Chapter 5
Introduction to Statistical Thermodynamics

Overheads with a **green outlined** title box are not examinable, but there for further explanation.

Chapter 5

What is entropy and how do you do thermodynamics predictively in the light of actual microscopic structure?

5.0 Classical v. statistical Thermodynamics

- Classical thermodynamics is a phenomenological theory: it provides empirical relations between experimentally observable quantities. **However, it does not predict these quantities on the basis of a microscopic model,** and cannot handle random fluctuations of state variables.

- For many applications (design of chemical plant, heat engines, liquefaction of gasses) classical thermodynamics is enough – and indeed the entropy *etc*. of materials is derived from measured p, V, T and heat capacities – more accurate than any value determined from theory/statistical thermodynamics.

- **Statistical Thermodynamics** provides the link between the microscopic description of a system of interacting atoms or molecules and thermodynamic observables such as pressure or temperature. It also gives the 'reason why'.

Story so far: state variables and irreversibility

- We are studying systems made of **large no of particles in internal flux** that allows an **internal equilibrium** to be established and with it a unique 'macro state' which can be characterised by **state variables**. In particular the state of such a system is defined by specifying its volume, contents and total energy.

- A key realisation was that **often we are only interested in the macroscopic properties of a system**, and have little use for the details of the motion of each atom.

- A **key property of such systems is that they show irreversible behaviour** on the macroscopic scale – *i.e.* as determined by their state variables. This arises because the changes we are considering are induced by changes in external constraints. If you reverse these, the motion of the individual particles continues to propagate forwards and so the state variables do not necessarily 'retrace their steps'. If you were to make a decent attempt at reversing the particle trajectories (it is very rare that this is possible), the system does indeed reverse – but this is limited by the accuracy with which you can reverse the particle trajectories.

- **A consideration of an archetypical process** – expansions and compressions in a reversible cyclic heat engine in the context of the second law (for example heat only flows from hot to cold), **lead to the formulation of a state variable, entropy, defined by** $dS = dq_{rev}/T$. For isolated systems in equilibrium, the entropy remains constant, but otherwise it increases and acts as a marker for how far down the 'irreversible road' an isolated system has progressed.

Story so far: the second law

● The second law was originally formulated by observing the properties of heat engines:

Carnot: a heat engine only produces work when heat flows from hot to cold.

Clausius: there is no process whose sole function is the transfer of heat from a colder body to a hotter one (*i.e.* heat flows from hot to cold).

Kelvin (attributed): no process whose sole function is the conversion of heat to work.

● More fundamentally it is a law that applies to any potentially irreversible process of a multiparticle system in internal flux and says:

A general statement of 2nd law: The direction of an irreversible process is a function of the states of the system.

2nd law applied to equilibrium: The nature of equilibrium for systems in a state of internal flux is a function of the states of the system. (This follows from the general statement: the irreversible process stops once equilibrium is achieved.)

2nd law in semi topical language: **Irreversible means irreversible!**   260

Key Questions

● What is the basis for the second law? Why does the direction of an irreversible process depend on the states of the system and not the details of the paths between the states and the rate of passage along these paths?

This can be answered fairly quickly in terms of the more fundamental principle of 'time reversible symmetry': in general you cannot tell which way to run a film of microscopic processes, both obey the laws of physics.

● What actually is entropy, and why does it increase for an irreversible process.

Answering this takes more doing, and has been the subject of enormous and at times heated debate since entropy was first formulated in the 19th century, but it is a core aim of this course to answer this question. Thermodynamics is a very powerful tool and can give indisputable results for complex systems, but very often both classical and statistical thermodynamics are not used when they could be because it is not commonly understood quite why they work, and hence when and how thermodynamics can be used.

Statistical thermodynamics road map

- **Derivation of second law from time reversibility.** Why is equilibrium a function of the states of the system and not how the system moves from on microstate to another?

- **States**: Why are we considering states and not the details of how you get between them? What are these states. Macro and micro states.

- **Equal *a priori* probability of micro states**, and hence most likely macrostate being the one with the most corresponding microstates.

- **Derivation and use the Boltzmann factor**, $\exp(-E/kT)$: gives relative probability of a system being in a microstate of energy E if it is in thermal equilibrium with a reservoir at temperature T.

- In order to help **understand what entropy actually is** we will look for expressions for entropy in stat. thermo. The complication is that the basic definition is for reversible heat transfer – *i.e.* for system in equilibrium contact with reservoir- and thus its energy is fluctuating (slightly).

- **Consider how the expressions for entropy derive from basic statistics**, and hence how the law of increase in entropy follows from statistics.

- **Use this knowledge** to understand the 3rd law, thermal radiation and kinetic theory of gasses in the subsequent sections.

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Non examinable material

- The aim of a science degree course is to teach and train scientists, but this process does not always fall nicely into courses that can be examined in their totality for credit at the end.

- The overall course is separated into subjects that are dealt with at particular times: this course is about the fundamentals of thermodynamics. But some of this material is at a level where it takes time to grasp it and is of complexity beyond what can be expected to be reproduced in a 1B exam. There is, however, no other 'home' for this material in the overall course structure at present and now is the time logically for it to be considered.

- It is fundamentally true that real understanding is gained by iterative study, and as such educationally it is sometimes necessary to outline material 'now' that can only really be understood 'later' – but if you do not start the process now, then later it cannot be grasped – the 'later' becomes the 'now'.

- All this does not fit with the school 'we are doing a course only to get a good exam result' mentality. At a university the educational process has moved on: the idea of the school was to enable you to get to the next stage (and for the school to look good in the league tables/meet government assessment targets), but once you are there the aim is to actually teach you the subject.

- In this course this issue is handled by having slides with 'green' outlined titles, with 'NE' appended on the slide title.

- The departments are continuously seeking to optimise this process and really need thoughtful and constructive feedback from the students.

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5.1 Basis of 2ⁿᵈ law. States v. kinetics: a simple illustration.

- Lets first consider an example of a way in which you can control the rate of passage between macro states. Consider three different sized boxes A,B,C, with a small hole connecting A and B but a large one connecting B and C
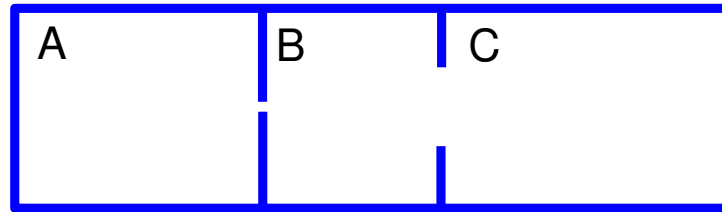
- Although the rate at which the pressure in C equilibrates with that in B is faster than the rate for A, they all end up at the same pressure, and the number of particles in each box is determined by their volume, NOT the rate at which they pass from one box to another.

- This sort of situation is very common, and the second law of thermodynamics (= what can happen *i.e.* direction of net particle flow, the nature of the equilibrium, is a function of state, not kinetics) is correctly cited as justification/proof.

- But why?? What lies behind the second law?? In this case it is obvious that if you increase the hole size to speed up passage from A to B then you will also speed up passage from B to A, but is this generally true? Its clearly what is needed to make the second law work and also must be a consequence of the second law – but why?

- (Of course we are not talking about things that are kinetically forbidden – *i.e.* where its not just a matter of how fast the transfer between macro states is, but where there is no actual path – for example no hole!)

The second law and time reversibility

- The 2ⁿᵈ law says that the direction of an irreversible change (and hence the nature of equilibrium) is a function of the states involved and NOT HOW YOU MOVE BETWEEN STATES, so in order to work out 'the reason why' at the microscopic levels, we only need to consider the states, and do not need to consider how you get from state to state. This is a truly remarkable and very powerful observation: the detailed way a system moves from state to state is usually very complicated, but what the states are is comparatively straightforward, but why is it the case?

- **Essentially the laws of physics show time reversibility** – *i.e.* if you found a piece of cine film which tracked the particles/wavefunctions properly at the fundamental level, you would not be able to decide which direction it should run: both directions obey the laws of nature. This means:

  - For every forward propagating state there is an identical backward propagating one, otherwise you could tell which way to run the film.

  - Any 'static' thing you change (size of aperture, reflectivity of a surface, area of an interface, but not 'moving constraints' which are not covered by time reversibility) must change the rate of the forward and backward propagating states in the same way, otherwise you could tell which way to run the film. Thus, if you change the 'kinetics' (size of hole) you do not change the position of equilibrium, and it must only therefore depend on the states themselves.

  - Since changing the kinetics changes equally the rates of forward and backward propagation, it only changes the rate of an irreversible process, not its direction.

The Second Law and the 'Arrow of Time'

● The 'arrow of time' is often cited as one of the major unsolved problems of physics, and the 2nd law and entropy almost invariably get a mention. Three aspects of this issue are typically raised.

● **Why does time only go forwards**: space and time are linked (relativity) and you can go backwards in space – why not in time?

(Indeed.. but one wonders how you could have any meaningful process if there was not the passage of time? Would the Universe be like a book - but with no prospect of reading it? A hard question – can we imagine a Universe w/o time as we know it?)

● **It is suggested that somehow the 2nd law could somehow be a reason for this**. (Not at all: the 2nd law is dragged in here because its workings are seen as a mystery, whereas we have shown it just follows from the laws of dynamics and the simple statistics used because you realise you don't need to track what happens to each particle in order to understand macroscopic behaviour: averages over such large numbers work.)

● **'Mystery of low entropy at start of universe'**
On the face of it there is no mystery: if you start with all the mass/energy of the Universe in one tiny space at a furiously high temperature with a lot of energy stored in the fields, this will be a low entropy state. Is the real mystery not the low entropy of this state, but the problem of he origin of the Universe itself? and the low entropy is the least of your worries? Of course it's the low entropy of the state, required by the necessity that entropy must increase, that is the killer fact that means citing a bigger universe as the origin does not solve the problem ultimately. Or is part of what's meant is the 'problem' that the Universe is subject to decay: the low entropy spring that drives all macroscopic scale change is gradually unwinding and it is heading for a cold sterile wilderness, or warm uniform soup? [266]

5.2 States: The second law and microstate probability

● The macrostates we observe (*e.g.* total particle number on 2 sides of a partitioned box) comprise a myriad of microstates, *i.e.* actual particle positions/wavefunctions.

● Once an equilibrium macrostate is established (the gas settles down after removing a partition) the second law means that the probability of the system occupying each microstate settles down and is determined by the nature of each microstate only.

● Microstates need not all have the same probability, it would depend on how the states were defined, but it is entirely conceivable that one might be able to define/find microstates which are equally probably, all other things being equal (*e.g.* if you don't have to worry about where to get the energy for the microstate) and indeed this proves possible, but one has to take care how the states are defined for it to be true.

● Irreversible change is triggered by the removal or change in a constraint: we remove a partition or make thermal contact between two objects which makes many more microstates 'accessible' – and the thermal fluctuations between microstates causes the system to 'spread out evenly' amongst the states (the gas fills the box)

● The change is irreversible because the original microstates are only a tiny subset of those available after the constraint is changed and the chance of being found back in them is slim. (see Slide 28).

'Proper' quantum mechanical micro states

● So: **what actually are these micro states**?? The 'correct' description of the world is a quantum mechanical one, and the only real option for states are the **eigenstates of the Hamiltonian** *i.e.* solutions to the time independent Schrödinger equation – of the form $\psi(\mathbf{x}_i) \exp -i\frac{E}{\hbar}t$, where $\{\mathbf{x}_i\}$ are all the coordinates of the system: 'stationary states' that just 'sit there' with measureable properties do not change with time.

● The Hamiltonian is an Hermitian operator so its eigenstates are mutually orthogonal, which means they are independent of each other with and each one does not contain any component of any of the others, and they form a 'complete set' – *i.e.* any state of the system can be fully described in terms of them.

● Thermodynamics however applies to systems in internal flux. Notionally then one starts with a Hamiltonian which does not include interactions between states – so these really do just sit there unchanged, then you add in an extra interaction potential that inter-connects the states and induces transitions between them. *e.g.* you add an molecule-molecule potential energy term that causes scattering between gas molecules, or a energy term that depends on gas molecule position and the amplitude of a vibrational mode of the walls.

Micro states: a classical mechanics approximation

● Many physics problems, however, have the characteristic particle wavelength less than the length scales of interest and can be well described by the much simpler classical mechanics.

● The state of a system **in classical mechanics** is defined by the position and velocity of each constituent particle - but the chance of finding a particle with exactly a particular position and velocity is zero. So notional **'states' are set up which are small boxes of uniform volume everywhere in space and velocity space**: if a particles position and velocity lie within a particular box, it is said to be 'in the state'.

A Classical Thermodynamics Single Particle 'State'
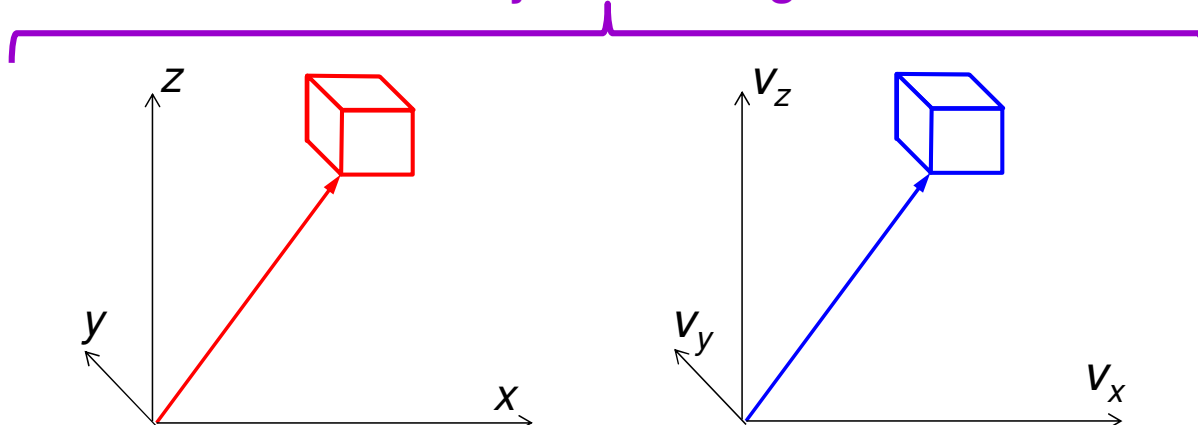
'States' in classical mechanics thermodynamics

- **We are not saying that space is quantised** – it's just a convenient trick that enables us to do statistical thermodynamics within a classical mechanics setting. If one is worried about the effect of the box size, just make it smaller- there comes a point when its size affects nothing in classical mechanics or thermodynamics based on classical mechanics.

- **It is simplest to set boxes so small that there is no multiple occupancy.**

- **All parts of space are 'just as good' as each other** – *i.e.* the chance of being at any one point, all other things being equal, is the same – **but the same applies to velocity space** – if any one point is special in one inertial frame – it will appear somewhere else when seen from another inertial frame.

- It is therefore reasonable to propose that **all these states are equally likely**, if you are not doing anything special, and are not constrained by anything else (*e.g.* where do the particles and energy come from and what is the chance that you will get them).

- This **'principle of equal *a priori* probability' (PEAP)** for classical states only applies to those carefully defined states for which it is true (!) – *e.g.* not for states defined by constant kinetic energy intervals in 1d since $\delta E = mv\delta v$, and states of uniform δv size, will have different δE sizes.

PEAP and quantum states (NE)

- In quantum mechanics, the thermodynamic 'states' are eigenstates of the Hamiltonian .

- If we then take the Hamiltonian of a 'non interacting' system, *e.g.* for a system composed of free non interacting particles enclosed in a box with perfectly reflecting walls (no-wall state interactions), we can find the associated set of system eigenstates. But thermodynamics does not apply: the system is not in a state of flux and once the system is in a state, it stays there.

- If we then add in interactions between the states, amplitude flows form one state to another and we have a system in flux, but we have changed the Hamiltonian. We could find a new set of rather complex eigenstates, made up of mixtures of our 'previously non interacting states'. Or, we describe what happens in terms of flux between the original states => thermodynamics.

- Whilst the interaction between each pair of states may be different, as we argued previously, changing these interactions cannot change the equilibrium occupation of the states. Taking the simplest case, where for some reason we only need to consider eigenstates that are of equal energy, all the eigenstates appear in the mathematical description in the same way, so there is no reason why the equilibrium/average occupation should be different and they will be of equal *a priori* probability. This equal *a priori* probability arises because the states are orthogonal.

- The world is quantum mechanical, so there is no point agonising too much over the requirement for precisely equal energy classical microstates. Perturbation theory (Part II QM) shows that if you switch on an interaction, then states that have an energy close to that of the original one also become involved, within an energy range roughly defined by the matrix elements of the potential that describes the interaction. In other words the eigenstates of the new 'original Hamiltonian + perturbation' Hamiltonian have components of the original states (our thermodynamics microstates) over a range of energies given by the matrix elements of the perturbation.

Quantum v. Classical States: separate spatial/energy states??

- In statistical thermodynamics using classical states, the energy (velocity) and position of the molecules are separate things and the statistics are associated with how you distribute the energy amongst the particles and how you distribute the particles between the spatial states. (Recall both energy and particle number are conserved, essentially positive scalars – so you cannot make them 'cancel out' – you have to put them somewhere)

- In quantum mechanics there is not this separation between energy and spatial nature of the states - an eigenstate has a particular energy and spatial form – so in QM the statistics are simply how the particles are distributed amongst the available energy eigenstates.

