

PREVIOUSLY ON

...*Thermodynamics*

- Positive specific heats and compressibility
- Negative elastic moduli and auxetic materials
- Clausius Clapeyron Relation for Phase boundary
- “Phase” defined by discontinuities in state variables
- Gibbs-Helmholtz equation to calculate G

There are five laws of Thermodynamics.



5,4,3,2 ... ?

Laws of Thermodynamics

2, 1, 0, 3, and ?

What is the entropy at absolute zero?

$$S = \int_0^T \frac{dQ}{T} + S_0$$

Unless $S = 0$ defined, ratios of entropies S_1/S_2 are meaningless.

The Nernst Heat Theorem (1926)



Consider a system undergoing a process between initial and final equilibrium states as a result of external influences, such as pressure. The system experiences a change in entropy, and the change tends to zero as the temperature characterising the process tends to zero.

Nernst Heat Theorem: based on Experimental observation

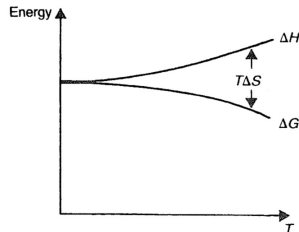
For any exothermic isothermal chemical process.

ΔH increases with T ,

ΔG decreases with T .

He postulated that at $T=0$,

$$\Delta G = \Delta H$$



As $T \rightarrow 0$, observed that
 $\Delta G \rightarrow \Delta H$ asymptotically

$$\begin{aligned}\Delta G = G_f - G_i &= \Delta H - \Delta(TS) \\ &= H_f - H_i - T(S_f - S_i) \\ &= \Delta H - T\Delta S\end{aligned}$$

So from Nernst's observation

$$\frac{d}{dT}(\Delta H - \Delta G) \rightarrow 0 \implies \Delta S \rightarrow 0$$



Planck statement of the Third Law:

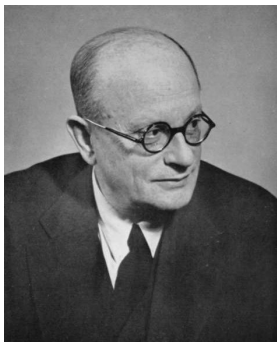
The entropy of all perfect crystals is the same at absolute zero, and may be taken to be zero.

Planck Third Law

- All perfect crystals have the same entropy at $T = 0$.
- Thermodynamics : choose this to be $S_0 = 0$
- Supported by experimental evidence.
- Microscopics : $S = k \ln W$ all atom positions uniquely defined.
- $W = 1$
- Permuting atoms doesn't count.

Last point comes from Ergodicity - atoms can't swap - or from indistinguishability: state is the same if they do swap.

Simon Third Law (1937)



Sir Francis Simon (ne Franz Eugen Simon)

Student of Nernst

- banned from working on radar.

Invented U^{235} separation via gaseous diffusion of UF_6 (Manhattan Project)

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

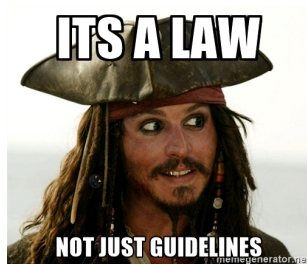
- “configurational entropy”: various arrangements of atoms on sites
- “vibrational entropy”: various positions of vibrating atoms.
- “magnetic entropy”: various arrangements of spins.

Isentropic process conserves TOTAL entropy.

Pause for thought

The Third Law, however stated, stems from

- *observation of properties of substances*
- *successful description of low temperature behaviour.*
- *no counterexamples or special conditions*



Vanishing Heat capacity

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

$$C_V = \left(\frac{\partial S}{\partial \ln T} \right)_V \approx \frac{\Delta S}{\Delta \ln(T)}$$

As $T \rightarrow 0$,

Third law: $\Delta S \rightarrow 0$

$\ln T \rightarrow -\infty \implies$ No constraints on $\Delta \ln(T)$

$C_V \rightarrow 0$

True for *all* specific heats for *all* materials.

n.b. The heat capacity for an Ideal gas is $c_v = 3R/2$...

... means that the ideal gas doesn't properly describe low-T.

The Schottky heat capacity for a paramagnet $c_B(T, B=0) = b/T^2$

... means that the Curie Law doesn't properly describe low-T.

Vanishing Thermal expansion coefficient, β

Using a Maxwell Relation..

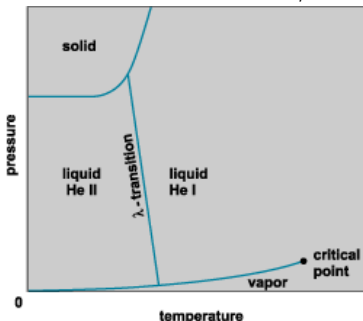
$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = -\frac{1}{V} \left(\frac{\partial S}{\partial P} \right)_T$$

- Isothermal derivative.
- Third Law, as T approaches zero, $\Delta S \rightarrow 0$,
...and so as T approaches zero, $\beta \rightarrow 0$.
- This is true *for any material*

Zero slope of the phase boundary for first order transition

$$\text{Clausius-Clapeyron: } \left(\frac{dP}{dT} \right)_{PB} = \frac{\Delta S}{\Delta V}$$

But $\Delta S \rightarrow 0$ as $T \rightarrow 0$, so the slope of the phase line must be zero.

