

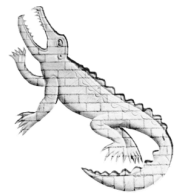
# Thermodynamics

## Kinetic Gas Theory & Transport Phenomena



Part 1B, Physics B

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### *Books and Acknowledgements*

**S.J. and K.M. Blundell** *Concepts in Thermal Physics* (OUP 2006)

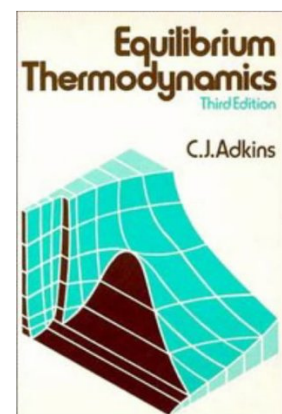
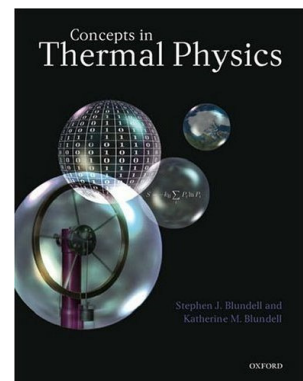
**C.J.Adkins** *Equilibrium Thermodynamics* (CUP, 1983)

H. B. Callen *Thermodynamics* (2<sup>nd</sup> ed. John Wiley & Sons, 1985)

R.Bowley and M.Sánchez *Statistical Mechanics* (OUP, 1996)

A.H.Carter *Classical and Statistical Thermodynamics* (Prentice Hall, 2001)

**These handouts draw on the excellent handouts of previous lecturers - Prof Erica Eiser and Prof David Ward, but the errors will be mine.**



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# Website, handouts & lectures

Copies of handouts/questions sheets are to be found on the Cavendish Teaching Information System.

There is no separate handout: these slides aim to be both 'slides' and 'handout' in the belief that it is easier to have just one resource to learn from.

The nature of the lectures: what is the story of the slides? I won't always go through every line of every derivation.

**Do watch the lectures and do take notes:** you need to be writing in a lecture if you are going to remember the material! This is a LECTURE course. The slides/handout are a summary of the main points, not a book on the subject.

**Do attend the 'in-person' lectures if you can:** whilst online has the advantage of 'pause/replay/ run faster in boring bits/don't get out of bed for 9am' in-person is totally different to online and much easier to learn from/remember. A live lecture is much more 'alive'.

All this is heading for Part II where (as now, actually) you need to 'study' the course – and not just attend lectures. **You need to spend time pondering/getting to grips with the lecture before the next one if you are going to understand this and indeed any other physics course.** TINA

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## How to study? (*≠ just going to lectures and doing supervision work*)

- **At the heart of science is problem solving:** 'knowing what to do when no one knows what to do' – either to understand new things, or applying current knowledge to unsolved problems (the light bulbs produced by the factory don't work today).
- But **this is very closely parallel to what we have to do continuously every minute of every day** to 'keep the show on the road', (e.g. walk or decide from our instantaneous first impression what reaction we expect from a stranger) and we are built with systems to enable us to learn how to do this either directly, or from others. The result is most people have a good gut intuition about basic science – after all if you are going to throw a ball, you need a pretty good instinctive understanding of mechanics.
- **Our 'automatic learning mechanisms' only get us so far:** some things are too complicated for the normal processes to work unaided, and we need to do experiments/learn from others/study more formally (lectures/supervisions/pondering), but the basic learning mechanisms remain.
- **Much of what we do in everyday life is (has to be) done 'on auto'** – i.e. 'the back room' comes up with ideas and solutions, which just seem to appear in our thoughts (if a tiger steps into your path you don't have to think whether/how to react), but it needs to be educated (face it out, don't run).
- **Some key steps in this natural process might seem to be:**
  - **Its iterative:** we are hard wired to look for/work out 'general rules', and we are designed to take notice of what we see often which by default is what is important/general.
  - **It involves pondering** – we need to mull over what we have seen.
  - **The 'back room' needs space and time to sort things out** – things are often clearer when you return after a break.
  - **The 'back room' gets hold of information much better when we output it** – so make sure you are writing during lectures, blog key ideas as you find them, produce ultra succinct summaries.
  - **We work best from 'stories'** – we are built to watch the world and for the 'back room' to work out/learn/use how things (e.g. tigers) work, so ask/find 'what is the story of the course'.

