies to the other end of the container, bonces back and the hits the moving wall again, and for adiabatic expansion (no heat transfer from walls) it keeps cooling.

Expansion of a real gas: what actually happens?

- The mean free path of molecules in real gases is rather short – in air at room temperature and pressure its 70nm, so **most molecules never get anywhere near the moving wall.**

- **Molecules bounce off their neighbours. If the gas is expanding these are, on average, moving away from the first molecule, and behave on average like a wall moving away**, so the gas cools uniformly throughout its bulk if the expansion is slow enough for the pressure to remain constant throughout the gas, *i.e.* there must be no big changes in velocity on a timescale of the size of the container divided by the speed of sound.

- For a cooling to actually occur, the atom molecule has to hit its neighbours – but if they are receding too fast, the slow ones won't be able to catch them and so will not cool – this in theory limits the speed of expansion if it is to be reversible, but given the short mean free path in air, however fast the expansion, the neighbours will have low mean relative velocities.

- In rapid adiabatic expansion, the gas ends up moving fast as a fluid – *i.e.* some *U* is converted not to work on the piston, but KE of the bulk fluid. When the expansion stops, unless you are very ingenious (*e.g.* in a gas turbine), this KE converts back to U as the fluid slops around in the container. If you then compress the gas slowly back to its original volume it will be warmer than it was at the start – *ie* the 1st expansion was irreversible

Section 1: Summary

- Thermodynamics seeks to describe the behaviour of many particle systems in terms of state variables, which characterise a 'macrostate' of the system.
- There are myriads of microstates (*i.e.* many different actual constituent particle positions and velocities) that correspond to a particular macrostate.
- The laws of thermodynamics are empirical, but can be derived by applying statistics to basic mechanics/ quantum mechanics.
- 0th law: thermal equilibrium (= no heat flow) defined by state of system with temperature as a state variable marker for thermal equilibrium. A useful temperature scale is the Ideal Gas/Absolute one which leads to the ideal gas 'equation of state', $pV = nRT$.
- 1st law: equivalence of heat and mechanical energy => conservation of energy. Useful to consider change in internal energy in terms of heat transfer and work done on system: $dU = đQ + đW$. $đQ$ and $đW$ depend on how you do the change *i.e.* are path dependent.
- There are many ways to do work on a system, but for convenience we standardly consider 'pdV' work – then swap variables for other types of work.
- Heat capacities: for ideal gas $C_p = C_v + R$ per mole. Extra heat needed to supply energy for the work required to push back surroundings as the gas expands if pressure is kept constant and V allowed to change.
- A reversible change is one that proceeds in infinitesimal steps from one equilibrium to another.
- Ideal gas expansions: isothermal ($pV = \text{const}$), needs to be slow to be reversible, but adiabatic (= no heat transfer) can be very fast and still essentially reversible. For reversible adiabatic $pV^\gamma = \text{const}$ (where $\gamma = C_p/C_v$)

Appendix to Ch. 1: Creation of Partial Derivatives

- We want: $C_p = \left(\dfrac{dQ}{dT}\right)_p$ and we have: $đQ = \left(\dfrac{\partial U}{\partial T}\right)_V dT + \left(\dfrac{\partial U}{\partial V}\right)_T dV + pdV$

- So, back off from the infinitesimal limit: $\delta Q \approx \left(\dfrac{\partial U}{\partial T}\right)_V \delta T + \left(\dfrac{\partial U}{\partial V}\right)_T \delta V + p\delta V$

- Divide by δT : $\dfrac{\delta Q}{\delta T} \approx \left(\dfrac{\partial U}{\partial T}\right)_V \dfrac{\delta T}{\delta T} + \left(\dfrac{\partial U}{\partial V}\right)_T \dfrac{\delta V}{\delta T} + p\dfrac{\delta V}{\delta T}$

- Specify a path: $\left(\dfrac{\delta Q}{\delta T}\right)_p \approx \left(\dfrac{\partial U}{\partial T}\right)_V \left(\dfrac{\delta T}{\delta T}\right)_p + \left(\dfrac{\partial U}{\partial V}\right)_T \left(\dfrac{\delta V}{\delta T}\right)_p + p\left(\dfrac{\delta V}{\delta T}\right)_p$

- And take the limit again:

$$C_p = \left(\dfrac{dQ}{dT}\right)_p = \left(\dfrac{\partial U}{\partial T}\right)_V \left(\dfrac{\partial T}{\partial T}\right)_p + \left(\dfrac{\partial U}{\partial V}\right)_T \left(\dfrac{\partial V}{\partial T}\right)_p + p\left(\dfrac{\partial V}{\partial T}\right)_p$$

$C_v \nearrow \qquad \nwarrow 1$

$$= C_v + \left[\left(\dfrac{\partial U}{\partial V}\right)_T + p\right]\left(\dfrac{\partial V}{\partial T}\right)_p$$