Topic 5 Entropy: Phys 347.

- Way back we said their were different types of energy – organized & disordered
- Organized energy is kinetic or potential and can do work
- Disordered energy is thermal & random and a poor source of work.
- For a closed system the disorder always tends to increase.
- We will now define this disorder ≡ entropy.

Disorder & Information

e.g. Flip a coin 1000 times → HTTHHTH....

- How many bits do you need to store it? (bit = H or T)
- Ans: you need 1000 bits, there's no way to compress a random sequence.
- It contains a lot of disorder.

e.g: the weather on each day of year $=$ RRRSSSRS..
where $R \equiv$ rain & $S \equiv$ sun.

- This sequence is less random because if its sunny, chances are that it will be sunny on the next day.

- Thus there is some predictability in the sequence.
$\Rightarrow$ it contains less disorder than the sequence of coin flips.

Idea: disorder $\equiv$ how hard is the sequence to memorize?

low disorder $\rightarrow$ easy to memorice
high disorder $\rightarrow$ hard to memorize

Proposal: Object exists in M equally likely states and we make a sequence of N observations.

$$\text{disorder} \equiv I = N \log_2 M = KN \ln M \; ; \; K = \frac{1}{\ln 2}$$

e.g. $M = 2 \equiv$ coin toss $\Rightarrow I = N \log_2 2 = N$

so the disorder is just the length of the sequence, as expected.

Why logarithm?

- gives us additivity – two uncorrelated sequences' disorder should add.

e.g. Roll a die & coin N times. $M = 6 \times 2 = 12$

so $I = KN \ln 12 = KN(\ln 2 + \ln 6)$

$\rightarrow$ disorder added.

Rewrite: # of states. $\Omega = M^N$

so $I = KN \ln M = K \ln(M^N) = K \ln \Omega$

$$I = K \ln \Omega$$

interpretation – the more states a system has, then the more disorder it has

Shannon Information:

- Above we assumed that all of the M outcomes were equally likely, i.e. $P_i = 1/M$.
- This isn't always the case, for instance in language the probability of a word is different for different words.

So let $P_j \equiv$ probability of the j^{th} outcome.

Then
$$\boxed{\frac{I}{N} = -K \sum_{j=1}^{M} P_j \ln P_j}$$

- this is the amount of disorder / letter.

e.g. for a coin, $P_j = 1/2$ & $M = 2$

so $$\frac{I}{N} = -K \sum_{j=1}^{2} \frac{1}{2} \ln \frac{1}{2} = 1 \equiv 1 \text{ bit}$$

For a one letter alphabet, where $P = 1$

$$\Rightarrow \frac{I}{N} = -K\, 1 \ln 1 = 0 \leftarrow \text{no disorder.}$$

Key property of Shannon's Formula:

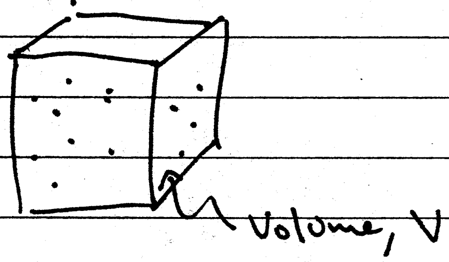
$\frac{I}{N}$ is maximum when all the P_j's are the same — or in words, every outcome is equally likely.

- this will be an important property in connecting information / disorder to thermodynamics.

Connection to Physics:

- Think of the series of coin flips as a series of physical measurements, where for each measurement the system can exist in one of M microstates.

e.g.:



N particles in closed box with total energy E.

the "state" will be the positions & velocities of the particles.

Statistical Postulate: equillibrium occurs when all the states become equally probable & thus the greatest possible dissorder.

in words — equilibrium corresponds to the greatest ignorance of the state of the system.

N.B.: equilibrium can take a very, very long time to reach.

Entropy: System exists in Ω states each having energy E.

$$\text{disorder} = I = K \ln \Omega \quad (\text{a big \#})$$

$$(\times \text{ by small \#}, \ k_B = 1.38 \times 10^{-23} \ldots)$$

Entropy, $S = k_B \ln \Omega$

→ more states ⟹ more entropy.

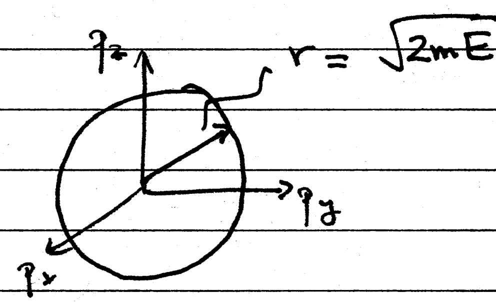
→ less states ⟹ less entropy

<u>Entropy of Ideal Gas:</u>

$$E = \sum_{i=1}^{N} \frac{m \vec{v}_i^{\,2}}{2} = \frac{1}{2m} \sum_{i=1}^{N} \vec{p}_i^{\,2} = \frac{1}{2m} \sum_{i=1}^{N} \left(p_{i,x}^2 + p_{i,y}^2 + p_{i,z}^2 \right)$$

eqn: $x^2 + y^2 + z^2 = R^2$, equation of a sphere.