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## *Outline of Course*

0. Basic concepts in thermodynamics
1. 'Fundamental Principle', Zeroth & First Law
2. Second Law & Entropy
3. Analytical Thermodynamics
4. (First Order) Phase Transitions
5. Foundations of Statistical Thermodynamics
6. Third Law
7. Thermodynamics of Radiation
8. Kinetic Gas Theory
9. Introduction to Transport Phenomena

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## *Chapter 0*

### Basic concepts in thermodynamics

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## Thermodynamics: some quotes

- *'Thermodynamics is the only physical theory of universal content which, within the framework of the applicability of its basic concepts, I am convinced will never be overthrown.'* **Albert Einstein**
- *'The law that entropy always increases, holds, I think, the supreme position among the laws of physics. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations – then so much the worse for Maxwell's equations. If it is found to be contradicted by observations – well, these experimentalists do bungle things from time to time. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation'* **Sir Arthur Eddington**
- Thermodynamics is sometimes regarded as a rather grubby subject – the realm of chemistry, engineering and applied science – but it is not. It is one of the most important tools in science, often essential if you wish to consider a system with more than 2 interacting particles. The aim of this course is to try and gain an understanding of it and how to use it at a fundamental level, most importantly **'what is the second law?'**, **'what is its use?'** and **'why is it so inviolable?'**.
- Thermodynamics, properly applied, has the unique position in science in its ability to give virtually undisputable answers in complex situations.

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## Nature functions on distinct length scales

- The fundamental forces have very different length scales: nuclear forces are large on the  $< 2.5 \times 10^{-15} \text{m}$  length scale. At larger distances, electrostatic forces (including as dipoles/multipoles – charge is rarely isolated) dominate, with atomic sizes and bond lengths determined by the magnitude of the electrostatic potential and the mass of the electron. Gravity kicks in on the  $10^{-5} \text{m}$  length scale giving 'super large' scale structures (Trees, mountains, planets, stars, galaxies, clusters of galaxies).
- At each scale we describe what happens on that scale, but it is controlled by the properties of smaller entities at the next scale down.
- This leads to a clear hierarchy of phenomena: there is no sense in trying to describe a cat in terms of the motion of each of its constituent quarks/electrons.
- You also need a certain size 'object' for it to 'function' as opposed to just sitting there doing nothing. There are limits on how small you can make a mammal given the functionality you require and cell has to be a certain size to be able to do all it needs to do. You cannot make a small volcano. Rocks are less constrained.
- This hierarchy of interaction and self assembly gives nature its richness and fascination, and science needs tools and methods that work at different levels: **this is why we have different sciences** – each tends to work at a different scale of complexity with different methods. But most have the same basic problem of describing what happens at one scale in terms of a myriad of objects at the next scale down – and this is what thermodynamics is designed to do.

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## *Nature: change on one scale produced by motion on another*

- So far in physics we have only dealt with simple objects, e.g. a 'bar'. It is a fixed structure, so if you push on one end, the other end moves. This is fine if you are describing a machine/ a system made of these 'fixed object parts'.
- Nature is not ultimately made of 'bars' at any level, it's components come, can morph and go. The fascination with nature is usually change, and if we have an object, the question is usually how did it get there and what is it good for.
- Change on the macro scale requires each of the tiny components of a system to move/change the way they move. If you compress gas in a cylinder, very few of the molecules go anywhere near the piston – and a gas molecule is not connected to anything – they just diffuse around influenced by their local environment– yet they do so in a way that the gas as a whole moves.