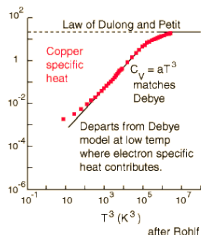
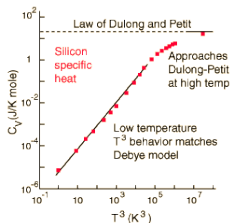


e.g. He^4 in the low temperature limit.
liquid phase II / solid phase transition

$$S = k \ln W$$

- Ground state ($W=1$). $S = 0$
- A finite amount of energy needed for excited quantum state.
- An infinitesimal change in temperature cannot provide this.
- Therefore, an infinitesimal process at $T = 0$ cannot change W
- Third law only manifest for kT close to quantised energy

Heat Capacity of Metals



For metals at low temperatures
 $c_v \approx c_p = aT + bT^3$

aT associated with the conduction electrons **aspect**,

bT^3 associated with the lattice vibrations **aspect**.

Using $\frac{c_v}{T} = \left(\frac{dS}{dT}\right)_v = a + bT^2$; and integrating we see that:

$$S(T) = aT + \frac{1}{3}bT^3$$

both contributions to entropy tend to zero as $T \rightarrow 0$

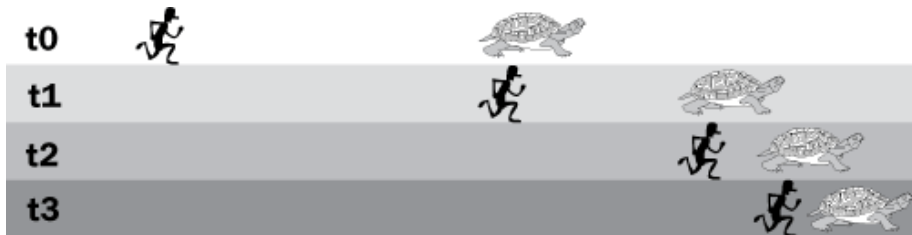
All electron states below E_F are occupied.

All lattice vibrations (quantum harmonic oscillators) in ground state.

Unattainability of absolute zero (Zeno statement)

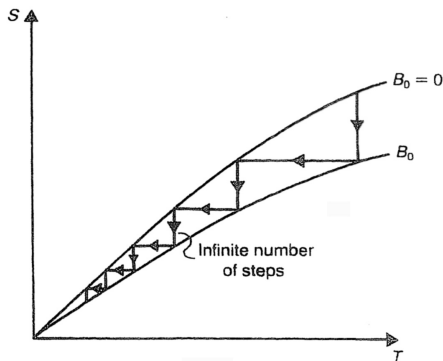
Another statement of the Third Law:

It is impossible to reach absolute zero in a finite number of processes.



Magnetic cooling again

- Cooling by adiabatic demagnetisation (Lecture 12).
- Field on: Reduce entropy by aligning spins
- Field off: Adiabatic equilibration = cooling.
- Repeat this **process**.
 $\Delta T_n \propto \Delta S_n$



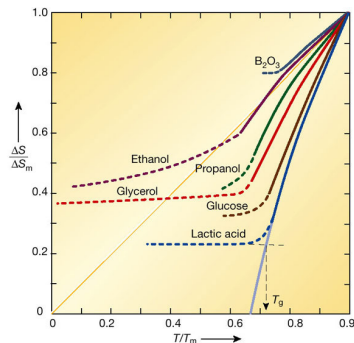
As $T \rightarrow 0$ entropy changes get smaller at each step.

Disobeying the Third Law?

Kauzmann's paradox

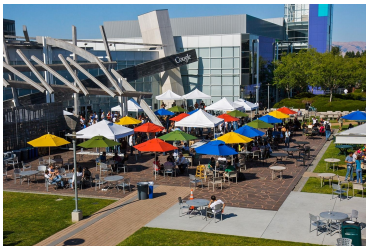
see also Nature 410, 259-267(2001)

Temperature dependence of the “heat content” (label $\Delta S/\Delta S_M$) between supercooled liquids and their stable crystals.



- Glasses look as if their entropy doesn't go to zero at 0 K
- Implication is they are *not* at equilibrium.

Permutation entropy: A very very big number



Take a microstate.
Swap two atoms around.
Is this another microstate?
How many ways?

A very very big number, vanishes



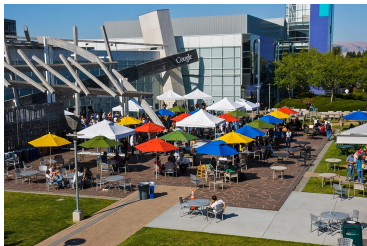
How many ways?

$$W = (N_A)!$$

Which is 1 followed by about Avogadro's
number of zeroes

Unless the particles are indistinguishable,
when

$$W = 1$$



Monty Hall Problem as an irreversible process

Entropy increases in irreversible process.



