



Some here are notes repeated from TOPIC 18, for material not done in lecture 18.

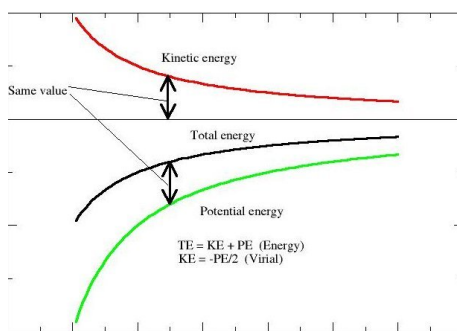
Synopsis

Limits of thermodynamics, Nonequilibrium thermodynamics. Fourth Law.

Equilibrium

Most of this course has considered systems in equilibrium, or constructed equilibrium pathways between initial and final states connected by irreversible processes. But most interesting systems, from the human body to the earth, to the Universe itself, are out of equilibrium.

Breaking the Law - Virial theorem and Self-gravitating clusters



Clausius derived the virial theorem...

If the force between particles of the system results from a potential energy that is proportional to some power n of the inter-particle distance r , the kinetic energy is $n/2$ times the total energy.

So for gravitational clusters ($n = -1$) the average kinetic energy is equal to minus half the average potential energy, where PE is negative and KE positive. So we can write:

$$KE = -PE/2 = -U$$

This is similar to the equipartition theorem - energy is equally divided between all degrees of freedom, but it applies to inhomogeneous systems. If we add some heat energy to the system, increasing the PE (to a smaller negative value), then the KE must decrease. If we also equate the KE to a temperature, then the temperature *decreases* as we add heat. *Negative heat capacity!*

This applies to systems such as self-gravitating star clusters floating in a vacuum ($P=0$), where the “Heating” might be the addition of a fast-moving star. Our proof of positive heat capacity from the second law doesn’t apply because the systems are inhomogeneous. The “boundary condition” is that the system self organises. They also *expand*, so while the intensive entropy may decrease, the total entropy does not. ¹

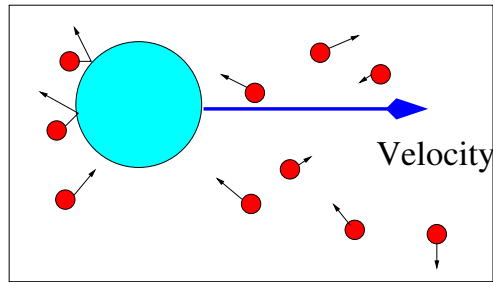
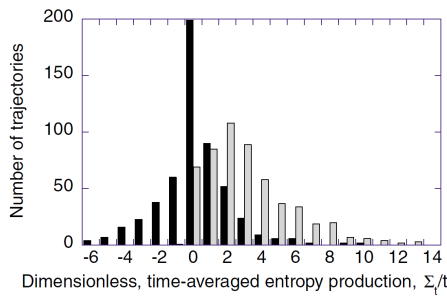
Breaking the Law - Fluctuation Theorem

The “fluctuation theorem” can be derived from statistical mechanics. It relates the probability that a process will produce entropy, S , to the probability that it will spontaneously reduce entropy by $-S$,

$$p(-S)/p(S) = e^{-St}$$

This was first shown in computer simulation (1993), proven analytically in 1994 and finally demonstrated experimentally in 2002. The experiment involved moving a tiny bead in an optical trap slowly through a solution of other beads and measuring the force needed to move it: this force fluctuates depending on whether more of the other beads hit it from behind or in front.

¹see paper by Mr and Mrs Lynden-Bell MNRAS, 181, 405 (1977)



Movement of the bead in the trap is regarded as *work*, movement of other beads as *heat*. On rare, and *unpredictable*, occasions work is done *on* the trap bead from the environment, violating the Kelvin statement. The resolution is that the Second Law is really statistical, and that *on average* work has to be done to move the trap-bead.

