School of Physics and Astronomy

Junior Honours **Thermodynamics**   GJA 2019-2020

Lecture TOPIC 15 (Finn: 11.1 11.3 11.4, 11.5, 5.10)
Synopsis: The Third Law of Thermodynamics. Entropy, probability, disorder.

The Third Law of Thermodynamics.

The Third Law defines the behaviour of entropy at absolute zero.
The Nernst Heat Theorem is an early statement, a compromise version of it is

> *Any system undergoing a process between equilibrium states as a result of external influences, such as pressure, experiences a change in entropy. This change in entropy tends to zero as the temperature characterising the process tends to absolute zero.*

Nernst made *experimental observations* as summarised in the diagram. He noticed that for many chemical reactions, the change in enthalpy ΔH, increased as T rose, while ΔG was reduced. Asymptotically, (at zero T) it appeared that they went to the same value, and with zero slope. From the definitions of G and H for the two curves

$$
\begin{aligned}
\Delta G \;=\; G_f - G_i \;&=\; \Delta H - \Delta(TS) \\
&=\; H_f - H_i - T(S_f - S_i) \\
&=\; \Delta H - T\Delta S
\end{aligned}
$$
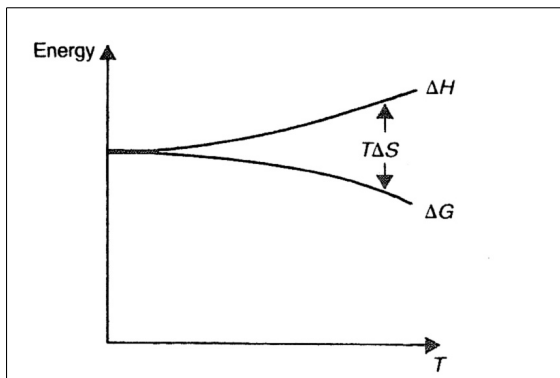
Obviously $\Delta H = \Delta G$ at T=0, but the curves only touch asymptotically if $\Delta S \to 0$.

An alternative statement of the Third Law, attributed to Planck, refers to a perfect crystalline state.

> *The entropy of all perfect crystals is the same at absolute zero, and may be taken to be zero.*

The key feature is that all perfect crystals would all have the same value of entropy at the absolute zero of the thermodynamic temperature T. That this value should be uniquely chosen is not just a matter of convenience. The choice $S_0 = 0$ at $T = 0$ allows a strong link to be made between thermodynamics and statistical mechanics where the same assumption is made **and supported by evidence from a very wide range of physics phenomena**.

All this leads naturally to a third statement of the Third Law, due to Simon :

> *The contribution to the entropy from each **aspect** of a system which is in thermodynamic equilibrium disappears at absolute zero.*

It is usually helpful to be able to separate out the various contributions to entropy (which is an "extensive" variable – so various contributions can be added). For a crystal, contributions come from the arrangements of atoms ("configurational entropy"), from the orientations of atomic spins, or molecular units, from nuclear properties ("nuclear spin") and from motion of all of these (eg lattice vibrations). As we saw in magnetic cooling, isenthalpic processes may involve entropy changes in individual components only the total is conserved.

The validity of the Third Law, however it is stated, stems from its derivation from properties of substances in general and its successful use in describing the low temperature behaviour of a wide range of processes and parameters.

Consequence: Vanishing Thermal expansion coefficient, β

Use a Maxwell's relation to get $\beta = \frac{1}{V}(\frac{\partial V}{\partial T})_P = -\frac{1}{V}(\frac{\partial S}{\partial P})_T$. n.b. the partial derivative is isothermal.

By the Nernst statement, as T approaches zero, $\Delta S \to 0$, and so $\beta \to 0$.

Consequence: Vanishing Heat capacity $C_V = T(\frac{\partial S}{\partial T})_V$.