What is the most likely macro state??

- Basic Proposal: A system in flux can move between a set of 'accessible microstates', and once it has had time to 'spread out' so as to be able to cover all these microstates (*e.g.* a gas has filled the box once a partition is removed) the chance of finding an isolated system at any particular one of the permitted microstates is the same (*i.e.* the PEAP).

- The chance of the system being in any particular macrostate (*e.g.* gas all on one side of a box) is given, therefore, by the number of microstates that correspond to it, divided by the total number of accessible microstates. The system does not need to have time to 'explore' all the states: all you are interested in is the chance of finding the system in any one of the microstates that correspond to your specified macrostate.

- Whilst we have given reasonable justifications for these proposal, the ultimate justification for these assumptions is that they give accurate predictions of how multiparticle systems work (*i.e.* the standard justification for a scientific laws: they are observed to work). The cornerstone however is the second law which means the relative probability of any state (macro or micro) is determined by the nature of the states, not how the system moves from state to state.

Summary of 'States'

- The fact that thermodynamics can be deduced from the properties of the system states without considering how you get from one state to another is a consequence of the 2nd law. More fundamentally it is a result of the time reversibility of the laws of nature (note 'CP' violation however).

- A 'proper' microstate is defined by quantum mechanics and is a eigenfunction of the time development operator, $\hat{H}$ (= the Schrödinger operator for low velocity systems). If we can approximate the motion of the constituent particles with classical mechanics, then we can use states that are small boxes in a 6 dimensional combined x and v space, best represented as requiring x to be in a small box in x space and v to be within a small box in v space. The boxes are made so small that no measureable property depends on the box size,

- We can show that the principle of equal *a priori* probability of 'correctly defined' microstates is reasonable and turns out to be incredibly 'powerful' (=useful). Ultimately it is justified on the same basis as all other scientific 'laws' – namely that it makes accurate predictions of how the world is observed to behave.

- The fact that all microstates are equally likely means that and the probability that a system at equilibrium is in a certain macrostate is proportional to the number of microstates that correspond to the macrostate. 274

# 5.3 Temperature: The division of energy between two systems

- **Consider an isolated system – fixed energy and fixed no of particles.** There are many, equally likely, microstates of the system with energy and particles arranged in different ways. The system can move from one microstate to another (thermodynamics applies to systems in flux) whilst keeping the same energy and no of particles.

- We can split an isolated system into 2 sub-systems in thermal contact. For a particular 'macrostate' in which the sub-systems have energies E_1 and E_2, the atoms and the way that energy is stored within each sub-system can be rearranged in many ways (Ω_1 and Ω_2 microstates respectively) without changing E_1 and E_2, giving a total number of corresponding microstates of the whole system, $\Omega = \Omega_1 \times \Omega_2$.

$$E_1 \quad E_2$$
$$\Omega_1(E_1) \quad \Omega_2(E_2)$$
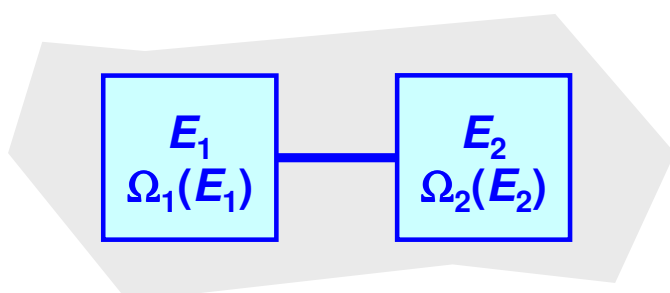
- The most likely 'macrostate' (here = division of energy between E_1 and E_2) is the one with the most corresponding microstates.

A simple example: store energy in fixed 'quanta'.

● Consider a box containing 3 distinct simple harmonic oscillators each with energy $E = \hbar\omega(N + \frac{1}{2})$ that are weakly interacting so quanta can flow from one to another, but the nature of the states is not affected by the interactions
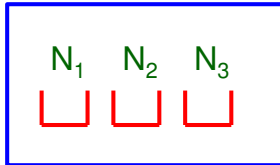
N_1	N_2	N_3
⊔	⊔	⊔

A macrostate of the systems is defined by the total number, N, of quanta in the box (i.e. the total energy in the box), but for each value of N there are a number of ways of arranging the energy (N_1, N_2, N_3) where $N_1 + N_2 + N_3 = N$

N=0 Ω=1 (000)

N=1 Ω=3 (100) (010) (001)

N=2 Ω=6 (200) (020) (002) (110) (101) (011)

N=3 Ω=10 (300) (030) (003) (210) (201) (120) (021) (102) (012) (111)

● As N rises Ω rises rapidly.

● General expression for M boxes and N quanta? How many ways can you line up M-1 walls and N quanta in a row?

No of ways of lining up N+M-1 different objects

QQWQQQQWQWWQQQWQQQWQ

N_1=2 N_2=4 N_3=1 N_4=3 N_5=3 N_6=1
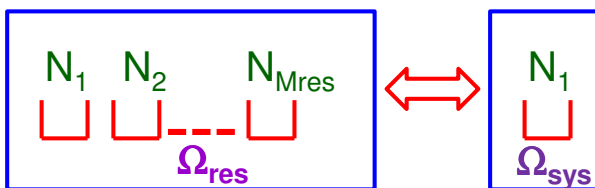
N_4=0

$$\Omega = \frac{(N + M - 1)!}{N!\,(M - 1)!}$$

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Reduce by no of ways identical objects can been arranged

Ω for system/reservoir: non degenerate system

● Consider two boxes – one with a lot (M_{res}) of oscillators – 'a reservoir' and one with a few (M_{sys}) – 'a system' – take case M_{res}=10, M_{sys}=1 and N=11. Ω is the total no of microstates for the whole system -

N_1	N_2	N_{Mres}
⊔	⊔---⊔	

Ω_{res}

N_1
⊔

Ω_{sys}

Using: $\Omega = \dfrac{(N + M - 1)!}{N!\,(M - 1)!}$

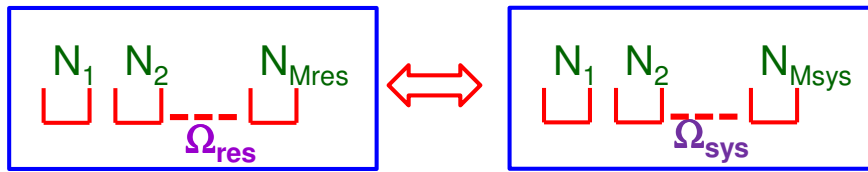| N_{sys}	Ω_{res}	Ω_{sys}	$\Omega = \Omega_{res}\Omega_{sys}$
0	167960	1	167960
1	92378	1	92378
2	48620	1	48620
3	24310	1	24310
4	11440	1	11440
5	5005	1	5005
6	2002	1	2002
7	715	1	715
8	220	1	220
9	55	1	55
10	10	1	10
11	1	1	1

This macrostate has the largest number of microstates of the whole 'system+reservoir' so is the most likely one to be found.

As energy is removed from the reservoir Ω_{res} reduces – so it becomes less likely that this will be seen. This drop-off is what is quantified by the Boltzmann factor

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Ω for system/reservoir: degenerate system

● Take case $M_{res}=10$, $M_{sys}=3$ and $N=13$.

N_{sys}	Ω_{res}	Ω_{sys}	$\Omega=\Omega_{res}\Omega_{sy}$
0	497420	1	497420
1	293930	3	881790
2	167960	6	1007760
3	92378	10	923780
4	48620	15	729300
5	24310	21	510510
6	11440	28	320320
7	5005	36	180180
8	2002	45	90090
9	715	55	39325
10	220	66	14520
11	55	78	4290
12	10	91	910
13	1	105	105

Now the system has 3 oscillators inside so has many ways it can store N_{sys} quanta – and Ω_{sys} increases with N_{sys}

Although the most likely microstate of the system is still the one with all the energy in box 1, as N_{sys} increases Ω_{sys} rises and Ω peaks at the most likely system macrostate, $N_{sys}=2$. The average no of quanta in the system (averaging over all values of N_{sys}) is 3.

Temperature in statistical thermodynamics?

● The most likely macrostate (*i.e.* distribution of internal energy (E_A, E_B) between the two states) is the one with the max value of $\Omega = \Omega_A\Omega_B$ and thus is the condition when $T_A = T_B$. (cf 0th law).

● To look for a condition on E and Ω that can be related to the classical thermodynamics concept of temperature, maximise $\Omega_A\Omega_B$ *w.r.t.* E_A :

$$0 = \frac{d}{dE_A}\left(\Omega_A(E_A)\Omega_B(E - E_A)\right) = \Omega_A'\Omega_B - \Omega_A\Omega_B'$$

$$\Rightarrow \frac{\Omega_A'}{\Omega_A} = \frac{\Omega_B'}{\Omega_B} \quad \Rightarrow \quad \frac{d\ln\Omega_A}{dE_A} = \frac{d\ln\Omega_B}{dE_B}$$

● So – the relation between U (= E here) and Ω that must be the same for two systems in thermal equilibrium, and thus must relate to the classical thermodynamics concept of temperature is:

$$\boxed{\beta = \frac{d\ln\Omega}{dE}}$$

Real systems: a 'continuum' of microstate energies

● $\Omega(E)$ gives the degeneracy of the system when it has energy E, *i.e.* the no of states of identical energy. The previous definition also assumed that the spacing between energy levels in systems A and B was the same (for exact energy transfer).

● In practice we usually have a myriad of finely spaced energy levels, which we can characterise by a 'density of states' $g(E) = \frac{dN}{dE}$ – *i.e.* how 'thick and fast' they come as you vary E, with the number of microstates, δN that have an energy lying between E and $E + \delta E$ being $\delta N = g(E)\delta E$.

● In the real world no two states will have the same energy, but, if only because of the time energy uncertainty principle ($\Delta E\Delta t \geq \frac{\hbar}{2}$) we can accept a range of energies, δ_E, as 'being equal' and say that at an energy E we have $\Omega(E) = g(E)\delta_E$

● Currently the 'age of the Universe' is estimated as 13.8 billion years, which gives us some sort of lower limit in the 'acceptable spread in energy around precise equality' of $\delta_{E,min}$=2.4x10^{-52}J. The entropy of water at 25C is 367J/Kg/K which corresponds to $g(E)$= 10$^{1.16e25}$/J so there are still plenty of states in the range $\delta_{E,min}$.

● These numbers are not astronomical, but 10^{astronomical}. Taking logs can help 'grasp' them, and see that the value of δ_E is normally irrelevant to $\log g(E)\delta_E$:

$$\log_{10}(g(E) * J) = 1.16 \times 10^{25} \qquad \log_{10}\big(g(E)\delta_{E,min}\big) = 1.16 \times 10^{25} - 51.6$$

β for a 'continuum' of microstate energies

● Revisiting the condition for the most likely distribution of energy between two systems, *i.e.* 'maximising $\Omega_A\Omega_B$ w.r.t. E_A :' but using density of states we have:
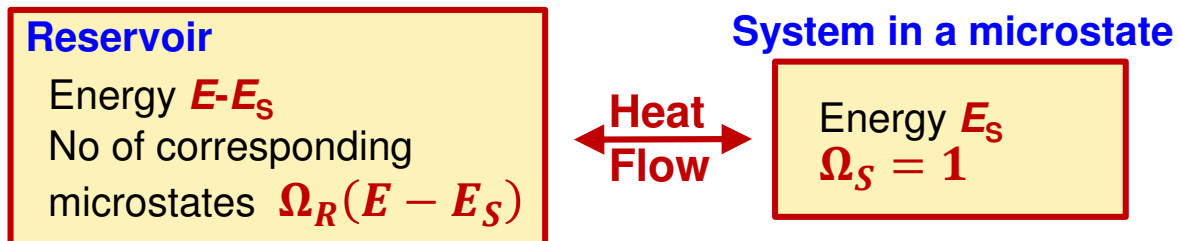
$$0 = \frac{d}{dE_A} \ln\big(\Omega_A(E_A)\Omega_B(E - E_A)\big)$$

$$= \frac{d}{dE_A} \ln \delta_E g_A(E_A) + \frac{d}{dE_A} \ln\delta_E \, g_B(E - E_A)$$

$$\Rightarrow \frac{d\ln g_A}{dE_A} = \frac{d\ln g_B}{dE_B}$$

● We thus have a 'temperature function' in terms of a systems energy density of states:

$$\boxed{\beta = \frac{d\ln g}{dE}}$$

5.4 The Boltzmann Factor: 'Reservoir' + 'System'

● A typical thermodynamics 'thought' experiment is a system in contact with a thermal reservoir (a 'heat bath') of such a high heat capacity that its temperature does not change when you transfer (small) amounts of heat in/out of it. (*In thermodynamics we want to consider equilibrium (requires at least 2 objects) but also change – something in equilibrium can only change if it is connected to something else.*)

Reservoir
Energy E-E_S
No of corresponding
microstates $\Omega_R(E - E_S)$

Heat Flow ←→

System in a microstate
Energy E_S
$\Omega_S = 1$

● To get us going, suppose that we give a relative probability of 1 to a microstate of the system with its lowest energy $E_S=0$ (a 'ground state'), with all the available energy (E) stored in the reservoir. The relative probability that the system will be in a 'excited' microstate of energy E_S is given by:

$$P_r(E_s) = \frac{\Omega_R(E - E_S)}{\Omega_R(E)}$$

(Note: P_r is determined by how Ω_R varies as you take energy out of the reservoir)

Derivation of Boltzmann factor

● The probability of a system having a certain energy will be related to the temperature (of the reservoir), so we need to relate $P_r(E_s)$ to β

$$\beta = \frac{dln\Omega}{dE}$$

● Given that E_s is small compared to the energy in the reservoir, and given we have an expression for β in terms of $\frac{dln\Omega}{dE}$, use a Taylor expansion to consider how $ln\Omega_R$ varies as energy is removed from the reservoir:

$$ln\Omega_R(E_R) = ln\Omega_R(E - E_S) \approx ln\Omega_R(E) - E_S \frac{dln\Omega_R}{dE}$$

$$= ln\Omega_R(E) - E_S\beta$$

Hence: $ln\Omega_R(E - E_S) - ln\Omega_R(E) = -E_S\beta$

● Relative chance of the system being in a microstate with energy E_S:

$$P_r(E_s) = \frac{\Omega_R(E - E_S)}{\Omega_R(E)} = e^{-\beta E_S}$$

(note: for clarity we have written this in terms of Ω, but for a continuum of states we simply write $\Omega(E) = g(E)\delta_E$ where δ_E is the permitted uncertainty in the deference of energy of two states which can be counted as having the same energy)

- Thermodynamics is formulated in terms of a very general notion of a 'reservoir' – quite what is it made up of is unspecified and unimportant, it just needs to be large enough for its temperature not to change when heat is transferred in and out of it.

- However, to get some idea of a typical 'form' of a reservoir $g(E)$ we can consider one in the classical mechanics limit made of an ideal gas, or a 'harmonic solid' – the latter is a good approximation to any solid not too close to its melting point as for small atomic displacements from equilibrium the forces are in general proportional to displacement.

- If there are N atoms in the system, we have 3N velocity coordinates, each giving a contribution of $\frac{1}{2}mv^2$ to the kinetic energy. For simplicity we could rescale these coordinates with the mass of each atom ($q_i = \sqrt{m_i}v_i$) to give a total kinetic energy of $\frac{1}{2}\sum_i q_i^2$. The potential energy stored in each normal mode of vibration varies quadratically with the displacement – so we could also scale these to give a total potential energy similarly of $\frac{1}{2}\sum_i q_i^2$ Thus, if we have a total of n coordinates (3N velocity for an ideal gas, 6N (velocity and displacement) for a harmonic solid), the total energy is simply $E = \frac{1}{2}\sum_{i=1}^{n} q_i^2$ and all the states with a certain energy lie on the surface of a 'n-ball' in n dimensional space radius $q = \text{sqrt}\left(\sum_{i=1}^{n} q_i^2\right)$. 284

- The volume of an 'n-ball' radius q is proportional to q^n so the increase in 'nD' volume with q is $dV \propto q^{n-1}dq$ which means the number, N_s, of classical 'states' (boxes in velocity and displacement space) covered as q increases rises similarly and we have: $$\frac{dN_s}{dq} \propto q^{n-1}$$

- The total energy of the reservoir is: $E = \frac{1}{2}\sum_{i=1}^{n} q_i^2 = \frac{1}{2}q^2$

  So: $\frac{dE}{dq} = q \Rightarrow g(E) = \frac{dN_s}{dE} = \frac{dN_s}{dq}\frac{dq}{dE} \propto q^{n-2} \propto E^{\frac{n}{2}-1}$

- For large n, $g(E) \propto E^{\frac{n}{2}-1}$ rises very rapidly, but taking the log gives:

$$\ln g(E) = \left(\frac{n}{2}-1\right)\ln E + const$$
$$\Rightarrow \ln g(E+\epsilon) \approx \ln g(E) + \left(\frac{n}{2}-1\right)\frac{\epsilon}{E} - \left(\frac{n}{2}-1\right)\frac{\epsilon^2}{2E^2}$$

For a large reservoir, where $E \gg \epsilon$, the first order Taylor expansion is a good approximation, giving the relative probability of a state that takes energy ϵ from the reservoir: $P_r(\epsilon) = e^{-\beta\epsilon}$ where $\beta = \frac{d\ln g(E)}{dE} = \left(\frac{n}{2}-1\right)\frac{1}{E}$

$P_r(\epsilon)$ is anything but linear in ϵ , so Taylor expanding $g(E)$ would not have been successful. The key requirement is that the reservoir is 'big', *i.e.* the temperature (relates to gradient $\frac{d\ln g(E)}{dE}$) does not change with energy transfer, *i.e.* the second and higher derivatives of $\ln g(E)$ can be neglected.   285

Connection between of β and T?