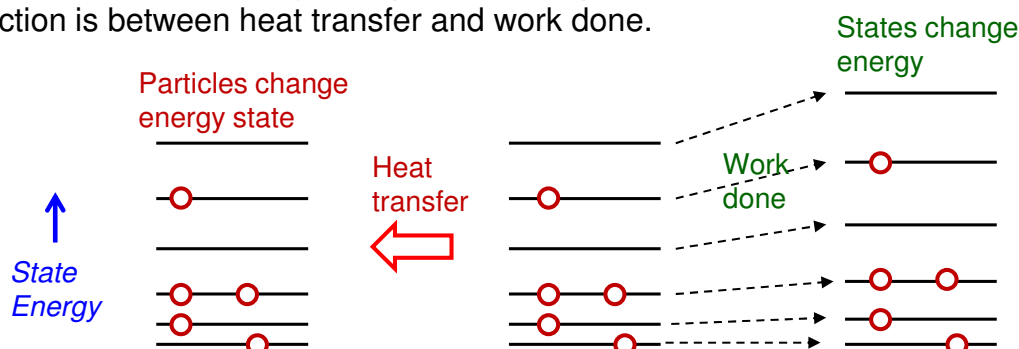
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## *Why 'thermo - dynamics'*

- Thermodynamics started as the study of heat, and heat flow. A central question was 'how to build a better steam engine' – hence 'thermo-dynamics'.
- From a classical perspective there are 3 ways change occurs on the macro scale:
  - Move heat.
  - Move particles.
  - Create/annihilate particles.

We shall see that the drivers that 'cause' heat to flow in a multiparticle system turn out to also 'cause' particles to move.

- Thermodynamics can 'handle' the effects of particle creation/annihilation.
- In classical mechanics where a particle is and what its energy is are separate questions. In a QM framework they are just aspects of the quantum state. We shall see a more useful distinction is between heat transfer and work done.

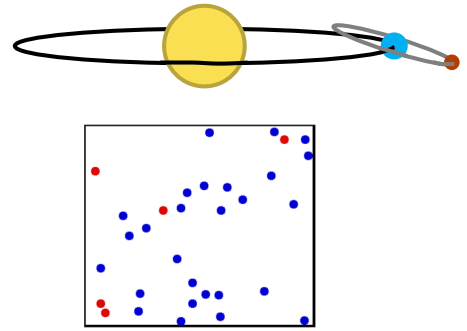


- We shall see that 'entropy' changes can be quantified by a heat transfer. Entropy relates to the distribution of the particles across the states: the wider the distribution the higher the entropy.

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# The multiparticle problem

- A fundamental problem in physics is dealing with any problem involving more than 2 particles. Even the ‘three body’ problem (e.g. motion of Sun, Earth, Moon system) cannot be solved analytically – let alone matter with  $10^2$ - $10^{80}$  constituent particles, yet the vast majority of things of interest in nature involve more than 2 particles!



- One approach is to try and decompose the system into semi independent ‘single particle like’ parts – for example the normal modes method in dynamics, or the concept of a ‘hole’ in semiconductor physics. – *i.e.* you work out how to duck the issue and make approximations that allow you to keep only considering single particle behaviour.
- An alternative is to give up trying to follow the motion of individual components of the system, and describe it in terms of ‘state variables’ – density, pressure, temperature, energy *etc.* – and this is the thermodynamic approach. It is amazing how successful and powerful this approach can be.
- Once you start thinking about multiparticle problems you realise that you really DO NOT want to know and think about what the individual atoms are doing – you want measures of overall behaviour. – consider a simple example (lecture computer simulation demo of a 2D gas of interacting particles)

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## Problems with direct simulations