Use $\frac{d}{dT}\ln T = \frac{1}{T} \Rightarrow d\ln T = \frac{dT}{T}$ to get $C_V = (\frac{\partial S}{\partial \ln T})_V$.

As $T \to 0$, $\ln T \to -\infty$, so for a given small change ΔT, $\Delta S \to 0$ but $\Delta(\ln T)$ may still be quite large. That means that $\frac{\Delta S}{\Delta \ln T} \to 0$. and $C_V \to 0$ as $T \to 0$. The same conclusion is found for all specific heats.

Experimentally, for metals at low temperatures $C_P = aT + bT^3$ where a and b are constants. The first term is associated with heat uptake by (or release from) the conduction electrons **aspect**, the second is associated with the lattice vibrations **aspect**.

Consequence: Zero slope of the phase boundary for first order transition

Recall the Clausius Clapeyron derivation $\left(\frac{dP}{dT}\right)_{PB} = \frac{\Delta S}{\Delta V}$

Since $\Delta S \to 0$ as $T \to 0$, so the slope of the phase line must be zero. This is observed experimentally, e.g. for the liquid phase II / solid phase transition for He^4 in the low temperature limit.

The Third Law: unattainability of absolute zero

Another statement of the Third Law:

> *It is impossible to reach absolute zero using a finite number of processes.*

Example: Magnetic cooling again

Different aspects of entropy were illustrated by refrigeration using adiabatic demagnetisation (Topic 11). In this method, a paramagnetic salt is first magnetised at constant temperature - extracting entropy from the magnetic aspect. It is then demagnetised adiabatically, shifting thermal entropy into the magnetic aspect, whereupon its temperature falls. The repeating two stages, isothermal magnetisation plus adiabatic demagnetisation, is a process which cannot reach absolute zero according to Third Law.

Aside: The Schottky relation $c = b/T^2$ (Topic 11) does not obey the Third Law. That's because at low enough T, paramagnets acquire spontaneous magnetisation (Curie-Weiss Law) for which the Schottky heat capacity is $c = b/(T - T_c)^2$. Below T_c, heat capacity drops

Consider a succession of these processes between zero and a fixed value of magnetic field. With the final temperature of one process being the initial temperature of the next, the temperature drop becomes progressively smaller. The two curves of entropy versus temperature, one for zero field ($B = 0$) and the other for fixed field $B = B_0$, both end on $T = 0$ with $S = 0$ according to the Nernst statement of the 3rd law. Graphically it is seen that the decrease of entropy in successive processes becomes smaller in such a way that for a finite number of processes neither the entropy nor the temperature reaches zero.
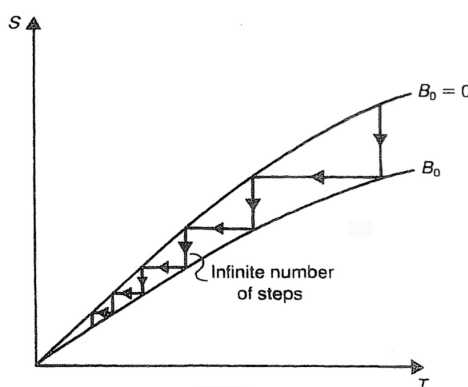
Disobeying the Third Law: Ideal Gas Entropy and Free Energy

The heat capacity for an Ideal gas is $c_v = 3R/2$, independent of temperature.

Using $\frac{c_v}{T} = (\frac{dS}{dT})_V$ and a Maxwell relation $(\frac{dS}{dV})_T = (\frac{dP}{dT})_V$ we can easily calculate changes in ΔS:

$$\Delta S = \int_{T_0}^{T} \frac{C_v}{T}dT + \int_{V_0}^{V} \left(\frac{\partial P}{\partial T}\right)_V dV = \int_{T_0}^{T} \frac{3NR}{2T}dT + \int_{V_0}^{V} \frac{NR}{V}dV = NRc_v \ln\frac{T}{T_0} + NR\ln\frac{V}{V_0}$$

Which implies that the entropy difference between absolute zero and finite T for an ideal gas is infinite. Obviously this is nonsense: the absolute value of Entropy (and Free Energy G, and F) are undefined for an Ideal Gas. The best we can do is find their value relative to some reference state.[1]

Glasses: Kauzman's Paradox

Glasses look as if their entropy cannot be reduced to zero even if they can be cooled to 0 K - the figure[a] shows data derived from specific heat measurements for various supercooled liquids.