- Temperature in classical thermodynamics was defined initially (and arbitrarily) in terms of ideal gas properties (*i.e.* the ideal gas law: **$pV=nRT$**) and then, equivalently, in terms of the heat transfers to a reversible heat engine operating between two heat reservoirs at two different temperatures $Q_2/Q_1 = \Theta_2/\Theta_1$.

- In order to determine the connection between of β and T, all we need is a temperature dependent property derived using both statistical and classical thermodynamics.

- The kinetic energy of an ideal monoatomic gas (in 3D) is $\frac{3}{2}RT$ per mole. Dividing the gas constant R (8.314J/K/mol) by the Avogado number gives Boltzmann's constant k_B=1.381x10^{-23}J/K and the mean energy per monatomic gas atom of $\frac{3}{2}k_BT$. We will show later that statistical thermodynamics gives this energy as $\frac{3}{2\beta}$, hence:

$$\boxed{\beta = \frac{1}{k_BT}}$$

Unpacking the Boltzmann factor

- Applies to a system in contact with a heat reservoir and gives chance of that the system is in a particular microstate relative to the chance that the system is in a ground microstate.

- It arises because as you transfer heat out of the reservoir, the number of microstates available to the reservoir drops.

- The temperature of a reservoir is defined in terms of the rate at which its number of accessible microstates changes as heat is transferred out of the reservoir – so provided the reservoirs you consider are at the same temperature, they will give the same Boltzmann factor and the Boltzmann factor is independent of the nature of the reservoir.

- **The most likely system microstate is the ground state.**

- In practice one usually is interested in the probability of a particular system macrostate, and one must multiply the chance that the system is in one of the macrostates constituent microstates (which is given by the Boltzmann factor), by the number of microstates in the particular system macrostate.
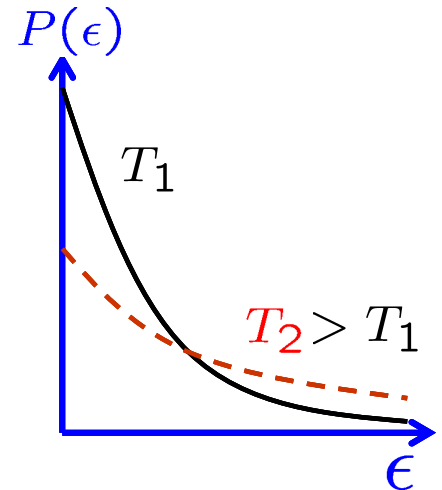
Normalisation of Boltzmann distribution

Now we still need to normalize the Boltzmann distribution:

● If need to sum the unnormalised probability over the individual microstates:

$P(\epsilon)$

$E - \varepsilon$
$\Omega(E - \varepsilon)$
T

reservoir

ε
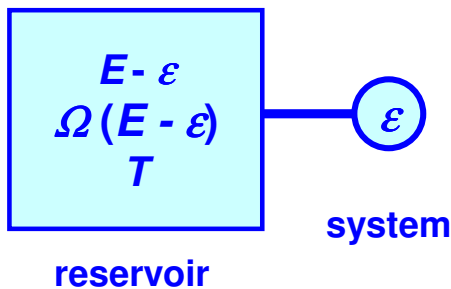
system

$P(\epsilon) \propto e^{-\epsilon/k_B T}$

● If the system is in microstate **r** with energy E_r, then:

$$P(\text{microstate } r) = \frac{e^{-E_r/k_B T}}{\sum_i e^{-E_i/k_B T}}$$

and $Z = \sum_i e^{-E_i/k_B T}$ is called the **partition function.**

('*Zustandsumme*' in German)

● $1/Z$ gives the probability of the system being in the ground state.

Normalisation of Boltzmann dist.: degenerate states

● If we decide to work with macrostates – for example we take as a macrostate all the microstates with the same energy ϵ, we need to know the number of microstates (Ω) in the macrostate. Since we are talking about states of equal energy, this is referred to as the 'degeneracy' of the macrostate, *g*.

$E - \epsilon$
$\Omega(E - \epsilon)$
T

reservoir

ϵ

Degeneracy = g
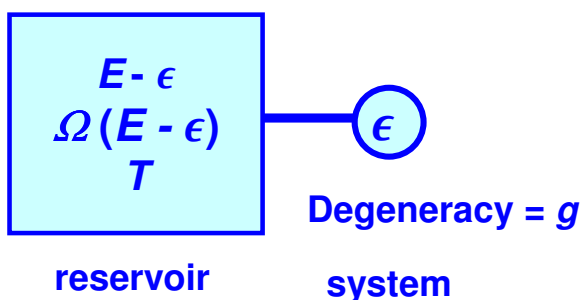
system

Relative probability that the system is in macrostate **q** with energy E_q:

$$P(\text{macrostate } q) \propto g_q e^{-\epsilon_q/kT}$$

$$P(\text{macrostate } q) = \frac{g_q e^{-\epsilon_q/kT}}{\sum_i g_i e^{-\epsilon_i/kT}}$$

and $\quad Z = \sum_i g_i e^{-\epsilon_i/kT}$

Consider a system with only 2 possible states: One with energy $\epsilon_1 = 0$ and the other with energy $\epsilon > 0$.

The probabilities to find the system in the lower and energy are

$$P(0) = \frac{1}{1 + e^{-\beta\epsilon}} \qquad P(\epsilon) = \frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}}$$

with $\beta = \dfrac{1}{kT}$

Note: at high temperature $(\beta \to 0)$ $P(\epsilon) \to \frac{1}{2}$.
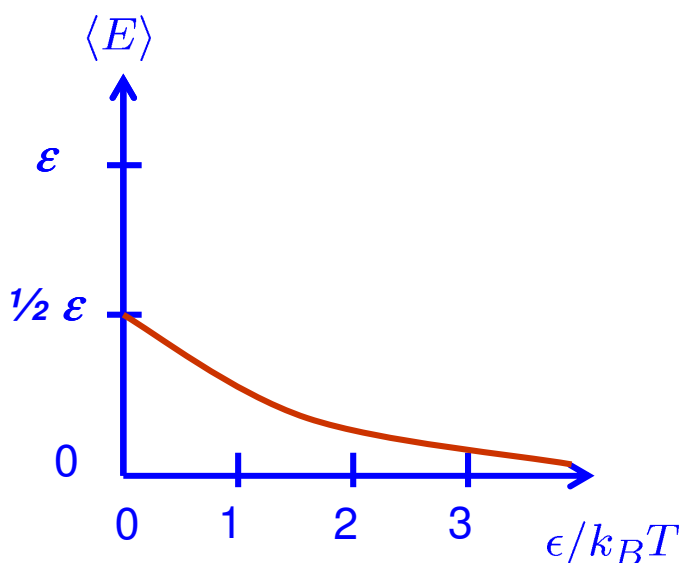
$\Rightarrow$ average energy *<E>* of the system is

$$\langle E \rangle = 0P(0) + \epsilon P(\epsilon)$$

$$= \epsilon\frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} = \frac{\epsilon}{e^{\beta\epsilon} + 1}$$

Example: The 2 state system

The average energy is: $\langle E \rangle = \dfrac{\epsilon}{e^{\beta\epsilon} + 1}$

The expression for *<E>* behaves as expected:

- At low *T*, we have $k_B T << \epsilon$, thus $\beta\epsilon >> 1$, and *<E>* $\to$ **0**.

- At very high *T*, we have $k_B T >> \epsilon$, thus $\beta\epsilon << 1$, and *<E>* $\to$ ½ ϵ.

- Temperature is a measure of the 'price' in terms of entropy drop for the reservoir when heat is extracted from it. At high temperature the entropy hit, $dS = \frac{dQ}{T}$ when heat dQ is extracted from the reservoir becomes very small, so both states become equally likely.

Example: Isothermal atmosphere
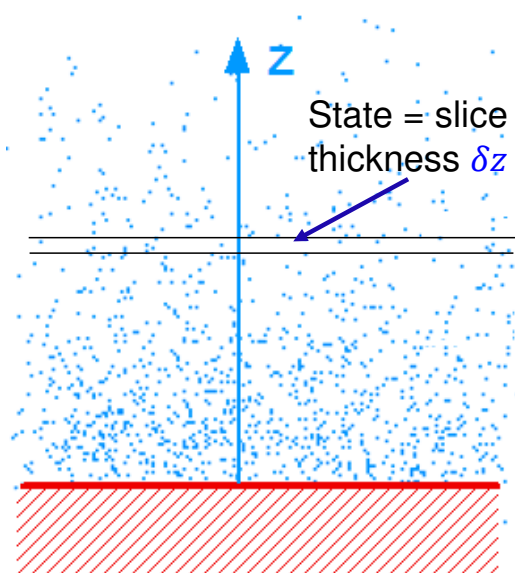
Consider:

- A molecule in an ideal gas at temperature **T** in the presence of gravity

- Microstates are horizontal 'slices' of uniform, infinitesimally small width δz, all equally likely.

State = slice thickness δz

- The probability of the molecule of mass **m** being at height **z** is therefore given by:

$$P(z) \propto e^{-mgz/k_B T}$$

with potential energy **E_{pot} = mgz** .

- The number density **N(z)** at height **z** is proportional to **P(z)**, so:

$$N(z) = N(0)e^{-mgz/k_B T}$$

- Compare with the result derived from drop in pressure considerations:

$$p(z) = p_0 e^{-\frac{mgz}{kT}} \quad \text{and:} \quad N = \frac{n}{V} = \frac{p}{kT}$$

Internal energy, *U*, in statistical thermodynamics

- **Use 'canonical' (='normal') approach** – *i.e.* consider system in thermal contact with a generic reservoir at temperature T and use the Boltzmann factor to give the relative probability of system microstates. Then the internal energy is found by summing the contribution for all the system microstates (given an index *i*):`

$$U_{sys} = \sum_{Sys.\,\mu states} p_i E_i = \frac{\sum E_i e^{-\frac{E_i}{kT}}}{\sum e^{-\frac{E_i}{kT}}} = \frac{\sum E_i e^{-\frac{E_i}{kT}}}{Z} \qquad (p_i = e^{-\frac{E_i}{kT}}/Z)$$

As before, normalising sum, known as the partition function is give by:

$$Z = \sum_{Sys.\,\mu states} e^{-\frac{E_i}{kT}}$$

Using $\beta = \frac{1}{kT}$

$$U_{sys} = \frac{\sum E_i e^{-\beta E_i}}{\sum e^{-\beta E_i}} = \frac{-\frac{\partial}{\partial \beta}\sum e^{-\beta E_i}}{\sum e^{-\beta E_i}} = \frac{-\frac{dZ}{d\beta}}{Z} = -\frac{dln(Z)}{d\beta}$$

Energy of a simple harmonic oscillator: Planck formula

- Quantum mechanical treatment of a SHO gives energy for the nth state $E_n = (n+1/2)\hbar\omega$. We are interested in the energy above the ground state (n=0), *i.e.* the average thermal energy stored in the oscillator when it is in thermal contact with a reservoir of temperature *T*, so we take $E_n = n\hbar\omega$:

$$U = \frac{\sum E_n e^{-\frac{E_n}{kT}}}{\sum e^{-\frac{E_n}{kT}}} = \frac{\sum n\hbar\omega\, e^{-\frac{n\hbar\omega}{kT}}}{\sum e^{-\frac{n\hbar\omega}{kT}}} = \frac{\sum n\hbar\omega\, e^{-\beta n\hbar\omega}}{\sum e^{-\beta n\hbar\omega}} = \frac{-\frac{dZ}{d\beta}}{Z}$$

- The expression for the partition function is a geometric series:

$$Z = \sum_{n=0}^{\infty} e^{-\frac{n\hbar\omega}{kT}} = 1 + e^{-\frac{\hbar\omega}{kT}} + \left(e^{-\frac{\hbar\omega}{kT}}\right)^2 + \cdots = \frac{1}{1 - e^{-\frac{\hbar\omega}{kT}}}$$

Energy of a simple harmonic oscillator: Planck formula

$$Z = \frac{1}{1 - e^{-\beta\hbar\omega}} \qquad\qquad \frac{dZ}{d\beta} = -\frac{\hbar\omega e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2}$$

$$U = -\frac{1}{Z}\frac{dZ}{d\beta} = \frac{\hbar\omega e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})} = \frac{\hbar\omega}{(e^{\beta\hbar\omega} - 1)} = \frac{\hbar\omega}{\left(e^{\frac{\hbar\omega}{kT}} - 1\right)} \qquad \textbf{\textcolor{green}{Planck Formula}}$$

- At low temperatures (*i.e.* $kT \ll \hbar\omega$) $e^{\frac{\hbar\omega}{kT}} \gg 1$ and $U \approx \hbar\omega e^{-\frac{\hbar\omega}{kT}}$ since there is only a slight chance ($e^{-\frac{\hbar\omega}{kT}}$) of the SHO being in the first excited state.

- At high temperatures (*i.e.* $kT \gg \hbar\omega$) $e^{\frac{\hbar\omega}{kT}} \approx 1 + \frac{\hbar\omega}{kT}$ and:

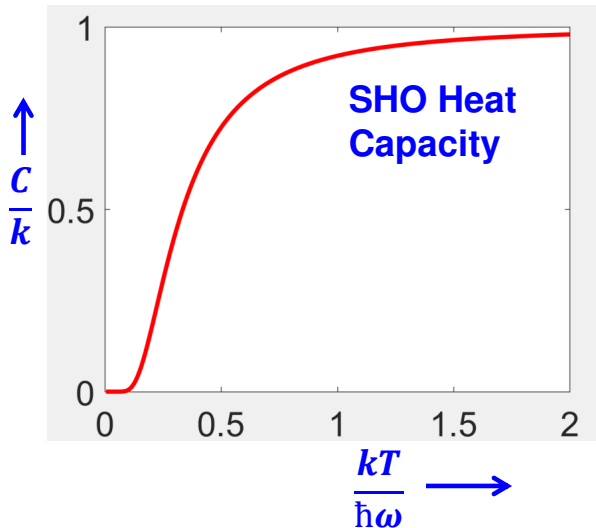$$U \approx \frac{\hbar\omega}{\left(1 + \frac{\hbar\omega}{kT} - 1\right)} = kT$$

i.e. we have moved over to classical dynamics where the energy level spacing is too small to have an effect and equipartition of energy holds - ½kT in both potential and kinetic energy.

Heat capacity of a simple harmonic oscillator

$$U = \frac{\hbar\omega}{\left(e^{\frac{\hbar\omega}{kT}} - 1\right)} \quad \Rightarrow \text{Heat Capacity} \quad C = \frac{dU}{dT} = \left(\frac{\hbar\omega}{kT}\right)^2 \frac{ke^{\frac{\hbar\omega}{kT}}}{\left(e^{\frac{\hbar\omega}{kT}} - 1\right)^2}$$

● At low temperatures (*i.e.* **$kT \ll \hbar\omega$**) $e^{\frac{\hbar\omega}{kT}} \gg 1$ and C tends to zero since there is only a slight chance ($e^{-\frac{\hbar\omega}{kT}}$) of the SHO being in the first excited state.