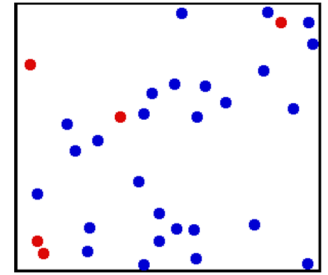
- Although the changes in structure and location shown by the system are caused by the motion of the individual atoms, **one is not at really interested in the details of this motion** – rather in the structures created and their properties.
- The time taken to compute a **classical ‘molecular dynamics’ simulation** like this scales as the number of particles (each particle only interacts with a certain number of neighbours) – for simple interactions and lots of computing power one might simulate **the motion of  $10^9$  particles** – roughly a cube of side length  $0.3\mu\text{m}$  of condensed matter – significant, but still rather small compared to most things of interest.
- The time and storage required to perform a ‘sledgehammer’ (ie no clever tricks/approximations) approach to a quantum system with  $N$  coordinates scales as  $N^N$  (!) **with a laptop you might be able to simulate the time development of the wavefunction of 2 particles** (20 digitisation points per coordinate requires 1GB to represent the wavefunction and would take 10’s of seconds for a single time step) – but not 3 ( requires 8TB storage) and the worlds most powerful supercomputer is not going to do much better.
- **A simulation is of limited use** anyway – it gives you the outcome of one set of initial conditions but other than giving you something you can watch and think about (ie an experiment you can do) – **gives you no insight into why the system does what it does – so you cannot generalise with confidence.** You need to do a new simulation for every new situation. As well as precise answers to ‘what happens’, you want ‘understanding’ to guide your thinking about the world – even if it only tells you approximately what happens.

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# The basic trick in thermodynamics: State Variables

- Rather than focus on the individual motion of all the constituents, with the system moving from one 'microstate' to another (each 'frame' in a very fast movie, with the position and velocity of all constituents defined, would be a different microstate) we look at the big picture - the 'macrostate' – characterised by 'state variables', properties such as temperature, pressure, density, latent heat, amount of material, derived from time averages over the different microstates the system explores.



- State variables work

**Either:** when thermal fluctuations are fast and an 'equilibrium' with well defined average properties is quickly established, at least locally, (hence the name 'equilibrium thermodynamics').

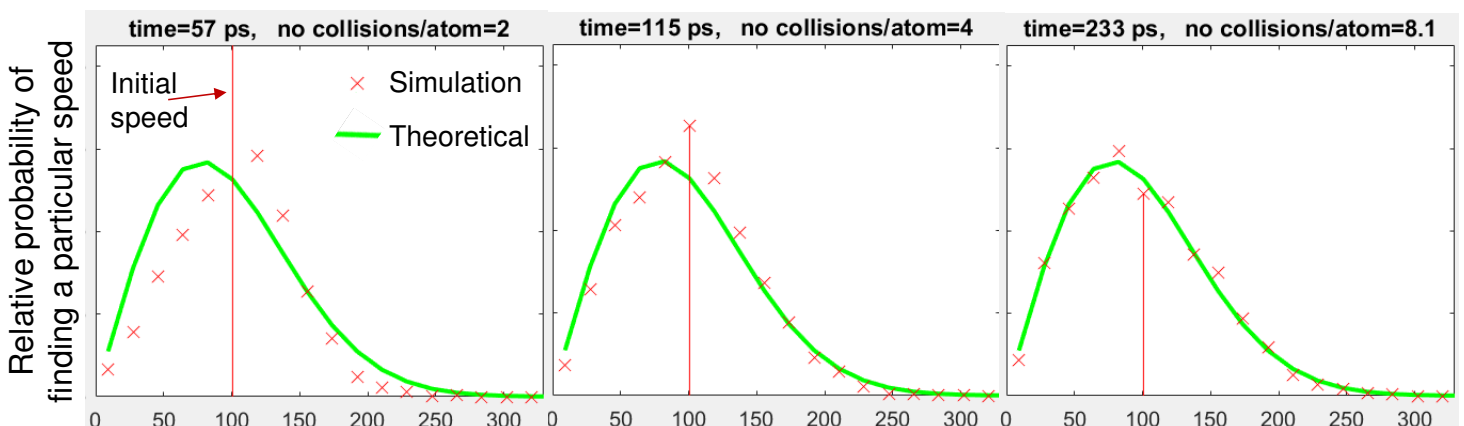
**Or:** when changes are so slow (cold crystal) that you can ignore them.