Hysteresis and Nucleation

Hysteresis is the phenomenon where a phase transition happens for a different value of the “driving parameter” on increase or decrease. e.g. supercooled liquid or pressurized diamond.

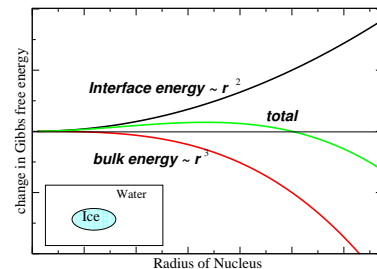
This cannot happen in equilibrium thermodynamics, but it is quite common in reality. One reason is that to create a nucleus of the new phase with lower Gibbs free energy, one must also create an interface of higher Gibbs free energy. For a spherical nucleus of ice, the balance of energy is:

$$\Delta G = 4\pi r^2 \Delta G_{interface} - \frac{4}{3}\pi r^3 \Delta G_{ice-water}(T)$$

Such the nucleus can only occur spontaneously for $R > 3\Delta G_{interface}/\Delta G_{ice-water}(T)$.

In practice, there is some probability of such a “critical nucleus” appearing by chance, at which point it will grow and trigger the transition. The probability of such a chance event is proportional to $\exp(-\Delta G/kT)$, and for positive $-\Delta G$ this may require many years.

So in practice, on steady cooling, the phase transition happens after $\Delta G_{ice-water}(T) < 0$. The same argument applies to steady heating. Hysteresis also occur in magnetic transitions. It is not reversible, the integral around the cycle gives a positive value, so net work must be done to drive the system through the transition and back.



“Laws” for nonequilibrium processes

Von Neumann referred to the search for nonequilibrium as akin to “a theory of non-elephants”. The point being that in equilibrium we needed a different potential (U,H,F,G) for each equilibrium boundary condition - how many more ways are there of being out of equilibrium? For some boundary conditions we have perfectly good nonequilibrium Laws, such as Ohms Law.

Nonequilibrium systems lead to more empirical “Laws” relating flows to driving forces which can’t be derived from thermodynamics. e.g.

Fourier’s Law of heat conduction $J_q = -\kappa \nabla T$

Fick’s Law of diffusion $J = -D \nabla n$

Ohm’s Law $I = V/R$

Newtons Law of cooling $\frac{dT}{dt} = -K(T - T_s)$

Actually, these “Laws” are really only Taylor expansions valid for small driving forces.

Dynamical Transitions

There is an important distinction between “Equilibrium” and “steady state”. Both are unchanging in time, but a system in equilibrium with its surroundings produces no entropy or work. By contrast a viscous fluid flowing through a pipe continuously dissipates heat (creating entropy), while a steadily-running engine produces work. “Steady state” systems can have “dynamical” phase transitions: e.g. from laminar flow to turbulent flow.

One of the curious features of dissipative systems is the spontaneous formation of ordered structures. These can have transitions between different states of macroscopic order, some of which are hard to define, like consciousness and death.

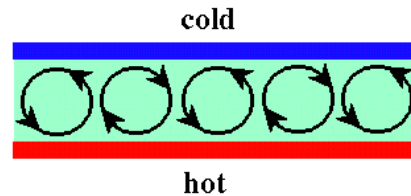
Convection

Consider a fluid contained between a hot plate and a cold plate. Heat can flow from hotter to cooler according to simple heat conduction:

$$\frac{dQ}{dt} = -k\nabla T$$

where k is a material property, the thermal conductivity.