SHO Heat Capacity

● At high temperatures (*i.e.* $kT > \hbar\omega$) $e^{\frac{\hbar\omega}{kT}} \approx 1 + \frac{\hbar\omega}{kT}$ and:

$$C \approx \left(\frac{\hbar\omega}{kT}\right)^2 \frac{k\left(1 + \frac{\hbar\omega}{kT}\right)}{\left(1 + \frac{\hbar\omega}{kT} - 1\right)^2} \approx k$$

Equipartition of energy

● Consider a case in the classical dynamics limit and a coordinate *u* with classical states correspond to equal intervals ε (*e.g.* distance, velocity, momentum, normal mode coordinate, angular velocity, angular momentum), and for which the energy is a quadratic function of u ($E=\alpha u^2$). The number of states in an interval u-> u+δu is δN=δu/ε The internal energy is given by summing over δu intervals:

$$U = \frac{\sum \alpha u^2 e^{-\frac{\alpha u^2}{kT}} \delta N}{\sum e^{-\frac{\alpha u^2}{kT}} \delta N} = \frac{\sum \alpha u^2 e^{-\frac{\alpha u^2}{kT}} \delta u/\varepsilon}{\sum e^{-\frac{\alpha u^2}{kT}} \delta u/\varepsilon} = \frac{\int_{-\infty}^{\infty} \alpha u^2 e^{-\frac{\alpha u^2}{kT}} du}{\int_{-\infty}^{\infty} e^{-\frac{\alpha u^2}{kT}} du} \Bigg\rangle \text{ Parts}$$

$$= \frac{\overbrace{\left[-\frac{kT}{2} u e^{-\frac{\alpha u^2}{kT}}\right]_{-\infty}^{\infty}}^{=0} + \frac{kT}{2}\int_{-\infty}^{\infty} e^{-\frac{\alpha u^2}{kT}} du}{\int_{-\infty}^{\infty} e^{-\frac{\alpha u^2}{kT}} du} = \frac{kT}{2}$$

e.g.	*u*	*E*
Spring PE	*x*	½*kx²*
Translational KE	*v*	½*mv²* (each dimension works as a separate coordinate)
Rotational KE	*ω*	½ *I ω²*

Equipartition of energy comments

- Works if the expression for total energy separates into the addition of separate terms that depend quadratically on a coordinate because then the integral over microstates itself separates. *e.g.* for a 1d simple harmonic oscillator a state is a box of size ε_x and ε_v in x and v spaces respectively. The sum over microstates is performed by the 2D integral in x and v space. In an integration interval $\delta x \delta v$ the number of microstates is $\delta x \delta v / \varepsilon_x \varepsilon_v$ and so the average energy is given by the integral:

$$U = \frac{\sum \left(\frac{1}{2}kx^2 + \frac{1}{2}mv^2\right) e^{-\left(\frac{1}{2}kx^2 + \frac{1}{2}mv^2\right)/kT} \delta N}{\sum e^{-\left(\frac{1}{2}kx^2 + \frac{1}{2}mv^2\right)/kT} \delta N}$$

$$U = \frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left(\frac{1}{2}kx^2 + \frac{1}{2}mv^2\right) e^{-\left(\frac{1}{2}kx^2 + \frac{1}{2}mv^2\right)/kT} dx dv / \varepsilon_x \varepsilon_v}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\left(\frac{1}{2}kx^2 + \frac{1}{2}mv^2\right)/kT} dx dv / \varepsilon_x \varepsilon_v}$$

Equipartition of energy comments

$$U = \frac{\int_{-\infty}^{\infty} \frac{1}{2}kx^2 e^{-\frac{1}{2}kx^2/kT} dx \int_{-\infty}^{\infty} e^{-\frac{1}{2}mv^2/kT} dv}{\int_{-\infty}^{\infty} e^{-\frac{1}{2}kx^2/kT} dx \int_{-\infty}^{\infty} e^{-\frac{1}{2}mv^2/kT} dv}$$

$$+ \frac{\int_{-\infty}^{\infty} e^{-\frac{1}{2}kx^2/kT} dx \int_{-\infty}^{\infty} \frac{1}{2}mv^2 e^{-\frac{1}{2}mv^2/kT} dv}{\int_{-\infty}^{\infty} e^{-\frac{1}{2}kx^2/kT} dx \int_{-\infty}^{\infty} e^{-\frac{1}{2}mv^2/kT} dv}$$

$$U = \frac{\int_{-\infty}^{\infty} \frac{1}{2}kx^2 e^{-\frac{1}{2}kx^2/kT} dx}{\int_{-\infty}^{\infty} e^{-\frac{1}{2}kx^2/kT} dx} + \frac{\int_{-\infty}^{\infty} \frac{1}{2}mv^2 e^{-\frac{1}{2}mv^2/kT} dv}{\int_{-\infty}^{\infty} e^{-\frac{1}{2}mv^2/kT} dv}$$

Each energy term gives a separate integral, each of value ½ kT

- So provided we can ignore quantum mechanics (*i.e.* the spacing of the energy levels is small compared to kT), each quadratic term contributes $\frac{1}{2}kT$ of energy.

Relation between β and T

- Now we know enough to derive the connection between β and T.

- Suppose we did not know the relation between β and T we could still have done the derivation of equipartition but with a Boltzmann factor exp(-βE) instead of exp(-E/kT), and the mean energy per quadratic degree of freedom would have been:

$$U = \frac{\int_{-\infty}^{\infty} \alpha u^2 e^{-\beta \alpha u^2} du}{\int_{-\infty}^{\infty} e^{-\beta \alpha u^2} du} = \frac{1}{2\beta}$$

and therefore the mean energy of a 3D ideal gas, with 3 quadratic degrees of freedom ($E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$) would be $^3/_{2\beta}$.
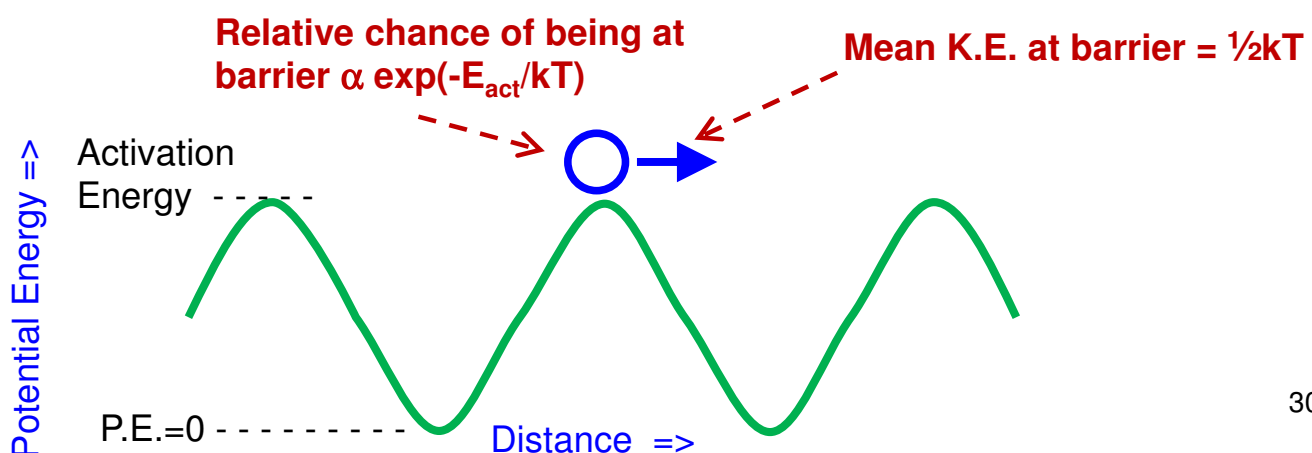
- Remember our temperature scale, T, was defined (arbitrarily and for our convenience) in terms of the properties of ideal gasses, and then more fundamentally, in terms of the efficiencies of reversible heat engines. In Handout 1, on slides 46-47, it was shown that the internal energy of a monatomic ideal gas is $^3/_2 kT$, so we have:

$$\frac{3}{2\beta} = \frac{3kT}{2} \qquad \text{and} \qquad \beta = \frac{1}{kT}$$

Consequences of equipartition of energy

- Remember – equipartition applies to particles behaving classically where energy is a quadratic function of coordinate.

- Mean speed and K.E. (and indeed velocity distribution) same for solids liquids and gasses => notion of *K.E.* as a measure of *T* irrespective of state.

- Even for particles moving in a varying potential energy, at any point the mean kinetic energy, velocity (and velocity distribution) are the same.(!)

- These ideas very useful when deriving a theory of 'activated processes' such as chemical reaction/diffusion, since the rate of barrier crossings depends on the number at the barrier and their velocity at the barrier:

Relative chance of being at barrier α **exp(-E$_{act}$/kT)**

Mean K.E. at barrier = ½kT

Potential Energy =>

Activation Energy

P.E.=0

Distance =>

Internal energy, heat capacity, equipartition

- For a system in contact with a reservoir, the internal energy is given by summing over all system microstates:

$$U_{sys} = \sum_{Sys.\,\mu states} p_i E_i = \frac{\sum E_i\, e^{-\frac{E_i}{kT}}}{Z} = \frac{-\frac{dZ}{d\beta}}{Z} = -\frac{dln(Z)}{d\beta}$$

- Heat capacities: $C = \dfrac{dU}{dT}$

- If energy level spacing is small *c.f. kT*, we can replace sum by an integral and equipartition of energy holds: ½ kT of energy per quadratic degree of freedom: requires energy to be a quadratic function of a coordinate such as x, v, p, ω, L for which the classical states are uniformly distributed, and for energy terms to simply add.
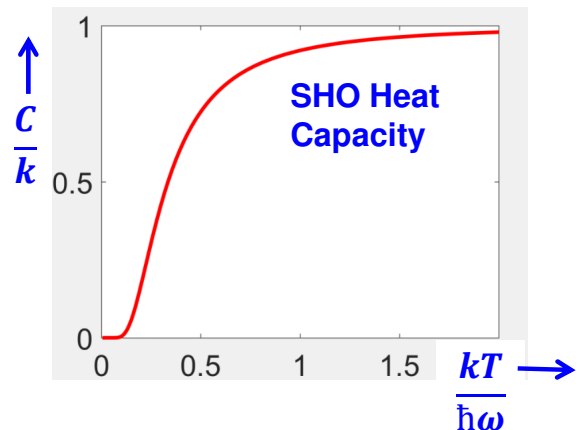
kT< level spacing: mode not 'fully excited', cannot approximate sum as an integral, see effect of QM
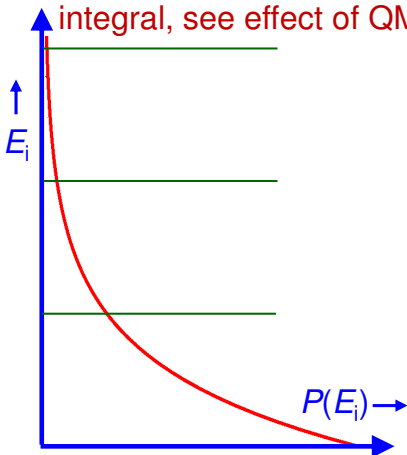
kT> level spacing: can treat as a continuum of levels: classical.
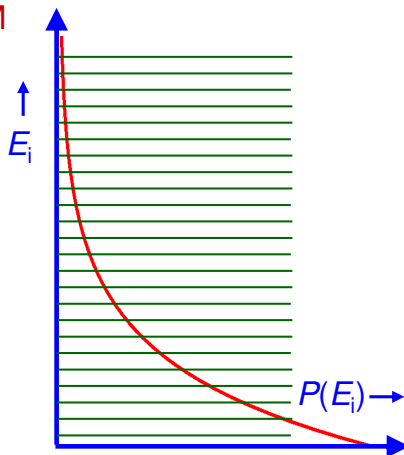
For simple harmonic oscillator (slide 296) when *kT*=level spacing the heat capacity has risen to 92% of its classical value

Heat capacity of gases

- Translational/rotational degrees of freedom contribute kinetic energy - ½*k* per degree of freedom/particle (= ½*R* per mole).

- Vibrational has both kinetic and 'Hooke's law spring' energies – giving *k* per vibrational mode (=*R* per mole of particles).

- The temperature has to be high enough for the modes to be excited (kT >energy difference between states)– vibration is more spatially localised than rotation, which is more localised than translation- so the second derivatives of the wavefunction and hence energy level spacing decrease in that order.

Schematic diatomic gas $C_{v,mol}$/R v. T
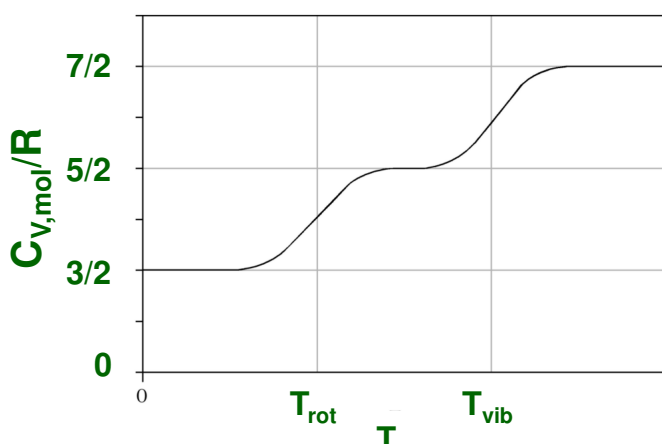
e.g. Diatomic Gases

Low temperatures: 3 translational degrees of freedom, KE only, $C_{v,mol}$=3/2R – only seen for hydrogen –lowest rotational level at E/k=28K=T_{rot} and it boils at 20K.

Intermediate temperatures: add 2 rotations, KE only $C_{v,mol}$=5/2R.

High temperatures: add 1 SHO vibration with KE +PE, so $C_{v,mol}$=7/2R.

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Actual diatomic gas molar heat capacities

Halogens – vib. mode highly excited at high T, so deviations from harmonic potential $C_{v,mol} > 7/2\ R$

Halogens – relatively massive and low vib. freq. – so vib. mode excited at 250K

H_2 and HCl dissociate before vib. gets to classical limit (=never 'fully excited')
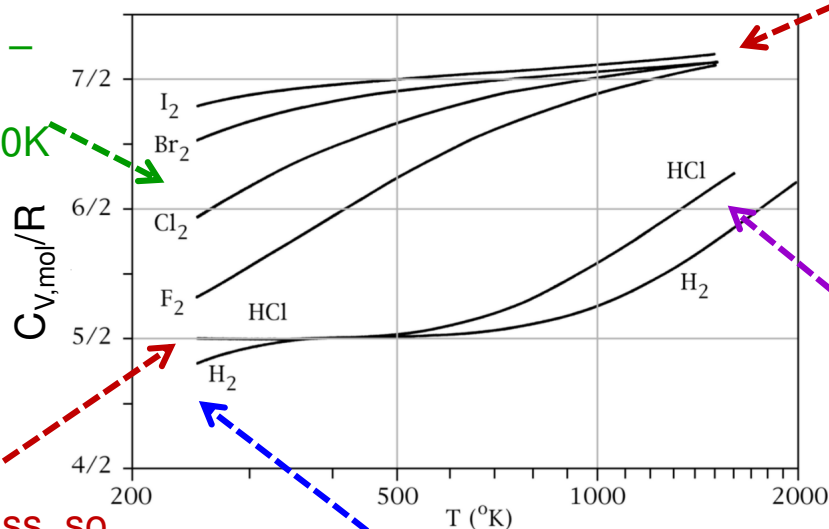
HCl – low reduced mass, so high vib. freq., so vibrational mode not excited till over 500K

H_2 1st rotational excitation energy (J=0 to J=1)/k is 28K – need to go just above boiling point (20K) to see $C_{v,mol}=3/2R$

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5.6 Entropy in statistical thermodynamics

- We now will use statistical thermodynamics to shed light on what entropy actually is by looking what $dS = dq_{rev}/T$ translates to in statistical thermodynamics terms.

- This takes some careful thought and argument – but if we skip this, we will never understand why entropy is what it is, but just have to accept (approximate) statements like '$S = k \ln \Omega$', with no understanding of where they come from and why. It also enables us to rigorously derive the law of increase in entropy from basic notions.

- Need to consider carefully the original definition of entropy: it is defined in terms of reversible heat transfer- *i.e.* heat transfer between a system in thermal equilibrium with a reservoir. This means that the system's energy is constantly fluctuating.

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Need to average over fluctuations

- Entropy is defined as a concept in classical thermodynamics in terms of reversible heat transfer – *ie* for a system in continuous contact with a reservoir:

$$dS = \frac{dQ_{\text{reversible}}}{T}$$

- The energy is therefore continuously fluctuating – and the change in internal energy, for example, is the difference between the average internal energy before and after the 'event'.
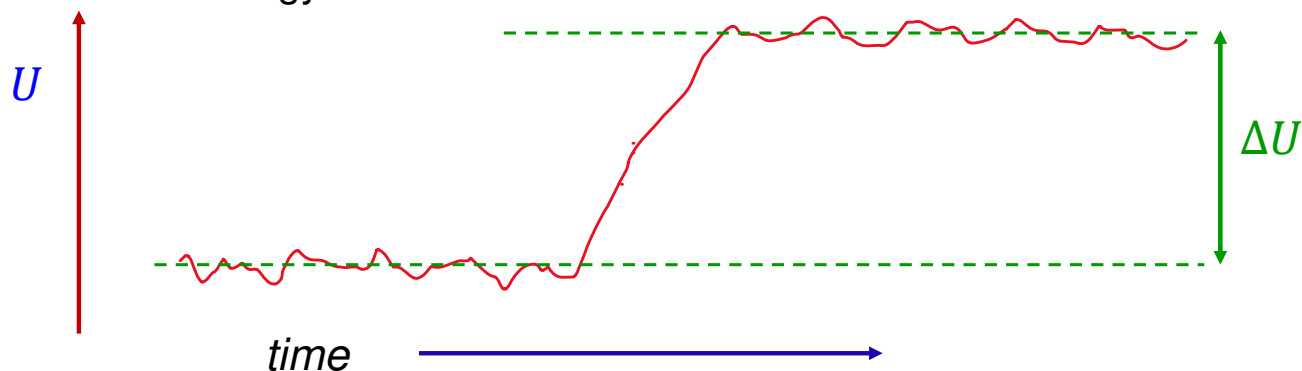
- We thus need to consider changes in $\quad U = \sum p_i E_i$

- The fact that the 'state' of our system is fluctuating means that every state variable, including the entropy, must be expressed an appropriately weighted average over configurations (microstates) of the system.