E.g. if you mix hydrogen and oxygen gas, they quickly inter-diffuse and establish a uniform mixture, but at room temperature and pressure they don't react on time scales of interest, so this 'aspect' of their properties can be left out of the consideration.

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## Rapid 'thermalisation' illustrated by 2D ice puck gas

- If you take a set of 'ice pucks' - hard disks with no long-range interactions and impulsive collisions - and start them all moving with the same speed but in random directions you find that after an average of just 4 collisions per ice puck, the velocity distribution is quite close to the theoretical one, and after 8 it is indistinguishable. The velocity has been 'thermalized' and 'memory' or the initial state erased. If you have not kept track of the process, 'information has been lost' – you know less about the velocity of each particle than at the start.

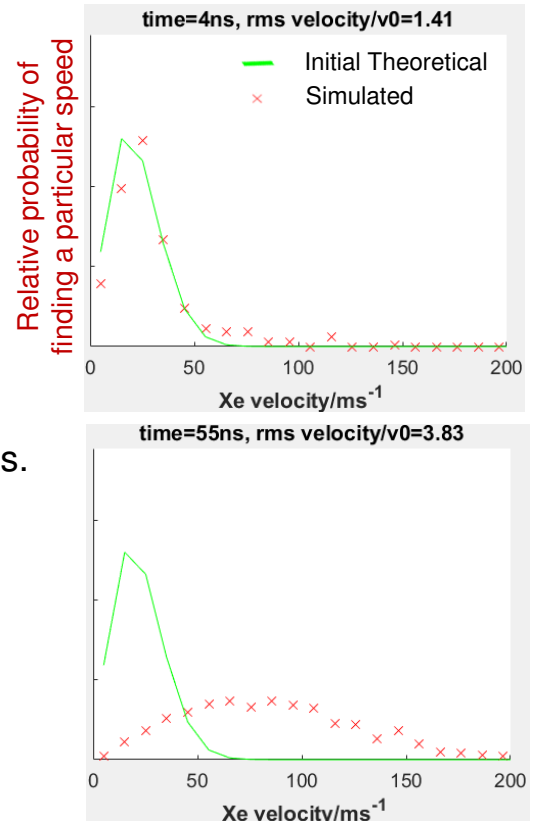


- We will see later that at 300K and atmospheric pressure, the mean free path of molecules in air is about 70nm. The mean velocity 470 m/s, and 4 collisions take about 0.6ns, so there is no macroscopic process in air for which the average speed and the velocity distribution (and hence temperature, pressure) is not locally well defined irrespective of initial conditions.

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# *A 'simple' example: condensation from 2D gas*

- **The small print:** the demonstration is a simulation of the atomic motion in a 2D gas of 400 interacting atoms, with parameters based on Xenon weakly adsorbed on a close packed metal surface (eg Pt(111)) at temperatures where the lateral variation of the adsorption potential is small enough to ignore (which can be realistic) and we consider what would happen if no energy is exchanged with the substrate (which is not realistic). The simulations starts with isolated atoms all moving at the same slow speed. As time progresses they start to cluster together.
- Starting with all atoms moving at the same speed, at first it just looks like the ice puck simulations – rapidly establishing a standard velocity distribution. *At short time scales we can ignore cluster formation (too slow)*
- On a longer time scale, small clusters form: the drop in PE gives a corresponding increase in KE.
- Eventually, if the box is not too big, the clusters coalesce into one crystallite, surrounded by 2D gas.
- *For a given box size and initial speed, the fraction of atoms in the crystallite at the end is independent of the atom's initial location and the direction of their velocities – thought the crystallite itself can be anywhere in the box, have a range of structures and indeed performs Brownian motion.*



# *The fundamental principle of thermodynamics*

*'The state variables of a system in internal flux are defined by specifying its volume, contents and energy and any constraints on the internal fluctuations.'*

(i.e. just leave it to fluctuate and it will settle down in some average 'equilibrium state')