3 doors, two goats, one car.

Pick one door (3), Monty opens another (1) to show a goat.

Is the car more likely to be in (2) or (3)?

Initial Entropy: $k \ln \frac{1}{3} = 0.4771k \dots$

$W \ni [GGC, GCG, CGG]$

Final Entropy: $k \ln \frac{1}{2} = 0.3010k \dots$

$W \ni [GGC, GCG] ?$

NO, $-k(\frac{2}{3} \ln \frac{2}{3} + \frac{1}{3} \ln \frac{1}{3}) = 0.2764k$

What changed? - TWO bits of extra information...

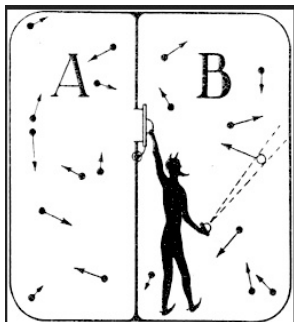
If Monty chose at random (may have revealed a car), no advantage switching

If Monty chose a goat-door, more information, some advantage switching

Breaking the law: Maxwell's Demon

If the Second Law of Thermodynamics is statistical, then...

There's a *chance* of breaking it.



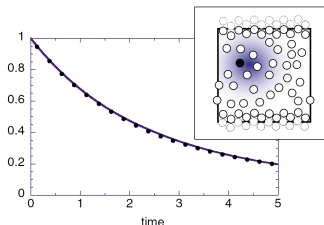
- Demon moves shutter ... only lets fast atoms go $A \rightarrow B$.
- Moves heat to hotter side
- Violates Clausius 2nd Law

Demon needs *information* about atom velocity: Demon itself creates entropy.

Moral. The 2nd law of thermodynamics has the same degree of truth as the statement that if you throw a tumblerful of water into the sea, you cannot get the same tumblerful of water out again. Maxwell, 1874

(BONUS) Breaking the Law

Small system, small time, *possible* to violate the Kelvin statement,



- Drag a micron sized particle.
- Measure piconewton forces.
- $\text{Work} = \text{force} \times \text{distance}$.
- *Sometimes* moving particle gets hit from behind more than in front.
- Extract work without supplying heat.
- Second Law violations *not predictable*

G.M. Wang, E.M. Sevick, E. Mittag, D.J. Searles & D. J. Evans (2002). "Experimental demonstration of violations of the Second Law of Thermodynamics for small systems and short time scales". *Physical Review Letters* 89 (5): 050601

(BONUS) Phase space: counting by integrals

- Full microscopic description: N particles, $3N$ positions, $3N$ momenta
- Represent system position+momentum by point in $6N$ -dimensional space.
- Space is divided into countable blocks of size.

$$\prod_{i=1}^N (\Delta \mathbf{r}_i \cdot \Delta \mathbf{p}_i) = (\hbar/2)^{3N}$$

Heisenburg uncertainty principle: Cannot count less than 1.

(BONUS) Other definitions of entropy beyond this course

- The probability interpretation the Gibbs Entropy: $S = -k_B \sum_i p_i \ln p_i$
- Quantum probability interpretation: von Neumann entropy
 $S = -\text{tr}(\rho \ln \rho)$, With ρ the density matrix.
- Shannon Entropy $H = -\sum_i p_i \log_b p_i$
Quantifies how much information is contained in a message (and therefore, how much the message can be compressed with gzip).

Remarkably, they are all the same, and the missing entropy in Maxwell's Demon is the information in the Demon's brain!

From Microstate to Thermodynamics

DEFINITION: A micro-state...

a way the particles could be arranged at one instant in a given phase.

DEFINITION: A macro-state means...

a group of microstates which correspond to the same thermodynamic quantities, P , V , T , phase etc.

DEFINITION: Ergodicity means...

it is actually possible to move from any microstate to any other.

- If $S = k_B \ln W$, zero entropy means unique arrangement ($W = 1$).
Electrons in insulator: all fermion states below E_F occupied
Bose condensate: All bosons in ground state
- Third Law: at $T=0$, $S=0$ only one microstate, the ground state.
- Negative entropy impossible for quantised system $\implies W < 1$
- $S = k_B \ln W$ implies all W states equally likely
- More generally, Gibbs Entropy $S = -Nk_B p_i \ln p_i$

Counting up to two, three times

Three particles, two partitions A and B. State defined by N_A

- $W(N_A = 0) = 1(BBB)$;
- $W(N_A = 1) = 3(ABB/BAB/BBA)$
- $W(N_A = 2) = 3(AAB/ABA/BAA)$
- $W(N_A = 3) = 1(AAA)$

W for N particles: $\binom{N}{k}$ Binomial coefficient, given by Pascal's triangle.

“Average” state is VASTLY more likely

As $N \rightarrow \infty$, width of the peak goes as $1/\sqrt{N}$