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dU=đQ+đW in statistical thermodynamics

- We are looking for an equivalent function in stat. thermodynamics to **S** in classical thermodynamics. Start with the definition of entropy: defined in terms of reversible heat transfer:

$$dS = \frac{dQ_{\text{reversible}}}{T}$$

- We have:

$$U = \sum p_i E_i \implies dU = \sum E_i dp_i + \sum p_i dE_i = dQ + dW$$

- The internal energy can conceptually be changed in 2 ways:

Move particles to other states- *i.e.* transfer energy (heat) to particles
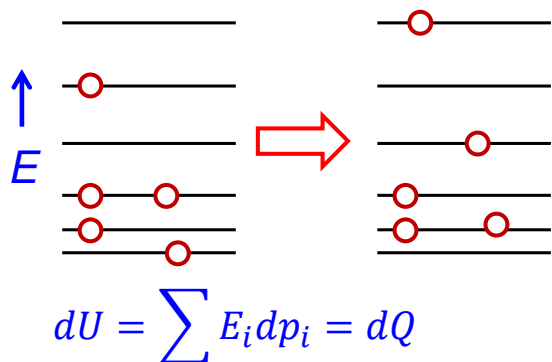
Keep state occupation the same, but change state energies – *i.e.* do work on the system

(suppose system was constrained to be in just one state: cons. of energy dictates that the energy change of the state is the work done on it – and $\sum p_i dE_i$ is just averaging over occupied sates)

$$dU = \sum E_i dp_i = dQ$$

$$dU = \sum p_i dE_i = dW$$
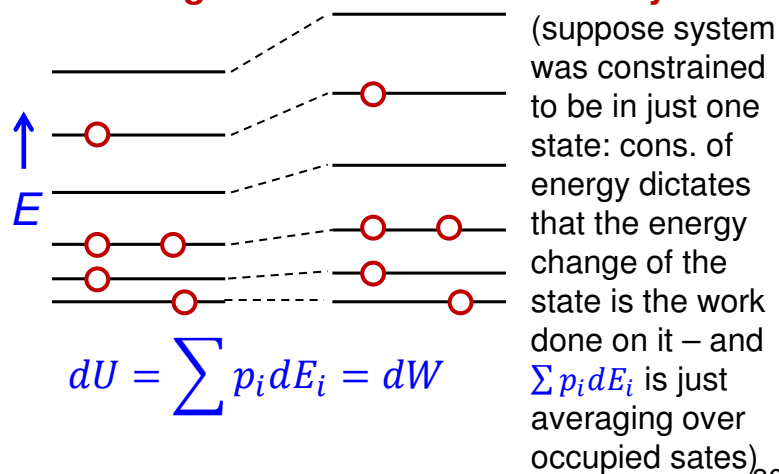
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Example of work in stat. thermo. : ideal gas

- Consider, for example, translation states of monatomic gas in a cubic box of side length L:

$$\lambda_n = \frac{2L}{n}$$

$$k_n = \frac{\pi n}{L}$$
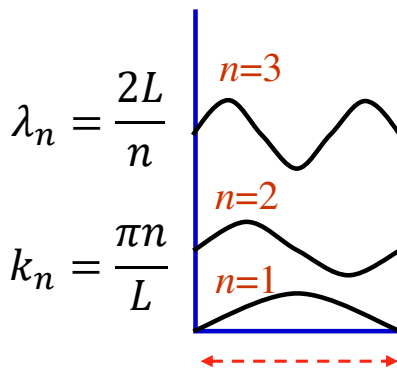
- If you slowly change L, the states 'morph' with it: if you start in *e.g.* $n = 2$, then the state can adapt to the slowly changing length, but if you 'instantly' double the size of the box, one would need to express the old $n = 2$ state as a combination of the new ones.

- This slow change means the work is done reversibly, but the decomposition into new states of the fast change cannot be undone by changing L.

- Wave-vector: $k \propto \dfrac{1}{L}$

- So for every state: $\text{KE} = \dfrac{\hbar^2 k^2}{2m} \propto \dfrac{1}{L^2}$ and $U = \text{KE} \propto \dfrac{1}{L^2} \propto V^{-\frac{2}{3}}$

- Compare with expression for temperature/volume dependence in adiabatic expansion of a monatomic gas:

$$TV^{\gamma-1} = \text{const.} \quad \Rightarrow \quad U \propto T \propto V^{1-\gamma} \propto V^{-\frac{2}{3}} \qquad (\gamma = \frac{C_p}{C_v} = \frac{R + C_v}{C_V} = \frac{1 + \frac{3}{2}}{\frac{3}{2}} = \frac{5}{3})$$

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Temperature change when work is done.

- When an external constraint (*e.g.* size of box) is changed, the quantum states change in energy, in general getting wider spaced as the box size decreased because the 'curvature' of the wavefunction ($\frac{d^2\psi}{dx^2}$) has to increase as the wave form is fitted into a smaller space.

- Therefore, as the box size decreases the density of states, $g(E)$, decreases and given the state occupation does not change and

$$\frac{1}{kT} = \frac{d \ln g(E)}{dE}$$

the temperature increases.
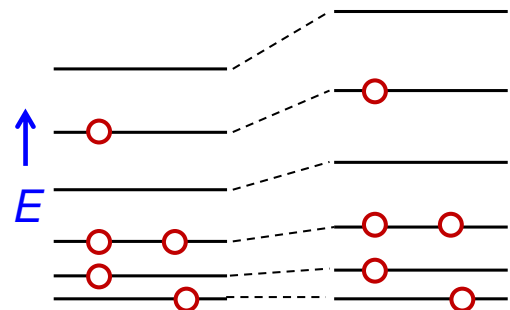
- This temperature increase can also be seen simply from the fact that the whole energy distribution is roughly scaled to larger energies.

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Entropy in statistical thermodynamics

- So, for a general 'slow' change where both work is done and heat transferred:

$$dS = \frac{dQ_{rev}}{T} = \frac{\sum E_i dp_i}{T}$$

- We need to relate E_i to p_i:
$$p_i = e^{-\frac{E_i}{kT}}/Z \quad \Rightarrow \quad \ln p_i = -\frac{E_i}{kT} - \ln Z$$

(Remember *dS* is defined in the context of reversible heat transfer – *i.e.* a system connected to a reservoir, so p_i is given by a Boltzmann factor where *T* is the fixed temperature of the reservoir.)

So, substituting $\frac{E_i}{T} = -k\ln p_i - k\ln Z$

$$dS = \frac{dQ}{T} = -\sum k\ln p_i dp_i - k\ln Z \sum dp_i \qquad \text{(but } \sum p_i = 1 \Rightarrow \sum dp_i = 0)$$

$$S = -\sum \int k\ln p_i dp_i \qquad = -k\sum p_i\ln p_i - k\underbrace{\sum p_i + \text{const.}}_{\text{constant}}$$

(recall $\int \ln x\, dx = x\ln x - x + \text{const}$)

- Setting the constant to zero (see 3rd law later) we get the Gibbs expression:

$$\boxed{S_{\text{Gibbs}} = -k\sum p_i \ln p_i}$$

(The sum is over system microstates and p_i is the probability of the system being in state i microstate when in contact with a thermal reservoir)

Entropy change and heat transfer

- We have:
$$U = \sum p_i E_i \implies dU = \sum E_i dp_i + \sum p_i dE_i$$

- For a REVERSIBLE change: $\sum p_i dE_i = dW$

and hence: $\sum E_i dp_i = dQ$

i.e. for a REVERSIBLE process, essentially work changes the energies of the microstates, and heat transfer changes the probabilities of occupying the microstates.

- Since entropy is defined in terms of microstate probabilities:

$$S_{\text{Gibbs}} = -k\sum p_i \ln p_i$$

we see why entropy change can be associated with reversible heat transfer.

- We looked for the most likely distribution of energy between two systems by maximising $\Omega = \Omega_A \Omega_B$ *w.r.t.* E_A :

$$0 = \frac{d}{dE_A}\left(\Omega_A(E_A)\Omega_B(E - E_A)\right) \quad \Rightarrow \quad \frac{d\ln\Omega_A}{dE_A} = \frac{d\ln\Omega_B}{dE_B}$$

  showing that $\beta = \frac{dln\Omega}{dE}$ and subsequently that $\beta = \frac{1}{kT}$

- Comparing $dE/T = d(kln\Omega)$ to the definition of entropy $dQ_{rev}/T = dS$ suggests that, $S = kln\Omega$ but this is false. dE is the energy change when one goes from one well defined division of energy between A and B to another, whereas dQ_{rev} is the average heat transfer from the average state before the change to the average state after. *i.e.* $dQ_{rev} \neq dE$

Summary of path to Gibbs entropy from $dS = dq_{rev}/T$

- Start with the 2nd law – which is based on (thought?) experiments

- The 2nd law implies there is a function of state that marks the progression of a system along a path of irreversible changes. Use consideration of heat engines to deduce that this function is defined by $dS = \frac{dQ_{rev}}{T}$

- Consider no. of microstates in an observable macrostate, Ω, made of two subsystems, and deduce most likely state is when $\beta = \frac{dln\Omega}{dE}$ ($= \frac{dln\, g(E)}{dE}$ for a continuum of states) , and by comparison with our arbitrary definition of temperature in classical thermodynamics, deduce $\beta = \frac{1}{kT}$,

- By considering transfer of energy from a reservoir to a system, show that the probability of the system being in a microstate of energy E_i is given by the Boltzmann factor $p_i \propto exp(-\beta E_i) = exp\left(-\frac{E_i}{kT}\right)$

- Show: $dQ = \sum E_i dp_i$ and using $dS = \frac{dQ}{T}$ deduce $S_{\text{Gibbs}} = -k\sum p_i \ln p_i$

- *i.e.* **we have found a mathematical expression in stat. mech. that maps on to the classical thermodynamic expression for *S*.**

$S_{\text{Gibbs}} = -k \sum p_i \ln p_i$, but why?

- Entropy is '-' the weighted average (*i.e.* something multiplied by p_i) of the log of the probability of being in one of the microstates. ('k' is just a scaling constant to cover how we have defined energy and temperature.)
- If a system starts in some subset of the microstates (*e.g.* one side of a box) and a constraint is moved making microstates accessible, the system will explore more microstates and the probability of being in any one of them will drop. In general terms we can see why the average value of $-\ln p_i$ will/must rise in an irreversible change: decreasing p_i is a marker for increased spread over more microstates.
- All other things being equal, microstates are equally likely and no averaging of p_i is needed, but if to change the system microstate you need to take heat from somewhere, the associated change in microstates in the heat source changes the relative probabilities of the system microstates and so averaging is needed. (If the system has not 'settled down' to its equilibrium state, but is in the process of getting there, then the p_i will also not have their equilibrium values.)
- The question then becomes 'why is the log of the probability the appropriate thing to average here'.
- A good place to start is to realise that $\sum p_i \ln p_i$ is the log of the 'time averaged geometric mean' probability of the system being in one of its constituent microstates *i.e.* the time averaged 'multiplicative effectiveness' of the state probability.
- In general terms probabilities 'stack up' multiplicatively, so the 'average multiplicative effect' would seem a good guess as to what you want.

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Time averaged geometric mean (TAGM) probability

- Take a sequence of n snapshots of the system, with the time separation being sufficient for the state of a system not to depend on the state in the previous snapshot. State probability given by p_i. Suppose we have 2 states with probabilities 0.8 and 0.2, then for example we might have:

State	1	1	2	1	2	1	1	1	1	1	•••
State probability	0.8	0.8	0.2	0.8	0.2	0.8	0.8	0.8	0.8	0.8	•••

Time ⟶

- The mean number of occurrences of the i$^{\text{th}}$ state in the sequence will be $n_{i,av} = np_i$, and for large values of n, probable values of n_i, the actual no of occurrences of the i$^{\text{th}}$ letter are fractionally very close to np_i. The total probability of getting a particular 'long' sequence is therefore:

$$P_T = \prod_i p_i^{np_i} = p_{TAGM}{}^n, \qquad P_{\text{Example}} = 0.8^8 0.2^2 = p_{TAGM}{}^{10}, p_{TAGM} = 0.61$$

where p_{TAGM} is the time averaged geometric mean probability.

- Taking logs we have

$$n \ln p_{TAGM} = \sum_i np_i \ln p_i \quad \Rightarrow \quad \ln p_{TAGM} = \sum_i p_i \ln p_i$$

and: $\qquad S_{\text{Gibbs}} = -k \sum p_i \ln p_i = -k \ln p_{TAGM}$

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TAGM probability $\geq$ average probability

- If we have n states/outcomes the arithmetic mean probability is: $\quad p_{AM} = \frac{1}{n}\sum_1^n p_i = \frac{1}{n}$

- Stationary values of the TAGM probability w.r.t. variations in p_i values may be found using the method of Lagrange multiplies, with normalisation of the probabilities being a constraint:

$$L = p_{TAGM} - \lambda\left(\sum_{i=1}^n p_i - 1\right) = \prod_i^n p_i^{p_i} - \lambda\left(\sum_{i=1}^n p_i - 1\right)$$

Since $\quad \frac{d}{dx}x^x = \frac{d}{dx}e^{x\ln x} = (1 + \ln x)x^x \quad$ we have

$$\frac{\partial}{\partial p_j}\prod_i^n p_i^{p_i} = \prod_{i\neq j}p_i^{p_i} \cdot \frac{\partial}{\partial p_j}p_j^{p_j} = (1 + \ln p_j)\prod_i^n p_i^{p_i} = (1 + \ln p_j)p_{TAGM}$$

and for stationary points of L: $\quad \frac{dL}{dp_j} = (1 - p_j)p_{TAGM} - \lambda p_j = 0$

Since this is the same formula for all p_j, they must be equal and $p_j = \frac{1}{n}$ and there is only one extreme value of p_{TAGM} which is equal to p_{AM}.

- On the next slide we show that if one microstate dominates $p_{TAGM} \approx 1 > 1/n$ so p_{TAGM} must be *minimised* when it equals p_{AM}

- As in irreversible change progresses towards thermal equilibrium, the microstate probabilities converge to their mean value and p_{TAGM} is minimised, so the entropy $S_{Gibbs} = -k\ln p_{TAGM}$, is maximised.

Time averaged geometric mean: examples

Probabilities	TAGM	
$0.5, 0.5$	$0.5^{0.5} \cdot 0.5^{0.5}$	$= 0.5$
$0.6, 0.4$	$0.6^{0.6} \cdot 0.4^{0.4}$	$= 0.51$
$0.8, 0.2$	$0.8^{0.8} \cdot 0.2^{0.2}$	$= 0.61$
$0.9., 0.1$	$0.9^{0.9} \cdot 0.1^{0.1}$	$= 0.72$
$0.99, 0.01$	$0.99^{0.99} \cdot 0.01^{0.01}$	$= 0.95$
$0.59, 0.39, 0.01, 0.01$	$0.59^{0.59} \cdot 0.39^{0.39} \cdot 0.01^{0.01} \cdot 0.01^{0.01}$	$= 0.46$
$0.4, 0.3, 0.2, 0.1$	$0.4^{0.4} \cdot 0.3^{0.3} \cdot 0.2^{0.2} \cdot 0.1^{0.1}$	$= 0.28$

- $1/p_{TAGM}$ gives an 'effective average number of states involved'. *E.g.* for the last two entries in the table $1/p_{TAGM} = 2.2$ and $1/p_{TAGM} = 3.6$. Maximising the entropy maximises the number of microstates over which the system has spread.

- Taking a case where predominantly only one microstate is occupied, and set $p_1 = 1 - (n - 1)\delta$ and $p_{j\neq 1} = \delta$ which for small δ gives

$$\ln p_{TAGM} = \sum_{i=1}^n p_i \ln p_i = [1 - (n-1)\delta]\ln[1 - (n-1)\delta] + (n-1)\delta\ln\delta$$

$$\approx -(n-1)\delta[1 - (n-1)\delta] + \boxed{\delta(n-1)\ln\delta} \quad \longleftarrow \text{Tends to 0 as } \delta \to 0$$

$$\underset{\delta\to 0}{\text{Lim}}\ln p_{TAGM} = 0 \quad \text{and} \quad \underset{\delta\to 0}{\text{Lim}} p_{TAGM} = 1$$

So, what then is entropy? I

- Entropy is a quantity discovered and defined in classical thermodynamics in terms of heat transferred reversibly which increases for an irreversible change and has the definition:

$$dS = \frac{dQ_{rev}}{T}$$

(Remember: to determine the entropy change for an irreversible process, for example of an isolated system, find an equivalent start/end point reversible path)

- For both classical and quantum mechanical descriptions of the world one can define microstates for which it is reasonable to propose that they would be of equal *a priori* probability. (The validity of this is demonstrated by the correctness of predictions based on it.)

- The direct translation of the classical thermodynamics concept of S into statistical thermodynamics notions gives the Gibbs expression for entropy:

$$S_{\text{Gibbs}} = -k \sum p_i \ln p_i$$

where p_i is the probability that our (sub) system is in microstate i.

As expected for reversible heat transfer, which implies thermal equilibrium between two bodies, entropy is a weighted average of some property of the microstates the system when it is in thermal contact with a another body. Thermodynamics applies to macrostate properties of systems in internal flux: you always have to average over microstates.

- If initially some constraint (a partition in a box or two sub-systems not in thermal contact) prevents access to all microstates by thermal fluctuations then one starts with a microstate probability distribution that is not uniform: many are zero, and the time averaged geometrical mean microstate probability, and hence its log ($= \sum p_i \ln p_i$) are larger than they would be if all states were equally occupied.

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So, what then is entropy? II

- Once a constraint is removed an irreversible macroscopic change occurs as the system moves to the macrostate corresponding to all accessible microstates occurring with equal probability (the gas fills the box) and $\sum p_i \ln p_i$ is minimised.

- The final state can take some time to be achieved, but during the change, 'local' fluctuations occur allowing the p_i to still be characterised: if you remove a partition in a box the rapid collisions mean the local temperature and hence the p_i distribution of the local subset of microstates are more or less defined.

- The ability to monitor the global $\sum p_i \ln p_i$ whilst an irreversible change occurs relies on local equilibrium being approached on a shorter timescale and implies it must be possible to regard the global irreversible change as a sum of a series of local irreversible changes that establish some sort of temporary local equilibrium on the way. This means that locally $\sum p_i \ln p_i$ is approaching a local minimum, and thus globally, if you can establish $\sum p_i \ln p_i$ during an irreversible change, it must be continuously decreasing as the system moves towards a global minimum $\sum p_i \ln p_i$.