- This applies to state variables describing the aspects of the system which fluctuate on the timescale of interest (e.g. intermixing of H<sub>2</sub> and O<sub>2</sub>, but not water formation if we are at 300K).
- In the 2D condensing gas example the temperature, the mean C.o.M. kinetic energy of the crystallite, the fraction of atoms as isolated atoms, as clusters of a certain size or in the crystallite, or the mean ratio of crystallite edge to its area are all defined once the volume, no of atoms and initial energy are specified.
- If you have particle creation, transfer, heat flow or volume change, then the 'source' of the energy/extra volume and the location of the particle creation must be within 'the box'.
- We do not consider the total linear momentum because we traditionally think in the center of mass frame. If the whole system is rotating, then one would need to also specify the total angular momentum as another conserved quantity.
- **This is the foundational principle of thermodynamics**, and works because state variables ARE DEFINED as time averages over the microstates the system can 'explore', and for systems containing a large number of particles, the deviations of the 'instantaneous' state variables around their mean values are very small. This is observed experimentally. A detailed justification comes from statistical thermodynamics.



# *Irreversibility and multiparticle systems*

- The condensing 2D gas simulation illustrates the way that for multiparticle systems a well defined change in macroscopic properties (e.g. moving from gas to gas + condensate) is always an irreversible process: once formed, the crystallite does not re-evaporate into a 2D gas.
- If there was more energy in the system, then starting with a crystallite, it would fly apart into a 2D gas and never reform: an irreversible process, but in the other direction.
- A central property of multiparticle systems is that they show irreversible behaviour: Heat flows from hot to cold – never the other way unless ‘pushed’. A gas expands into a vacuum – and only returns if ‘pushed’.
- This illustrates a very fundamental principle. **If a system has two macro states**, then, provided the system moves ‘by itself’ (i.e. is isolated and hence not driven by some external agent), **the path from one to the other is irreversible (i.e. the system can only go one way)**. i.e. the direction of this permitted path is determined only by the nature of the initial and final states, and not by the details of how the system moves or can move from one state to another. **This is actually a good general statement of the second law of thermodynamics...**

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## *Any defined ‘result’ is achieved by an irreversible process*

- If a macroscopic process is achieved or can be achieved (if not driven) by the microscopic ‘fluctuating’ motion of its constituents, then unless the process is irreversible, there is nothing to stop these fluctuations undoing what they have just done. We therefore conclude:

*Any process of a macroscopic object which results from the microscopic motion of its constituents and induces a macro scale change with some permanence is a result of an irreversible process.*

(After all by ‘change’ we often mean something that changes – i.e. does not just wander back to where it has come from.)

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## *Irreversibility can be harnessed to 'create' energy*

- Whatever 'drives' an irreversible change can be harnessed to produce work which can be stored as energy.
  - An expanding gas can be made to push on a piston.
  - A steam engine harnesses the flow of heat from hot to cold.
  - $\text{H}_2 + \text{O}_2$  burn irreversibly – but the reaction can be directly harnessed in a fuel cell to produce electrical power.
  - The mixing of fresh and salt water when a river flows into the sea is irreversible – but could power be produced from this? (Answer: yes - enough to supply the worlds electricity requirements if you could work out how to harness it).
- This raises the question as to what is doing the 'driving' and how much work can a particular irreversible process produce. These notions are quantified by the concept of 'entropy'.

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## *Energy can be used to work against/reverse an otherwise irreversible process*

- In a multiparticle context. macroscopic moving objects dissipate energy to the surrounding particles: an irreversible process. Once friction has stopped an object moving, the energy dissipated does not return 'all at the same time; and push the object over whatever energy barrier is constraining it. But a force can be applied and work done to act against this dissipation and create and maintain motion.
- Work can be used to drive an otherwise irreversible process backwards:
  - A piston can compress a gas.
  - A heat pump can move heat from cold to hot (eg a refrigerator).
  - Water can be electrolysed to produce  $\text{H}_2 + \text{O}_2$ .
  - Seawater can be desalinated by reverse osmosis.
- Energy is the ultimate resource. Multiparticle processes either occur 'just by themselves' in which case they are irreversible, or they can be driven by the expenditure of energy. Everything 'constructive' we see (ie things that work against dissipation: plant growth, thunder storms, animal function, mining, ore smelting) is driven by energy.