There are many ways to arrange the atoms to still be a glass. A glass does not have the long range order of a crystalline substance. It has entropy "frozen-in". It is well known (if often untrue) that – like a liquid – glass can flow (though extremely slowly) with structure gradually crystallising.

So the get-outs are that ideal gases aren't quantised, and glasses are not equilibrium systems!

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[a]Debenedetti Nature 410, 259-267, 2001, after Kauzman
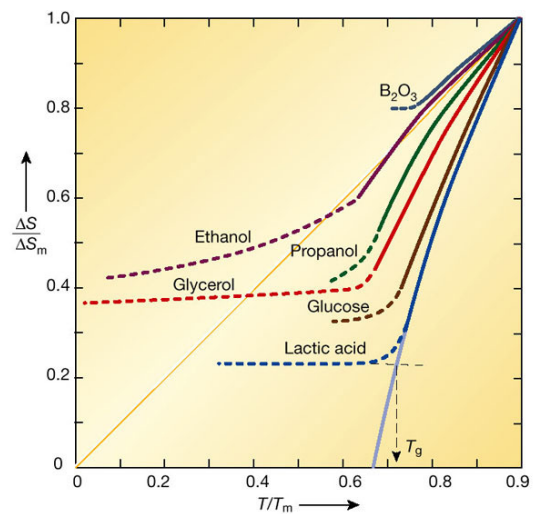
Thermodynamics at the microscale: Statistics, entropy, probability and disorder

DEFINITION: A micro-state as *a way the particles could be arranged at one instant in a given phase*
DEFINITION: A macro-state is *a group of microstates which correspond to the same thermodynamic quantities, P, V, T, phase etc.*
DEFINITION: Ergodicity means that *it is actually possible to move from any microstate to any other.*
DEFINITION: Equipartition means that *any microstate in an isolated system is equally likely.*[2]

Note that thermodynamics is *not* just a consequence of microscopic statistical mechanics. Macrostates can only be defined at the macroscopic level, and without knowing what the macrostate is, one cannot count its microstates. The number of microstates W is a rapidly increasing function of the energy. In the Boltzmann definition, $S = k_b \ln W$, so zero entropy means there is only one way of arranging the atoms ($W = 1$). At the lowest temperature there will eventually only be one state, the quantum ground state, and entropy $S = k_B log(1) = 0$.

Microstate as a point in multidimensional "phase space"

A full description of a system at give time requires six coordinates per particle, three postional and and three for momentum ("six degrees of freedom"). For a gas in equilibrium, the molecules are distributed uniformly in space. Their momentum directions are also uniformly distributed in "momentum space" $\mathbf{p}=(p_x, p_y, p_x)$. The distribution for momentum magnitude p has a single maximum, and is known as the Maxwell-Boltzmann distribution.

A countable (quantised) volume of the phase space is $\Pi_{i=1}^{N}(\Delta\mathbf{r_i}.\Delta\mathbf{p_i}) = (\hbar/2)^{3N}$

Equivalently, we can consider N points representing N particles in a 6D space. It may be that two particles are in the same place.

Ergodicity and large numbers are essential to this argument: the particles must be able to move from one microstate to another. This ensures that if each microstate is equally probable, for a large sample there is an overwhelming probablity of observing the system in one or another of a very large number of equivalent microstates which make up the highest entropy *macrostate*[3].

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[1]This is why "Standard Temperature and Pressure" has such iconic status in chemistry.