- The creators of classical thermodynamics stumbled upon a 'recipe' in terms of macroscopic variables (reversible heat transfer and temperature) that worked as a marker of irreversible change because, in microscopic terms, it is a scaled version of $\sum p_i \ln p_i$, namely $S = -k \sum p_i \ln p_i$. The sign Clausius assigned to entropy was arbitrary and as it happened it is proportional to the negative of $\sum p_i \ln p_i$, so the entropy he defined rises as an irreversible process proceeds.

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- A realisation that a global irreversible change involves local ones that approach equilibrium faster strongly suggests $\sum p_i \ln p_i$ decreases monotonically, but it would be good to have more algebraic justification: there might be some way redistribution of probability during an irreversible process might lead to a temporary increase in $\sum p_i \ln p_i$ even though ultimately it has to be minimised.

- Ultimately the world is quantum mechanical. The actual wavefunction can be written as a linear combination of basis states (the microstates) with transfer of amplitude between them. It can be shown that the rate of change of the probability, q_i, of being in a certain state can we written as a sum of pairwise connections with other states:

$$\frac{dq_i}{dt} = \sum_j v_{ij}\,, \quad v_{ji} = -v_{ji} = -\frac{2}{\hbar}\mathrm{Imag}(C_i K_{ij}^* C_j^*), \quad K_{ij} = e^{\frac{i}{\hbar}(E_i - E_j)t}\langle i|V|j\rangle C_j$$

C_i and E_i are the amplitude and energy of basis state i and V is the potential that links microstates and induces transitions between them. The thermodynamical microstate probabilities p_i are either time averages of q_i or average values of q_i taken by averaging over different starting conditions.

- In this context the key point is that the rate of change of q_i, and hence of its time averaged value p_i, can be considered is a sum of pairwise terms giving the rate of probability transfer from state j to i, and we can write:

write sum with i,j swapped and add

$$\frac{d}{dt}\sum p_i \ln p_i = \sum \ln p_i \frac{dp_i}{dt} + \sum \frac{dp_i}{dt} = \sum_{ij} \alpha_{ij} \ln p_i = \frac{1}{2}\sum_{ij} \alpha_{ij}(\ln p_i - \ln p_j)$$

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$$\frac{d}{dt}\sum p_i \ln p_i = \frac{1}{2}\sum_{ij} \alpha_{ij}(\ln p_i - \ln p_j)$$

α_{ij} is not necessarily a constant – just something which is a function of the two states, the potential that connects them, and some time average of their amplitudes. Use has been made of the fact that $\alpha_{ij}(= -\alpha_{ji})$ as it is some time average of v_{ij} $(= -v_{ji})$ for some particular p_i, p_j pair.

- The fact that the interactions are pairwise strongly limits the scope for 'strange' (collaborative) effects. We just have to think how two states behave. The question is 'on average does probability flow from a more to a less probably micro state'.

- The second law dictates that what happens to the averaged probabilities p_i is independent of the kinetics (the direction of an irreversible change is a function of the states of a system), so we can set all rates to be very slow except for one pair. Coupling a pair of states causes oscillation between them, so the states' respective probabilities q_i, q_j. will oscillate around their time average: $\frac{1}{2}(q_i + q_j)$, and the time average of every pair, $\frac{1}{2}(p_i + p_j)$, converges.

- Therefore, for $\sum p_i \ln p_i$ as a whole not to be monotonically decreasing there must be many pairs, for which, if left in their current state but solely connected to each other, the time averaged probabilities as they oscillate about their mean values would not be tending towards their time average, which seems very hard to conceive.

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- The fundamental principle is that all microstates are equally likely, but for this to be true they need to be equal energy microstates of the whole isolated 'setup' not just part of it, otherwise we have to factor in the effect of sourcing the energy from another part of the system (typically a reservoir, as per $dS = dq_{rev}/T$ definition).

- Consider 'whole isolated setup' microstates, specified by indices i (system part of microstate) and j (reservoir part of microstate), probability p'_{ij}.

- The equilibrium macrostate is the one for which all the p'_{ij} are the same and is found by minimising $\sum_{ij} p'_{ij}\log p'_{ij}$ as the whole setup comes to equilibrium.

- For the ith system microstate there are a corresponding set of Ω_i reservoir states which give the required total system+reservoir energy, and we can assume that at equilibrium these will occur in conjunction with system state i with equal probability (an allowed assumption since they are of equal energy and we know we are heading for uniform p'_{ij}). Thus the probability of finding the system in a particular state is given by $p_i = \Omega_i p'_{ij}$. As always the probabilities must normalise, so for equilibrium we are looking for stationary points of:

$$L = \sum_{ij} p'_{ij}\log p'_{ij} + \alpha[1 - \sum_{ij} p'_{ij}] = \sum_i p_i \log \frac{p_i}{\Omega_i} + \alpha[1 - \sum_i p_i]$$

$$= \sum_i p_i \log p_i - \sum_i p_i \log \Omega_i + \alpha[1 - \sum_i p_i]$$

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- As before, when we were considering temperature in stat. thermo., Taylor expanding the log of the number or reservoir states when the system is in state i with energy E_i about the log of the number of reservoir states for the system is in its ground state ($\ln \Omega_0$) gives:

$$\ln \Omega_i \approx \ln \Omega_0 + \frac{d \ln \Omega}{dE} E_i$$

Substituting gives: $L = \sum_i p_i \ln p_i - \sum_i p_i \left(\ln \Omega_0 + \frac{d \ln \Omega}{dE} E_i \right) + \alpha[1 - \sum_i p_i]$

$$L = \sum_i p_i \ln p_i - \ln \Omega_0 - \frac{d \ln \Omega}{dE} \sum_i E_i p_i + \alpha[1 - \sum_i p_i]$$

And looking for stationary points of L and w.r.t p_i gives:

$$\frac{\partial L}{\partial p_i} = 1 - \alpha + \ln p_i - \frac{d \ln \Omega}{dE} E_i] = 0, \qquad \Rightarrow p_i \propto e^{-\frac{d \ln \Omega}{dE} E_i}$$

- One could also try to impose the constraint on the system by recognising that the reservoir forces a well defined average energy on the system, *i.e.* $E_{\text{av,system}} = \sum E_i p_i$ and thus we would look for stationary values of a 'system only' expression:

$$L_2 = \sum p_i \ln p_i - \beta \left[E_{\text{av,system}} - \sum E_i p_i \right] + \alpha \left[1 - \sum p_i \right] \Rightarrow p_i \propto e^{-\beta E_i}$$

- Thus we see that if the first term of the Taylor expansion suffices (i.e. the reservoir is 'large' so its temperature does not change with heat transfer), considering only system microstates and the imposing the 'reservoir constraint' via an average system energy is equivalent to a full treatment of system +reservoir microstates. 323

$S_{Classical}$ v. S_{Gibbs}

- We have shown that $\sum p_i \ln p_i$ decreases continuously and is minimised as an irreversible change occurs and a 'equilibrium' macrostate is achieved. This is universally true provided one is accounting for all the 'connected' microstates, which therefore must make up some isolated system. Thus $S_{\text{Gibbs}} = -k \sum p_i \ln p_i$ always increases for an isolated 'setup'. We have illustrated that a 'connected' setup can be handled by putting an appropriate constraint (*eg* known E_{Mean}) on the maximisation of S_{Gibbs}.

- Classical thermodynamics found a quirky method of working out entropy, S, under a specific circumstance – reversible heat transfer, and the notion of S increasing was for processes for which equivalent start and end macrostates could be found that were achieved by reversible means, but the system start and end points do have to be connected to something that can act as a reservoir. There is therefore, strictly speaking, something of a restriction on the use of classical entropy: it is not set up to deal with the case of isolated system start and end conditions

- We will see that the change in entropy when the reservoir is disconnected is astronomically small, but still, formally, the classical notion does not apply for isolated start and end conditions. There is, however, no such limit on the statistical thermodynamic derivation of $S_{Gibbs} = -k \sum p_i \ln p_i$. We thus see that under the restricted conditions under which classical thermodynamics is defined, it is entirely equivalent to $S_{Gibbs} = -k \sum p_i \ln p_i$, but that $S_{Gibbs} = -k \sum p_i \ln p_i$ is a more general concept for a state function that acts as a marker for irreversible change that applies in all circumstances, including those with isolated start and end states. 324

Is S_{Gibbs} extensive?

- Take the classical entropy situation and have a system composed of two subsystems connected to a reservoir.

'System'
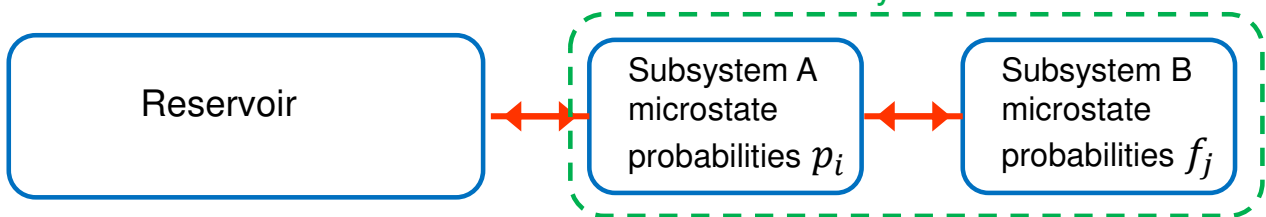
- A 'system' microstate is specified by a (i, j) pair and has probability $p_i f_j$ and the 'system' macrostate has the entropy:

$$S_{\text{Gibbs}} = -k \sum_{i,j} p_i f_j \ln(p_i f_j) = -k \sum_{i,j} p_i f_j \left[\ln(p_i) + \ln(f_j) \right]$$

If p_i and f_j are uncorrelated – *i.e.* if the probability of occupation of states in A is independent of B state occupation, is it will be if both are connected to a large reservoir:

$$= -k \sum_j f_j \sum_i p_i \ln(p_i) - k \sum_i p_i \sum_j f_j \ln(f_j)$$

$$= 1$$

$$= S_{\text{Gibbs,A}} + S_{\text{Gibbs,B}} \quad \text{and } S_{\text{Gibbs}} \text{ is properly extensive.}$$

- If however the 'AB' system is isolated, energy must be conserved, so the microstates of the two systems cannot be freely chosen. Whilst one can use S_{Gibbs} to define the entropy of both separately, which must rise for irreversible change, technically they will not sum to get the overall entropy (though the error is miniscule). 325

Expression for entropy of an isolated system?

- For an isolated system, with no connection to a heat reservoir, once equilibrium has been established, all microstates have the same probability $p_i = 1/\Omega$:

$$S_{\text{Gibbs,equilibrium,isolated}} = -k \sum_i p_i \ln(p_i) = k \sum_i \frac{1}{\Omega_i} \ln(\Omega) = k \ln(\Omega)$$

which is Boltzmann's expression for entropy.

- The Boltzmann expression is very useful conceptually – showing how entropy is related to the number of microstates, but it cannot be used for 'connected' systems or systems away from equilibrium.

- As previously, recognising that real systems do not have perfectly degenerate energy states, and have a 'permitted uncertainty' δ_E in their energy we have:

$$S_{\text{Boltzmann}} = k \ln(\Omega) = k \ln(g(E)\delta_E) = k \ln(g(E)) + k \ln(\delta_E) \approx k \ln(g(E))$$

which is a often a more useful expression for the entropy of an isolated system.

- Because the Boltzmann expression is not algebraically equal to the classical expression, one cannot prove that it is… which explains a lot of the trouble historically with thermodynamics.

- The Boltzmann expression is also not properly extensive. If two isolated systems have degeneracies Ω_1 and Ω_2, then when they are in contact, because energy can flow between them there will be additional states still with the same total energy but a different distribution of energy between A and B *i.e.*

$$\Omega_{\text{Combinded}} > \Omega_1 \Omega_2 \quad \Rightarrow \quad \ln \Omega_{\text{Combinded}} > \ln \Omega_1 + \ln \Omega_2$$

Boltzmann's formula for entropy

Boltzmann had extreme difficulty in persuading the physicists that his statistical expression for entropy was 'correct'. This was not because of a serious flaw in his approach (though there were subtle flaws: the Gibbs expression is actually the direct translation of the classical thermodynamics concept of entropy), but because the leading physicists seriously did not believe the atomistic view of the world, despite the fact this had been well accepted with powerful evidence in chemistry for many (6-7) decades by people in the same, prestigious universities. Boltzmann even proposed that the atomistic view be used just as a 'model that worked' so that progress could be made, but despite the fact that this is the basis for pretty much all of physics theory, even this was not acceptable. Oh the benefit of hindsight and the folly of our forebears! (hmm…)

His expression was famously, and tragically, inscribed on his grave stone in Vienna. 327

- To gauge the magnitude of the approximations in using different formulae for entropy, we will first evaluate S_{Gibbs} for a system connected to a reservoir in terms of $g(E)$.

- Firstly we recall that the Gibbs expression for entropy is:

$$S_{\text{Gibbs}} = -k \sum_{\text{All pos. } \mu\text{states}} p_i \ln p_i = -k. \text{ average value of } (\ln p_i)$$

(Recall $\bar{x} = \sum_i p_i x_i$ where p_i is the probability of x_i)

We are going to use the fact that for a sharply peaked distribution the most probable value of $\ln p_i$ is also its average value.

- How can we do the sum over all microstates? It is useful to characterise the microstates by their energy (since their relative probability depends on their energy via a Boltzmann factor), and then use the concept of a density of states, $g(E) = \frac{dN}{dE}$ – i.e. how 'thick and fast' they come as you vary E, i.e. the number of microstates, δN that have an energy lying between E and $E + \delta E$ is:

$$\delta N = g(E)\delta E$$

The sum over states becomes an integral over energy giving:

$$S_{\text{Gibbs}} = -k \int g(E)p(E) \ln p(E) \, dE$$

No of states in energy interval dE

Where the prob. that the system is in a microstate of energy E is:

$$p(E) = e^{-\frac{E}{kT}}/Z \quad \text{and} \quad Z = \sum_i e^{-\frac{E_i}{kT}} = \int e^{-\frac{E}{kT}}g(E)dE$$

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$$S_{\text{Gibbs}} = -k \int g(E)p(E) \ln p(E) \, dE$$

- Remember, this expression is being used to find the average value of $-k \ln p$, and we can see that $g(E)p(E) \, dE$ gives the chance of being in the macrostate defined by the energy interval E to $E + dE$.

- $p(E) = e^{-\frac{E}{RT}}/Z$, drops rapidly with E, whereas (as illustrated on slides 277-8), $g(E)$ (the density. of microstates at energy E) rises very rapidly with E – the result is that $g(E)p(E)$ peaks very sharply (for all but the smallest systems) at the average energy of the system (E_{av}).

- *E.g.* consider a system of M oscillators connected to a reservoir with a temperature such at that the average energy, *E*, is 1 quantum per oscillator:
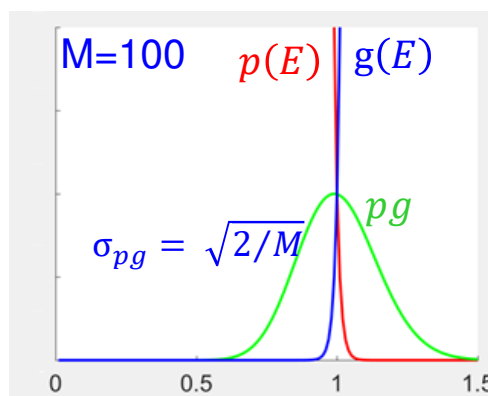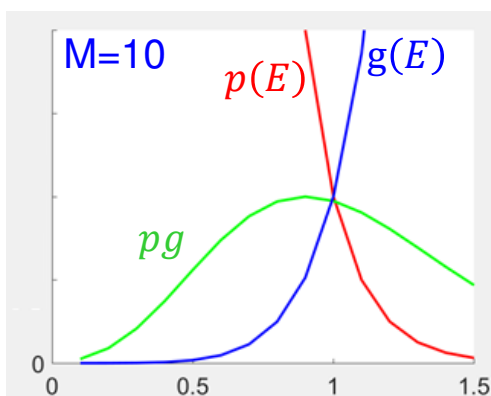
Width of $g(E)p(E)$, σ_{pg} ,scales as $1/\sqrt{M}$ – for 1 mole relative width $\approx 10^{-12}$

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$$S_{\text{Gibbs}} = -k.\text{ average value of } (\ln p_i)$$

- $g(E)p(E)$ peaks very sharply at the average energy E_{av}, so the mean of $\ln p(E)$ is simply $\ln p(E_{av})$, and:
$$S_{\text{Gibbs}} \approx -k\ln p(E_{av}) = \frac{E_{av}}{T} + k\ln Z \quad (\text{recall } p(E) = e^{-\frac{E}{RT}}/Z)$$

Now $Z = \sum_i e^{-\frac{E_i}{kT}} = \int e^{-\frac{E}{kT}} g(E)dE$, the integrand of which is, as before, very

sharply peaked - width ΔE, defined so its integral is $e^{-\frac{E_{av}}{kT}} g(E_{av})\Delta E$

The expression for S for a system connected to a reservoir therefore becomes:

$$S_{\text{Gibbs}} = \frac{E_{av}}{T} + k\ln\left(e^{-\frac{E_{av}}{kT}} g(E_{av})\Delta E\right) = \frac{E_{av}}{T} - \frac{E_{av}}{T} + k\ln(g(E_{av})\Delta E)$$

i.e. $S_{\text{Gibbs}} = k\ln(\text{Number of states covered by peak}) = k\ln g(E_{av}) + k\ln\Delta E$

- For 1 mole of gas at room temperature, for example, $\ln\Delta E$ is of the order of -12, but S is typically of the order of 100J/K – so $\ln g$ is of the order 10^{25} (!)

