Thermodynamics 1

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This lecture

- Temperature
- Heat and work
- Zeroth law
- First law
- States
- Entropy
- Second law
- Ideal gas

Introduction

- Thermodynamics concerned with efficiency of steam engines. A phenomenological study.
- The properties investigated during the early days can now be explained through **statistical mechanics**. Statistical mechanics looks at motions of individual molecules in a bulk medium.
- We usually observe averages of distributions of properties and not individual particles because there are so many particles.

Temperature

- What is temperature?
- The thing you measure with a thermometer
- How do you use a thermometer and what does it do?

Temperature

After a time, the thermometer is the same temperature as your armpit.

- If two things have been in contact for long enough, they will have the same **temperature**.
- The things are in **thermal equilibrium**.
- In contact? Exchange energy as **heat**.
- Temperature describes the tendency of an object to give up energy spontaneously to its surroundings. It tells you in which direction heat will flow.

Temperature scales

- SI unit for temperature is the **kelvin**, K.
- temperature in kelvin = temperature in degrees celsius + 273.15
- For a temperature scale we need reference points. Degrees Celsius sometimes called degrees centigrade: freezing water $\rightarrow$ 0 °C, boiling water $\rightarrow$ 100 °C.
- These numbers are arbitrary!
- 0 K = absolute zero

Heat and work

Heat is the spontaneous energy flow caused by a difference in temperature (doesn't matter how this happens). We use Q.

Work describes any other energy transfer. Denoted W.

These are not stores of energy, but energy flows.

Rub hands together!

Equilibrium and the zeroth law

- Thermal equilibrium: when two things have the same temperature
- If there is no nett heat flow, and no work done by one system on another, then no energy will be transferred between the two.
- **Zeroth law of thermodynamics**: if two systems are each separately in thermal equilibrium with a common third system, then they are in thermal equilibrium with each other.
- Sounds obvious but if wasn't the case we would have some trouble defining temperature!

Check!

Answer me these questions three

- Is temperature extensive or intensive?
- Is temperature an energy?
- Should you use $^{\circ}$C or K for thermodynamics calculations?

First law

- Conservation laws are one of the real joys of physics!
- This is a statement of conservation of energy
- When work *is done on* and heat *is added to* a system, the **internal energy** U increases by an amount equal to the sum of the heat and the work.

$$\Delta U = Q + W$$

- Sign conventions: the one we use is heat added is positive, work done *on* the system is positive. Others work (!) fine. Consistency is key!

(Another sign convention: work done *by* system is positive so first law is written $\Delta U = Q - W$)

States

- Heat, work: change state!
- N particles with a certain amount of total energy – different microscopic arrangements
- Assumption: there is no preference for one state over another so all microscopic arrangements are equally likely
- If we have a giant collection of systems (an **ensemble**) the most commonly observed arrangement will be the macroscopic state
- **Multiplicity**, Ω, of a state is the number of **microstates** corresponding to a **macrostate**
- Short particles in boxes discussion

States

- **Functions of state** (aka state functions) relate **state variables**, which are properties of the present equilibrium state of a system.
- Pressure P is a state variable when we specify equilibrium state of a system with it.
- Pressure P is a state function when we discuss how P varies with V and T etc.
- State variable is determined by initial and final states, NOT how you get between them
- Internal energy is a state function; work and heat are not! Notation fuss time:

  $$dU, dT \text{ etc. for functions; } \;\; đW, đQ \text{ etc. for ``inexact'' functions}$$

Entropy

- Moodle time (thanks Matt)
- Entropy always increases!
- Things always tend towards disorder!
- Quantum mechanics? Information theory?!?!?!?!?!?

Entropy

- *Derivation was for constant volume*
- In thermal equilibrium no nett heat flow – so a small exchange of energy does not change the most probable state, i.e. number of states is constant.
- The **entropy** is the macroscopic quantity that tells us the most probable state. This quantity, $\ln w$, has derivative $= 0$.
- Need SI units so have Boltzmann constant k.

$$S = k \ln w$$

For fixed volumes: $\dfrac{\partial S}{\partial U} = \dfrac{1}{T}$

Second law

$$S = k \ln \Omega$$

"Statistically less probable macrostates do not occur spontaneously; systems evolve to their most probable macrostates."
Most probable?

For any process:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$$

If you have an isolated system: ΔS is still ≥ 0.

Ideal gas

- A joy of physics is the concept of the *ideal*
- An **ideal gas** is a low-density gas: average space between molecules $\gg$ size of a molecule
- There is no potential energy between the molecules. They can crash into each other but that's it.
- An atrocious approximation to a pizza
- The ideal gas has a certain **equation of state** – derivation up on moodle courtesy of Matt

Ideal gas law

$$PV = nRT$$

P = pressure, V = volume, n = number of moles of gas, $R = 8.31$ J mol^{-1} K^{-1}, T = temperature (in K!)

Ideal gas law

$$PV = NkT$$

N = number of particles, $k = 1.381 \times 10^{-23}$ J K^{-1}

k is the **Boltzmann constant**. Physics preferred (number of particles instead of moles)!

$$R = N_A k$$

N_A is Avogadro's number.

Check!

Answer me these questions three

- What is the first law?
- Which of the following cannot be state variables: N, P, Q, S, T, U, V, W?
- Entropy always increases. True or false?