[2]Equipartition is only true for isolated systems, in general the probability depends on the energy of the microstate. But for an isolated system, (fixed N,V,S), all states have the same energy.

[3]There is a hidden assumption here, that each microstate can be assigned to a macrostate, which isn't always straightforward

Example: Dividing particles between states

Consider a finite number of particles (N) which can move between states of similar energy (M). Ergodicity (freedom to move around) means each particle is as likely to be in range 1 as in range 2. The states may be, e.g., positions of a gas molecule, or quantum energy levels which are either degenerate or much closer together than the thermal energy $k_B T$.

Consider a system of only N=3 particles and M=2 states There is only one arrangement with all particles in state 1 [W=1]. However, there are three arrangements with one particle in state 1 and two in state 2, since the particle in state 1 can be any of the three available [W=3]. [4] In general the numbers of ways [W] with N particles in M states are given by the binomial coefficients $\binom{N}{M}$, (Pascal's triangle).

When all this is extended to a large number of particles and states the thermodynamic probability of finding all particles in a single state becomes minute compared with equal numbers in all states. Assuming ergodicity, the observed "equilibrium" will be most likely arrangement even if we start in an unlikely one. This is a microscopic model for irreversibility e.g. free expansion takes us from a low probability (entropy) arrangement to a high probability one, from which we never return, *even though the dynamics of the particles is time-reversible.*

In Statistical Mechanics, we will see how properties of a macrostate can be written as an average over its microstates. This statistical mechanics will involve sums and integrals. The integrand just defines a property. Solving the integral is just maths, the physics lies in *defining the limits* of the integral. But...

> There is, in general, no way to define whether a microstate "belongs" to a macrostate

Disobeying the Second Law: Maxwell's Demon

If the Second Law of Thermodynamics is as a statistical law, then there's a chance of breaking it.

Suppose it were possible to shift the more energetic molecules of a sample of gas to part of the containing vessel. Then energy would be transferred preferentially from the cooler part of the sample (which would become progressively cooler) to the warmer part (which would become progressively warmer). To violate the Clausius statement would require achieving this without doing any mechanical work. One idea was the intervention (proposed by Maxwell) of an "alert and well-informed finite being" in total control of a special massless shutter mechanism, who only let fast particles go from left to right, and slow particles from right to left. It became known (to Maxwell's disapproval) as Maxwell's demon.

For small systems in small timescales it is *sometimes* possible to violate the Kelvin statement, and extract work from a system without supplying heat. Imagine dragging an object through a cylinder containing ideal gas atoms. Microscopically, the internal pressure is supplied by atoms bouncing off the piston *at random*. Normally, there will be more collisions on the front side of the object. But, if there are few enough atoms, and short enough time, there is a *chance* the number of atoms striking the object from behind may be greater. In that case the net force will be in the direction of motion, the system doing work *F.dx*. The catch is that *more often* work is done on the system, and we can't predict when the "violation" will occur. This sort of thing has been shown experimentally.[5]

Other definitions of entropy beyond this course

The probability interpretation of entropy leads to yet another definition, the Gibbs Entropy:

$$S = -k_B \sum_i p_i ln p_i$$

where p_i is the probability of finding the system in microstate i. The generalisation of this to quantum mechanics gives the von Neumann entropy[6]. These are equivalent to the heat definition, and also to the Shannon Information Entropy which quantifies how much information is contained in a message (and therefore, how much a message or image can be compressed, e.g. using gzip). Remarkably, these aspects of entropy are all the same, and the missing entropy in Maxwell's Demon is the information in the Demon's brain!

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[4] Some people find this obvious, others say it defies common sense. Look up the "Monty Hall problem"

[5] Wang et al (2002). "Experimental demonstration of violations of the Second Law of Thermodynamics for small systems and short time scales". Phys. Rev. Letters 89 (5): 050601

[6] similar to Gibbs, using quantum mechanical probabilities, the so-called "density matrix" which you won't see in JH