- For an isolated system, $\Omega = g(E)\delta_E$, $S_{iso} = k\ln g(E_{av}) + k\ln\delta_E$
  In QM the 'minimum permitted spread in energy' of microstates (eigenstates of the unperturbed – ie no connections between microstates - Hamiltonian) is given roughly by the matrix elements of the potential that 'connects' the microstates $\langle i|V|j\rangle$. The magnitude of this, for example in a gas, may be estimated using the time/energy uncertainty relation on the mean time between collisions (1/7GHz for air at STP) $\approx 10^{-24}$J and $\ln\delta_E \approx$ -55.

- For both isolated systems and those connected to a reservoir, the error in the approximation $S \approx k\ln g(E_{av})$ is astronomically small.

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$S = k\ln(\text{Number of states covered by fluctuations})$

On the previous slide we had for a very sharply peaked $e^{-\frac{E}{kT}}g(E)$ distribution, to a very good approximation (*i.e.* assuming average value = peak value):

$$S_{\text{Gibbs}} = -k.\text{ average value of } (\ln p_i) \approx -k\ln p(E_{av}) = \frac{E_{av}}{T} + k\ln Z$$

(1) Integrate $Z = \sum_i e^{-\frac{E_i}{kT}} = \int e^{-\frac{E}{kT}} g(E)dE$ over the peak

(2) Work out an effective width ΔE, such that this integral equals $e^{-\frac{E_{av}}{kT}} g(E_{av})\Delta E$, and use this as a definition of the peak width (the states are overwhelmingly in the peak).

(3) The entropy is then seen to be:
$$S = k\ln(\text{Number of states covered by peak}) = k\ln\big(\Delta E. g(E_{av})\big)$$

(4) When this system is in contact with a reservoir, its energy fluctuates. If N is the number of system microstates covered by fluctuations in the range $E_{av} - \Delta E/2$ to $E_{av} + \Delta E/2$, *i.e.* a notional number of state covered by/involved in these fluctuations, then $S = k\ln(N)$. This confirms that $1/p_{TAGM}$ is indeed a good measure of the number of microstates involved (recall: $S_{Gibbs} = -k\ln p_{TAGM}$).

(5) Z is determined overwhelmingly by the contribution from states in the peak, all of which have pretty much the same energy, so same probability which therefore must be $1/N$, hence again $S \approx -k\ln p(E_{av}) = k\ln N$

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Expressions for entropy: Summary

- The original definition of entropy is found in the field of classical thermodynamics in terms of the reversible heat transfer to a system from a heat reservoir:

$$dS = \frac{dq_{rev}}{T}$$

- In statistical thermodynamics this is exactly equivalent to the Gibbs expression for entropy for a system in thermal equilibrium with a reservoir:

$$S_{\text{Gibbs}} = -k \sum p_i \ln p_i$$

Microstate probability p_i given by a Boltzmann factor normalised by dividing by the partition function, Z. The BF folds in the number of associated reservoir microstates.

- $S_{\text{Gibbs}} = -k \ln p_{\text{TAGM}}$. ($p_{TAGM}$ = time averaged geometric mean microstate probability)

- p_{TAGM} is minimised for an isolated system when all microstates are equally occupied and drops monotonically during an irreversible process. It, or its log can be used as a measure of 'how far along the irreversible path' an isolated system has moved. Whilst it was discovered in the context of reversible heat transfer in classical thermodynamics, it universally true as a marker for irreversible change.

- For 'connected' systems irreversible change and equilibrium may be characterised by minimising p_{TAGM} but subject to the constraints imposed by the connection.

- As always for state variables, the use of p_{TAGM} requires some sort of 'local' equilibrium to be established so p_i can be found during an irreversible change.

- The approximate (by an infinitesimal amount for large systems) formulae $S \approx k \ln g(E_{av})$, $S_{\text{Boltzmann}} = k \ln \Omega$ are often much easier to evaluate and to 'understand': you are not summing over states that barely contribute to the entropy. 332

An example : entropy of ideal gas/change on expansion

Classical Thermodynamics Approach

- We showed (slide 142, handout 1) that application of the fundamental definition of entropy:

$$dS = \frac{dq_{rev}}{T}$$

Gives an entropy change for *n* mol of ideal gas on volume change from V_0 to V_1 of:

$$\Delta S = nR ln \left(\frac{V_1}{V_0} \right)$$

- Whilst we shall see that the third law allows us to set the value for entropy to zero at absolute zero, we still cannot get a general theoretical expression from the classical approach because we would need to use:

$$\Delta S = \int_0^T \frac{n c_{V,m}(T)}{T} dT$$

but we do not have a general expression for the temperature dependent molar heat capacity $c_{V,m}(T)$. At high temperatures this is given by equipartition ($c_{v,m} = {}^1/_2\, k$ per 'quadratic' degree of freedom) at low temperature one needs to apply statistical mechanics on the actual quantum states to derive one. However changes in entropy from one finite temperature to another can be calculated (slide 132, Lent, Handout 2) 333

Exact Statistical Thermodynamics approach

- For non identical particles, the application of the Gibbs expression is straight forward, and since the Gibbs expression is extensive, we can work out the entropy of an ideal monatomic gas consisting of a single free atom, mass m, in a box of volume V in thermal contact with the walls, then multiply by the number of atoms in the gas, then apply correction for identical particles

- The sum in the Gibbs expression could be handled by converting it to an integral over the density of states calculated using the standard 'waves in a box' approach (see Condensed Matter course/ the thermal radiation section of this course), which for convenience we might write in terms of the wavevector of atom:

$$S_{\text{Gibbs}} = -k_B \sum_i p_i \ln p_i = -k_B \int g(E) p(E) \ln p(E) \, dE \qquad \text{where} \quad E = \frac{\hbar^2 k^2}{2m}$$

$$= -k_B \int g(k) p(k) \ln p(k) \, dE$$

with $\quad p(k) = e^{-\frac{\hbar^2 k^2}{2mk_B T}} / Z \quad$ and $\quad Z = \sum_i e^{-\frac{E_i}{kT}} = \int_0^\infty e^{-\frac{\hbar^2 k^2}{2mk_B T}} g(k) dk$

And for a spin 0 boson (no further degeneracy: see Radiation H/O) $\quad g(k) = \frac{Vk^2}{2\pi^2}$

- These integrals are tractable and will give the entropy assuming the constituents are distinguishable, which in general they are not, so we need to work out how to correct for this.

Exact Statistical Thermodynamics approach II, handling identical particles

- On slide 338 a very useful shortcut is given to the above maths: we can show
$$F = U - TS = -k_B T \ln Z \quad \text{and hence} \quad S = U/T + k_B \ln Z$$

- For an ideal gas with N atoms at anything other than nano kelvin temperatures:
$$U = \frac{3}{2} N k_B T$$

We also need to work out the partition function, (sum of un-normalized Boltzmann factors), Z correctly for identical particles, and either use this directly, or use it to show the correction needed to the entropy expression for non identical particles

- If we have non interacting gas atoms, then the un-normalised probability of a particular microstate P_I of the whole set of atoms is given by the product of the Boltzmann factors that give the un-normalized probability that each atom is in the particular state required for this overall microstate:

Un normalized probability that particle 1 is in state i_1.

$$P_I = p_{1,i_1} p_{2,i_2} \, p_{3,i_3} \, p_{4,i_4} .. = e^{-E_{i_1}/k_B T} e^{-E_{i_2}/k_B T} \, e^{-E_{i_3}/k_B T} \, e^{-E_{i_3}/k_B T} . = e^{-E_{TOTAL}/k_B T}$$

- The partition function is the sum over all combinations of individual atom states, but given the particles are identical these come in groups of $N!$ indistinguishable states, so a simple sum over all states overcounts by $N!$ and we see when you add in the condition that the particles are identical, the partition function reduces by a factor of $N!$ and the entropy derived for non identical particle by $k \ln N!$.

Exact Statistical Thermodynamics approach III, S for ideal gas

● So, single atom partition function for an ideal monatomic gas:

$$Z_1 = \sum_i e^{-\frac{E_i}{kT}} = \int_0^\infty e^{-\frac{\hbar^2 k^2}{2mk_BT}} g(k)dk = \int_0^\infty \frac{Vk^2}{2\pi^2} e^{-\frac{\hbar^2 k^2}{2mk_BT}} g(k)dk = V\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}$$

And hence (provided the temperature is high enough for the sum in the partition function to be replaced by the integral) for a gas containing N identical particles:

$$S = U/T + k_B \ln Z = \frac{3}{2}Nk_B + Nk_B \ln Z_1 - k_B \ln N!$$

$$= \frac{3}{2}Nk_B + Nk_B \ln\left[V\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\right] - k_B \ln N!$$

Stirling's approximation for $\ln N!$

$$= \frac{3}{2}Nk_B + Nk_B \ln\left[V\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\right] - k_B N \ln N + k_B N$$

● Thus we have the entropy of a monatomic ideal gas:

$$S = \frac{5}{2}Nk_B + Nk_B \ln\left[\frac{V}{N}\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\right]$$

(The Sackur–Tetrode equation, predicts 126.04J/mol for He, experimental value is 126.153 J/mol: He-He interactions have been ignored.)

An example : entropy of ideal gas/change on expansion

Use of $S_{\text{Boltzmann}} = k \ln \Omega_{max}$

● The Boltzmann approximate expression for S can only be used for degenerate (equal energy) states, so cannot be used to model the 'heat' part of the entropy of an ideal gas, but it can be used to model the 'spatial' part. Because this separation only works for classical states we are limited in this instance to using these classical states, and the arbitrary nature of the volume of our microstates means no absolute value of the spatial part of S can be derived. However, the expression can be used to derive the change in S when the volume of the gas is changed. The 'heat' (velocity) part of the entropy does not change on isothermal expansion.

● If we have a box of volume V with N spatial states volume δV and n atoms in it and if the states are small enough to ignore the possibility of multiple occupancy (if they are not, just make them smaller) then, allowing for the fact the atoms are identical, we have :

$$\Omega(n) = \frac{(N)^n}{n!} = \frac{(V/\delta V)^n}{n!} \qquad \text{where} \qquad N = \frac{V}{\delta V}$$

● Thus we have (including an unknown offset due to the arbitrary nature of δV):

$$S_{\text{Boltzmann}} = k \ln \frac{(V/\delta V)^n}{n!} = nk \ln V - k \ln(n!\,(\delta V)^n)$$

● The entropy change when the volume is changed from V_1 to V_2 is therefore:

$$\Delta S_{\text{Boltzmann}} = nk \ln \frac{V_2}{V_1}$$

● For a system in thermal equilibrium with a heat reservoir, there is a rather simple expression for the Helmholtz free energy:

$$S = -k \sum p_i \ln p_i = -k \sum p_i \left(-\frac{E_i}{kT} - \ln Z \right) \qquad (p_i = e^{-\frac{E_i}{kT}}/Z)$$

$$S = \frac{1}{T} \sum p_i E_i + k \ln Z \sum p_i = \frac{U}{T} + k \ln Z \qquad (U = \sum p_i E_i)$$

Hence: $\boxed{F = U - TS = -kT \ln Z}$

● This formula provides an extremely useful bridge between statistical and classical thermodynamics: *F* is a thermodynamic potential with very accessible natural variables, *T* and *V*. This means that the partition function, *Z*, takes a central place in statistical thermodynamics.

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5.7 Entropy and Maxwell's Demon

● In 1867 Maxwell proposed the following thought experiment that seemed to violate the second law of thermodynamics.

● Suppose we have two boxes connected by a trap door and a 'finite being' (could be an inanimate control system, but called a 'demon' by Kelvin) that opens the door if a fast molecule moving right to left is detected or a slow one moving left to right. With time the fast molecules end up on the left and the slow on the right – heat has flowed from right to left, but no work has to be done (apparently) in opening and shutting the door – you just have to slide it too and fro. A simpler version is that the door is opened if a molecule moving right to left is detected – so all the molecules end up on the left – again with a reduction in entropy.

● The Maxwell Demon problem is of interest because it is a representative setup in which the individual coordinates/states of the system are measured and manipulated, and the question is whether the 2nd law still holds when you do.

Trap door opened when particle is detected moving right to left
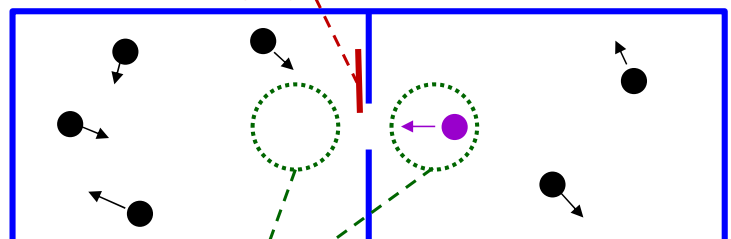

Particle detectors

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Explanations of Maxwell's Demon

- Initial efforts at explanation focused on the particle detectors – to detect the presence of a particle you need to do something irreversible like scatter a photon out of a light beam. This explanation fell out of favour when it was claimed that a counter example had been found (*i.e.* 'reversible process' detection of a particles position) Fundamentally any action that achieves a new state which stays put and cannot just wander back to its old one is irreversible – so measurement itself must be an irreversible process – *i.e.* result in entropy increase, and indeed inspection of the proposed 'reversible' measurement scheme shows it wasn't.

- This notwithstanding, the actuation of the trap door also produces an entropy increase – again you are achieving a result. The trap door will itself undergo thermal motion - Brownian motion - so you need to have an energy barrier between 'open' and 'shut' otherwise it will just diffuse between the two positions at random and be open half the time. You have to do work on the door to push it over the barrier – but once it is over you cannot recover this work as it descends on the other side –the work must be dissipated as heat, increasing the entropy of the surroundings

- Any system set up to recover the work, would have to be in mechanical equilibrium with the door, (think of collecting the work of a falling weight by connecting it with a string over a pulley to another weight) which removes the barrier. Indeed the whole point is that the descent from the barrier to the open position needs to be a one way process, *i.e.* irreversible (unless pushed back by the expenditure of more work)– and the energy needed to overcome the barrier is dissipated as heat –carried off an a random way that means it won't flow back and push the door back over the barrier.[340]

Switches/trap door mechanism

- **A switch has to have an energy barrier** between states in order to keep it located one way or another. (Otherwise it will drift from one state to the other and back by Brownian motion.)

State 1   **State 2**

E_b

- To change the state of the switch:
  - **Work is done against the switch** mechanism to push it to the top of the barrier.

  Work done on mechanism.

  - Once just over the barrier, this energy stored in the switch mechanism is converted to kinetic energy, which is then dissipated as heat when the switch hits state 2

  PE to KE

  - **The work has ended up in the as-good-as-random motion of the molecules** of the switch. The switch has no mechanism for keeping track of where this energy is: it has 'lost information' – the energy could be in any one of many microstates - and cannot direct the molecules to all bring the energy back at the same time so as to throw the switch back to state 1, so we have an irreversible change which stops the switch spontaneously moving back.

  KE to heat

[341]
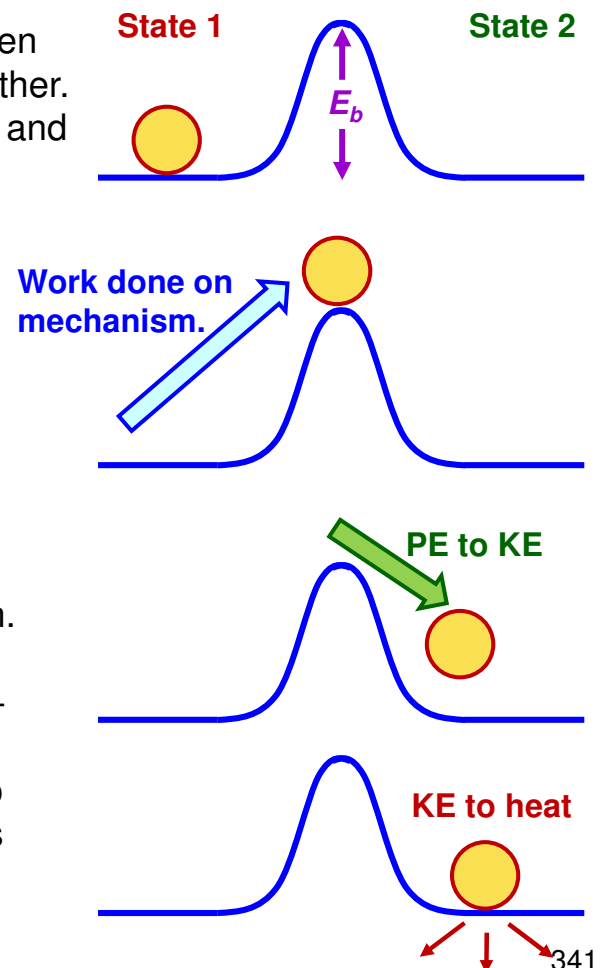
Maxwell's Demon: Trap door actuation

- Proposed door energetics: equal energy open and shut states separated by barrier:

Shut E_b Open
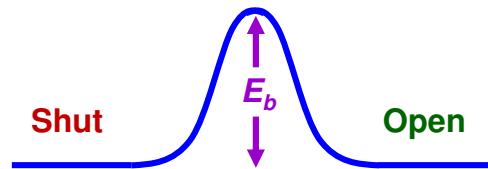
- If there are initially n_0 molecules on each side of the box ($2n_0$ in total) – then the entropy drop if they are all moved to the left side is $2n_0 k_B \ln 2$. To open and shut the door requires 2 barrier crossings, so work $2n_0 E_b$ is dissipated as heat giving an entropy rise of the surroundings of $2n_0 E_b/T$. For the second law not to be violated we require:

$$2n_0 k_B \ln 2 < \frac{2n_0 E_b}{T} \qquad \Longrightarrow \qquad E_b > k_B T \ln 2$$

Giving a Boltzmann factor of: $\qquad e^{-\frac{E_b}{k_B T}} < \frac{1}{2}$

- This means that for the second law to be violated the door would be spending more than 50% in a 'traveling over the barrier' state as opposed to located on one side or another – hardly a description of a well located door!