But for a real fluid, heat can also be transported by macroscopic processes, convection. If a fluid is heated from below, at some critical point the denser material at the top starts to fall, and the hotter material rises. It is obvious that the factors at play here are gravity (g), temperature gradient, thermal expansion (β), viscosity (ν) thermal diffusivity α . One can define a dimensionless quantity called the Rayleigh number balancing the gravitational and viscous forces.



the gravitational and viscous forces.

$$R = \frac{g\beta}{\nu\alpha}(T_b - T_u)L^3$$

The point at which *Rayleigh-Benard* convection starts depends on the boundary conditions, and can be found in two ways. Either through mechanical stability of the system, as Rayleigh did or, by measuring which out of convection and conduction produces entropy at the fastest rate. For free boundaries the solution turns out to be $R_c = 274\pi^4$.²

This convection instability occurs many times within the earth. Convection of molten iron in the core gives a magnetic field³. Convection of rocks in the mantle drives plate tectonics⁴. Convection in the oceans circulates nutrients from bottom to top. Convection in the atmosphere pushes air down and away from deserts and upwards and into tropics⁵.

²In theory - in practice if the pot has no bottom, the water will fall on the fire!

³The viscosity of iron in those conditions is about the same as water

⁴Non-infinite viscosity of rocks is due to *creep* - look it up!

⁵Hadley cells - there are six on earth. Nobody knows why

Turbulence

“When I meet God, I am going to ask him two questions: Why relativity? And why turbulence? I really believe he will have an answer for the first.” Heisenberg

When a fluid flows too fast, under specific and reproducible conditions it becomes turbulent. Is this to increase its entropy production by increasing mixing at the cost of flow rate?

At junior honours level, I’m afraid there’s little more to say. The transition to turbulence in a given geometry can be empirically associated with a specific value of the dimensionless “Reynolds Number” $Re = \rho v L / \mu$ (fluid density, fluid velocity, “Characteristic Length”, fluid viscosity). It also emerges from the so-called “Navier-Stokes” equation, which is a non-linear differential equation.

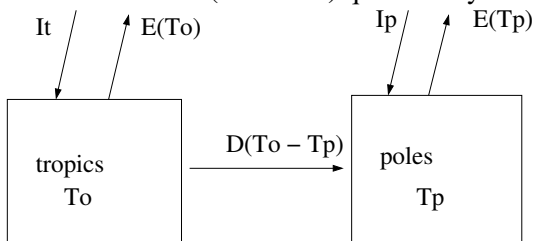
Principle of Maximum Entropy production

So it seems the nonequilibrium law might look like “Systems organise to maximise their rate of entropy production”. This actually works well in a number of cases. One of the nicest is a simple climate system.

Heat energy I_t on a planet arrives at high frequency from the sun (the hot reservoir) and is re-radiated back into space at lower frequency (Stefan radiation at the temperature of the planet σT^4). For the atmosphere, we have heat flow from the hot equator to the cold pole, $D(T_o - T_p)$. A simplified model balancing fixed heat flows is.

$$I_t - \sigma T_o^4 = D(T_o - T_p) = \sigma T_p^4 - I_p$$

Without worrying about details, we see we have two equations in three unknowns (D, T_o, T_p). D depends on a huge range of processes involving all the degrees of freedom in the earth. An entire global circulation model would be needed to calculate $D(T_o - T_p)$, and experimentation is impossible (or unwise). A simple assumption to treat the system as a heat engine, picking D to maximise $\frac{dS}{dt}$ turns out to describe the Earth (and Titan) quite nicely.



This flow of heat from hot to cold is ultimately the heat engine drives biology. Photosynthesis converts high frequency solar radiation to chemical energy and ultimately heat. A hard line on Maximum Entropy production would regard biology as the most efficient way of producing entropy.

Maximum Entropy Production is not fully accepted as being generally true, nor does it provide a recipe to say what emergent structures or processes would maximise entropy production.

The Lack of a Fourth Law of Thermodynamics

The Second Law tells us how systems equilibrate to a minimise of the appropriate thermodynamics potential. Newton’s Second Law tells us that force is a change in energy, directed towards equilibrium. It seems that there should be some “Thermodynamic” force to say *how* a system moves towards equilibrium. It is always possible given enough computing power to follow the behaviour of every particle and deduce macroscopic principles. A Fourth Law would shortcut this process by enabling us to deal with macroscopic quantities directly.

But there isn’t one.

Yet.