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## *The trade-off between space and energy*

- At high temperatures everything becomes a gas which expands into a vacuum – things tend to fill space.
- At low temperatures the system goes for the state of lowest energy – all gases condense to liquids or solids as they are cooled.
- At intermediate temperatures there is a trade off between the tendency to spread out into space, and the tendency to go to the lowest energy state – this is a fundamental issue of multiparticle behaviour that thermodynamics addresses.
- Consider an ‘isothermal atmosphere’ – gas at constant temperature with a pressure dropping as height increases. Gravity causes the gas molecules to accelerate downwards, but the density gradient balances this by causing net diffusion upwards. *A density gradient balances a force, even though there are no long range interactions between the molecules ... (!)*

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## *Classical and statistical thermodynamics*

- **All this talk of macroscopic behaviour being the average result of microscopic motion makes one think that the next step will be to start thinking about the statistics** of what is going on and derive state functions from them. This is the approach in ‘statistical thermodynamics’ and delivers ‘the reason why’.
- **BUT we are not going to do this just yet.** We are first going to look principally at ‘classical thermodynamics’ – an entirely empirical subject based on experimental observations of how ‘stuff’ behaves. Whilst this may seem counter intuitive, there is good sense in this. Before you study the explanation of how the world works, it helps to know what it actually does. More fundamentally, however, **the state functions that proved so very useful in describing out simulations are derived/developed/given meaning in classical thermodynamics** – and it is not at all clear how quickly, for example, you would hit on the idea of temperature if you only did statistical thermodynamics – its actually a pretty subtle concept – let alone something like entropy.

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# *The fundamental aims of the course*

- The aim of this course is to help you **to acquire a understanding of the central ideas of thermodynamics and in particular the concept of entropy** so that in Part II you can finally and definitively master the subject, but you will only gain this understanding if you take time to study the course outside lectures, pondering and trying to make sense for yourself of what is going on.
- Whilst classical thermodynamics is recognised as a perfectly rigorous development of the consequences of a set of experimentally observed empirical laws, statistical thermodynamics, and in particular the concept of entropy in statistical thermodynamics is often presented as based on a series of Ansätze. **This course aims to show that these assumptions are unnecessary and that thermodynamics follows simply and directly from the underlying classical/quantum mechanics.**
- (Maybe you will also come to understand why temperature is actually a more complex and subtle concept than entropy.)

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## *Section 0: Summary*

- Physics often deals with highly simplified situations – we want to understand what happens at a fundamental level – but the real world is complex and to use this knowledge to understand the universe we need to apply it in a context of multiparticle systems.
- The real world is hierarchical: what happens on one level is often determined by motion on a smaller scale. But we want to describe what happens on a large scale in terms of large scale parameters – not the individual motion of the constituents.
- The basic trick is to use ‘state variables’, which works because locally at least microscopic fluctuations/motion mean the constituent particles quickly ‘adjust’ their behaviour and configuration to fit the local conditions giving well defined macroscopic properties.
- Central to all this are irreversible processes, which can be harnessed to produce energy, and can be driven in reverse by the expenditure of energy. Any ‘change’ of a multiparticle system that is not then undone by microscopic fluctuations/motion is due a irreversible process. We notice that there seems to be a trade-off between space and energy in determining what happens.
- The whole universe and its many parts are largely driven by irreversible processes, and we need a measure of how far this irreversibility has gone: is state A (e.g  $\text{H}_2 + \text{O}_2$ ) or state B ( $\text{H}_2\text{O}$ ) of some local system further down the irreversible track?? Entropy is a measure of this and is central to thermodynamics.
- This course puts these notions on a quantitative footing, and starts to show how this can be used to understand and manipulate multiparticle systems.

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