- Whilst we have not proved definitively that a Boltzmann factor of 0.5 or less is needed to locate the door, it is clearly very reasonable – and there is no reason to say that this provides any real evidence for 2nd law violation.

- In practice, for example in a single bit memory, one needs a much larger barrier to stop the system jumping thermally over to the other state: the longer you want to store the information for, the higher the barrier needs to be.

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Maxwell's Demon: Other considerations II (NE)

- One final proposal would be to have a door that has no energy barrier, but slides freely, and then is clamped by the application of a normal force once it is in the right place which does no work (nothing moves when its clamped). But something must turn this normal force on and off and sooner or later a 'switch' is need that just stays where it is put, which will have its own energy barrier etc.

- The Maxwell demon problem is commonly explained in terms of information: it is postulated that the demon needs to store information in order to know to open the door, but this is just not true – the demon opens and shuts the door in response to the presence of a molecule, not with respect to some stored data. Even suppose the demon did wish to remember the state of the door – the door itself will tell you that – you might as well look directly where the door is as to the value of a record of where the door is!.

- The 'missing increase in entropy' is proposed to be due to the need to wipe the data in the register where the (actually unnecessary) information is to be stored – but wiping data means setting an indeterminate system to a known value (unless you propose to read the data first, another irreversible process) and is no different anyway to recording a known value– so this makes matters worse with another decrease in entropy –so the second law is invoked to say there must be some corresponding heat transfer somewhere that compensates for all this (forgetting the whole idea was to compensate for the entropy loss of the sorted gas, which thus remains uncompensated) and anyway giving a circular argument: Maxwell's objection to the second law cannot be valid because the second law requires that something works to sort it out!

- It is quite common for physicists to consider the effect of a conscious observer on a system – and indeed sometimes Maxwell's Demon is considered in this light. However, today virtually all measurements are made by rather simple machines that straightforwardly obey the laws of mechanics, QM and thermodynamics, and the interaction of a conscious observer would seem to be entirely spurious.

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Measurement is an irreversible process

● The Maxwell demon problem sparks a further train of understanding: measurement = determining/recording the state of a system – which, like the moving of the trap door in the MD problem, or the switching of a bit in a memory device, or indeed any process that achieves a well defined result has to be an irreversible process achieved by having a much higher number of available states on the 'I've recorded an event' side. If the 'well defined result' is produced by a reversible process the system can just diffuse back and undo the result: you have not achieved anything, least of all a measurement.

● At this point we have walked straight into what is arguably one of the major unsolved problems of science: measurement in QM – *i.e.* when you set up a device that records which of the component eigenstates a wavefunction is in (when actually it is a mixture of many) – you get a random, but definitive answer weighted according to the squares of the magnitudes of the coefficients of the component states. A key feature of all this is that a measurement occurs when the propagating wavefunction 'hits' or 'becomes linked to' an irreversible process (for example the triggering of a silver halide crystal on a photographic film to decompose into elemental silver and the halogen), and this is recognised as a key jigsaw piece in the QM 'collapse of the wavefunction/measurement' puzzle. Collapse of the wavefunction is a QM irreversible process, and maybe this realisation will assist in working out what 'collapse' is.

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Summary I

- The second law (direction of irreversible change, and hence nature of equilibrium is a function of system states not kinetics) is based on 'time reversibility': static constraints must change forward and backward rates equally.

- The second law means the relative probability of microstates is only a function of how the microstates are defined/set up, and we can find microstates in both classical and QM descriptions that are equally likely.

- The most likely macrostate is the one with the most corresponding microstates.

- We considered how the global no of microstates for a macrostate comprising two systems in thermal contact varies as energy is transferred, and deduced a condition for thermal equilibrium in terms of reservoir degeneracy/density of states: $\beta = \frac{d\ln\Omega}{dE} = \frac{d\ln g(E)}{dE}$ must be the same for each object in thermal equilibrium. By comparison with classical thermodynamics we showed $\beta = \frac{1}{kT}$.

- We showed that for the a system in thermal contact with a reservoir, the relative probability of the system being in a microstate of energy E is $\exp(-E/kT)$ and of its being in a macrostate of energy E and degeneracy g is $g.\exp(-E/kT)$.

- We showed how the Boltzmann factor could be used to deduce average energies and heat capacities of systems, and derived equipartition of energy for systems where energy is stored as a 'quadratic' function of coordinates.

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Summary II

- An irreversible change occurs when a constraint is removed and the macro state changes as the system moves to fluctuate over all the additional new microstates: the gas fills the box.

- $\sum p_i \ln p_i$ is the log of the time averaged geometric mean microstate probability p_{TAGM}, and $1/p_{\text{TAGM}}$ gives the mean effective number of occupied states which rises as a state changes irreversibly, 'spreading out' to give uniform occupation of all microstates. $\sum p_i \ln p_i$ has a minimum value when all p_i are equal, and drops monotonically as equilibrium (equal microstate occupation) is approached.

- If one can determine $\sum p_i \ln p_i$, (*i.e.* if local state variables can be defined) one has a marker for the progress of an irreversible change. The architects of classical thermodynamics stumbled upon a way of finding this quantity in terms of reversible heat transfer $dS = dQ/T = S_{\text{Gibbs}} = -k \sum p_i \ln p_i$, but the use of $\sum p_i \ln p_i$ applies generally.

- For isolated systems at equilibrium S_{Gibbs} simplifies to $S_{\text{Boltzmann}} = k \ln \Omega$ or $S = k \ln g(E)$ for systems with non-degenerate energy states. For large systems the change in entropy when extra freedom is afforded by connecting a system to a reservoir is astronomically small, but for small systems one should always use S_{Gibbs}.

- The normalising constant $Z = \sum \exp(-E_i/kT)$ turns out to be useful in its own right: $U = -\frac{d\ln(Z)}{d\beta}$ and $F = -kT\ln Z$

- Attempts at second law violation by sorting fail: any process with a defined result is itself irreversible and gives rise to entropy increase. 347

5.8 Entropy and Information

(non examinable)

This section is here for further explanation but is non examinable, so the overheads have a **green outlined** title box.

Information and uncertainty: background NE

- In the ground breaking, 1948, paper 'A mathematical theory of communication' C.E. Shannon established the foundations of information theory. A central point of the paper is to establish a link between information and an entropy like formula, and to make a start on this subject we need to see why it is reasonable to propose this mathematical formulation for information content, and we will do this by considering 2 examples where you need information- meeting someone at an airport and guessing a sequence of letters.

- The value of information always depends on a context: if it tells you something you either already know, or something you would have no trouble guessing, it is of little value, but if it is something you would 'never have guessed' it is of high value, and this notion is what the maths aims to encoded. It is very hard to see how you could define information without a context.

- A good place to start however, is to consider how you might seek to quantify uncertainty. As an opening gambit we could propose as a measure of uncertainty as something to do with the chance you hit the right answer/message with a single guess. Suppose someone wants you to meet them at the airport, and the pickup carpark can only be occupied for whole hours starting on the hour. Suppose they say they are coming in a non leap year February (28 days), and aircraft arrive with equal probability on all days/at all times, then since there are 28*24 parking slots in the month, the chance of getting it right per guess is 1/(28*24) Note all this relies on a previously known context – you knowing about the timing of the parking slots, and when flights arrive, that the person is coming this February in a non leap year.

- **We can think of information as reducing uncertainty** – so what would for example telling you that the person was coming on Monday do to your chance of getting it right – well it increases it by a factor of 7, which is the chance that your original guess lay within the constraints of the new information. We propose that the value of this new information has something to do with the number 7.

Information and uncertainty: initial proposal NE

- If you have two unrelated bits of information (the person is coming on a Monday, and flights from their airport arrive between 2 and 4, you multiply the 'information numbers together to get the combined effect, but actually you would like to be able to add whatever numerical measure we have of information: suppose you receive two letters, each increasing by the same factor the chance of guessing correctly, then you would like to say that with 2 letters you have twice as much information as one.

> Initial Proposal:
> Define:
> uncertainty, U = - log(chance, given what you know about the context, that you would guess the right answer with a single guess):
>
> Define:
> information, H = log(fractional increase in chance of a single random, but 'informed', guess being correct given use of this additional information):
>
> Then, after the arrival of information:
> New uncertainty = Old uncertainty - Information

- This definition chimes well with our instinctive understanding of the value of information. If 75% of holiday cottages in an area have the key under the door mat, then, if you know this and the letter from the agent tells you 'the key is under the door mat' you would say 'I could have guessed that, why bother telling me' – *i.e.* the information is pretty worthless, but if the letter says 'go back up to the top of the hill, across the carpark on the left, and you will find the key attached to a fishing float hanging on the back wall of the boat store' you would say 'that was worth knowing, I would never have guessed that'.

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Derivation of Shannon Entropy NE

- Suppose we have a range of things we can guess with different frequencies of occurrence – for example guessing the letters in a message (we will suppose that there is no further information to be had/known than just the letter frequencies). Again, we have a context – it is known that letters occur with certain frequencies.

- In order to determine the chance that we guess the message, we need first to determine what the optimum guessing strategy is. Suppose letters occur with a frequency $\{p_i\}$, $\sum_i p_i = 1$, what is the optimum guessing frequency, $\{f_i\}$, $\sum_i f_i = 1$ *i.e.* you guess the ith letter a fraction f_i of the time?

Mean no of occurrences of ith letter in sequence: $\quad n_{i,av} = np_i$

For large values of n, probable values of n_i, the actual no of occurrences of the ith letter are fractionally very close to np_i

To get the whole sequence correct, you have to guess each letter correctly. If you actually have letter i, the chance you would have guessed the letter i is (as always) f_i so, given the ith letter comes np_i times in the sequence, the chance of guessing the whole sequence correctly, P_T, is:

$$P_T = \prod_i f_i^{np_i}$$

Derivation of Shannon Entropy NE

To maximize P_T (and equivalently $\log P_T$) subject to the constraint $\sum_i f_i = 1$ we can look for stationary points of:

$$L = \log P_T + \lambda \left[\sum_i f_i - 1 \right] = \sum_i n p_i \log f_i + \lambda \left[\sum_i f_i - 1 \right]$$

$$\frac{\partial L}{\partial f_i} = n \frac{p_i}{f_i} + \lambda = 0, \qquad \frac{p_i}{f_i} = -\frac{\lambda}{n}$$

Since the ratio p_i / f_i is independent of i, and both sets of fractions are normalized, we have $f_i = p_i$ and have deduced that the optimum guessing strategy is to guess at the same frequency as the letters occur in the message. We thus have:

$$P_T = \prod_i p_i^{n p_i}$$

If we define, as proposed, uncertainty as:

$$U = \log(\text{"chance of guessing correctly, given what you know about the context"})$$

we have:
$$U = -\log P_T = -n \sum_i p_i \log p_i$$

If a message arrives telling you the sequence, it removes all uncertainty, so one would define the information content of the message as:

$$H = -n \sum_i p_i \log p_i$$

which is Shannon's definition of the information content of a message, which he called its 'entropy' because of the comparison with thermodynamical entropy.

Information and 'Surprisal' NE

- Information is widely defined (as per Shannon) as linked to the 'degree of surprise' or 'Surprisal' you experience on receiving the letter, defined as $-\log p(m)$ where $p(m)$ is the probability that message m is chosen from all possible choices in the message space M. This is equal to the change of you guessing the message if you know what the probability distribution function, i.e. values of $p(m)$ are (because you are then able to adopt the optimum guessing strategy of guess according to occurrence). However, it is not so easy to use this notion of how surprised you are to derive the Shannon entropy – and indeed Shannon had to add in extra limitations in order to deduce it. It is also not so easy to see what 'partial information looks like' – ie information that does not remove all uncertainty.

- This focus on 'surprisal' not withstanding, the Shannon entropy is widely seen as a measure of the uncertainty in an outcome if the probabilities of individual outcomes are known, as proposed here.

Shannon entropy and data compression NE

- If a message contains N characters, then the Shannon entropy (information content) of the message is:

$$H_N = NH_1 = -N \sum p_i \ln p_i$$

Where H_1 is the mean information content of a single character.

- Since digital data is stored in binary, it is more usual to use $\log_2$ in the context of information theory. It turns out that the Shannon entropy tells you the minimum number of bits needed to communicate the message without loss (N bits carry a base 2 Shannon information) of N).

- The Shannon entropy can be used to evaluate how good a particular data compression scheme is, and if it if is worth looking for a better one

- The simplest way of encoding English letters (ignoring capitols) is to give a number to each symbol – which would require 5 bits (32 possibilities) per letter. Letters, however, occur with very different frequencies, (p(e)=0.0913, p(z)=0.007, p(space)=0.19[1]) giving a Shannon entropy of 4.1, so it is possible, in theory, to use an average of 4.1 bits per symbol to transmit English text (ignoring capitols and punctuation!). Morse code has a simple version of data compression: the most frequent letters (*e, t*) have the shortest codes (dot and dash), keeping the average code length down.

- If you transmit data down a noisy line – this formalism can be used as a basis for working out the maximum data rate and assess schemes for dealing with the noise –for example how many times you would need to repeat the message to transmit a message with a given max uncertainty, if that was your chosen solution.

[1]Numbers taken from David Mackay's book 'Information Theory, Inference, and Learning Algorithms' (CUP, free to read online) which is widely seen as the definitive work on this subject.

Information and thermodynamics NE

- The question arises as to whether the similarity of formulae between the Gibbs and Shannon expressions for entropy sheds light on what thermodynamic entropy is: on the back of this similarity, in some quarters, thermodynamic entropy is seen as a measure of the information you have about the system, and entropy increase seen as the loss (or more emotively 'destruction') of information. Thermodynamics, however, is primarily about macrostates for systems in a state of internal flux. We never determine the microstates, just measure averages over them of a system in flux. Information is about messages and the whole point is that you do determine what the message is, in complete contrast to thermodynamics. Thermodynamics does not seem to be about anyone or anything knowing anything. It describes how the macrostate changes as a result of the system randomly exploring the available microstates. We consider microstates only to average over their properties to get state variables. Even if one does start actually looking at microstates, because we are talking about systems in flux, all you can know/wish to know is the probability of each state – the subject is never about determining the microstate, or in what microstate someone else has put it.

- A more direct connection would seem to be with the concept of uncertainty – the more microstates in a microstate the less 'certain' we are about the microstate it is in and in this context there is a conceptual mapping of the Gibbs entropy onto the Shannon one. Given information removes uncertainty, then we have the same formula for uncertainty as for information. The connection between the Gibbs and Shannon entropies becomes clear – both are $-average\ value\ of \log(probablity\ of\ finding\ the\ state)$

- Stephen Hawkings talked, apparently, about the destruction of information when matter falls into a black hole. This course offers no concrete understanding of this, but points rather to the connection between thermodynamic entropy and uncertainty as opposed to information. One however needs to be very careful here: for a model to work, it links into the existing understanding/world picture of the scientist, and one person's meat can be another person's poison: a law works in the appropriate context, but we all come to science from different starting points, so one ought to be very wary about being too dogmatic about terms used descriptively.

● Does seeing that the entropy corresponds to the information theory concept of uncertainty help understand entropy in thermodynamics. Does it explain why spontaneous (*i.e.* undriven) changes result in an increase in the entropy ? In one sense yes, if the uncertainty increases, you cannot recover the original position without the arrival of information –and to get information about the system you have to measure, but at this point we are again going to cite our knowledge of thermodynamics: measurement increases entropy which compensates for the information increase, but I am not sure if this view point assists understanding entropy and its use.

● There is quite a lot of interest in the question as to whether we as observers, by the act of observation, influence the world with highly respected scientists making comments such as 'we look forward to the day when consciousness is included in quantum mechanics'. One could perhaps immediately sound a note of caution: overwhelmingly, measurements ('observations') are made today by rather simple machines, simple physical systems, (such as a light sensitive grain on a photographic film) but the issue is of real interest. This context is, however, perhaps one reason why it is appealing to the modern mind to look for a connection between 'information', with all its connotations of measurement and consciousness, and entropy.

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Entropy and disorder NE

● It is common for introductions to entropy to talk about it as a measure of disorder. Order implies everything in a defined place – either one microstate or perhaps a very few, whereas disorder implies uncertainty as to where things are and the random occupation of many different configurations – all of which are directly linked to the more fundamental explanations of entropy, suggesting the notion that entropy is a measure of disorder is a good one.

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