For 1 particle:



- (p_x, p_y, p_z) reside on sphere with radius $\sqrt{2mE}$
- # of states is $\propto$ area of sphere
  $= r^2 \qquad = r^{(3N-1)}$
- N-dimensional hyper-sphere: $A_N \propto r^{3N-1} \approx r^{3N}$
- However for each set of p_x, p_y, p_z we can also put the particles at any position in the volume V
- # of relabeling of N particles $\sim V^N$

So the # of states for an N particle ideal gas.

$$\Omega \propto r^{3N} \cdot V^N = \left(\sqrt{2mE}\right)^{3N} V^N$$

so

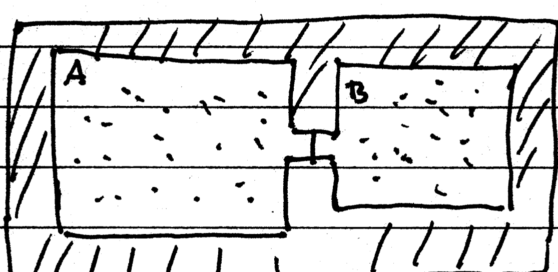
$$\boxed{S = k_B \ln \Omega = N k_B \ln\left(E^{3/2} V\right) + \text{const}}$$

so

bigger $V \to$ more S & more $E \to$ more S

- How can we get some of the well known results from this?

- Zeroth Law:



- Two boxes, N_A & V_A & N_B & V_B
- $E_{tot} = E_A + E_B$, fixed.

- ~~[illegible]~~ If E_A goes up then E_B must go down to maintain E_{tot}.

- @ equilibrium all states @ E_{tot} are equally probable.

- If we take a snapshot, what will the most likely value of E_A be? (Answer follows)

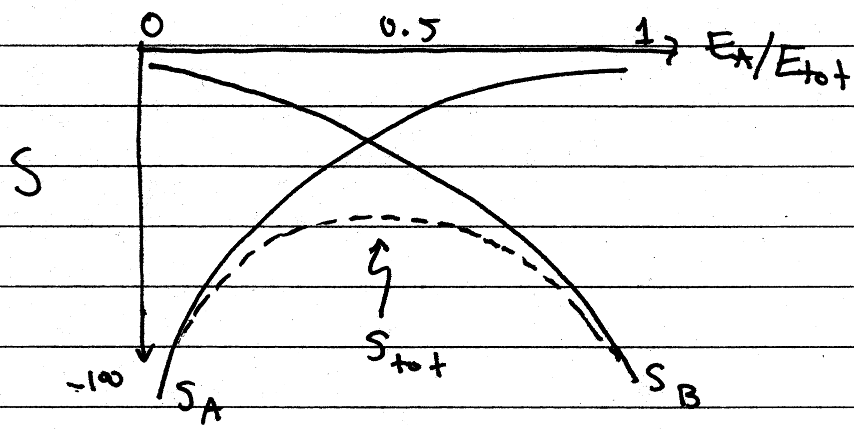
- Consider Total Entropy: $S_{tot} = S_A(E_A) + S_B(E_B)$

$$= S_A(E_A) + S_B(E_{tot} - E_A)$$

Using ideal gas S:

$$S_{tot}(E_A) = k_B\left[N_A\left(\frac{3}{2}\ln E_A + \ln V_A\right) + N_B\left(\frac{3}{2}\ln(E_{tot}-E_A) + \ln V_B\right)\right]$$
$$+ \text{const.}$$

Graphs:



- The most likely E_A occurs when S_{tot} is maximum which is where $dS_{tot}/dE_A = 0$

$$\Rightarrow \frac{3}{2}k_B\left(\frac{N_A}{E_A} - \frac{N_B}{E_B}\right) = 0$$

OR

$$\frac{E_A}{N_A} = \langle \varepsilon_A \rangle = \frac{E_B}{N_B} = \langle \varepsilon_B \rangle$$

but $\langle \varepsilon_A \rangle = \frac{3}{2}k_B T_A$ & $\langle \varepsilon_B \rangle = \frac{3}{2}k_B T_B$

so

$$\boxed{T_A = T_B}$$ zeroth law.

so the system is most likely to be sharing energy such that the temperatures are the same.

New definition of temperature:

equilibrium: $T_A - T_B = 0$

Define: $\boxed{T = \left(\frac{dS}{dE}\right)^{-1}}$

Check units: $[k_B] = \frac{[E]}{[T]}$ $\therefore \left(\frac{[S]}{[E]}\right)^{-1} = \left(\frac{1}{[T]}\right)^{-1} = [T]$

- Thus the two systems will exchange energy & entropy so that $T_A = \left(\frac{\Delta S_A}{\Delta E_A}\right)^{-1} = T_B = \left(\frac{\Delta S_B}{\Delta E_B}\right)^{-1}$

- So temperature only has a statistical definition, it is related to how much a system's disorder changes when we change the system's energy.

- if $\frac{\Delta S}{\Delta E} \gg 1$ then T is low

- if $\frac{\Delta S}{\Delta E} \ll 1$ then T is high

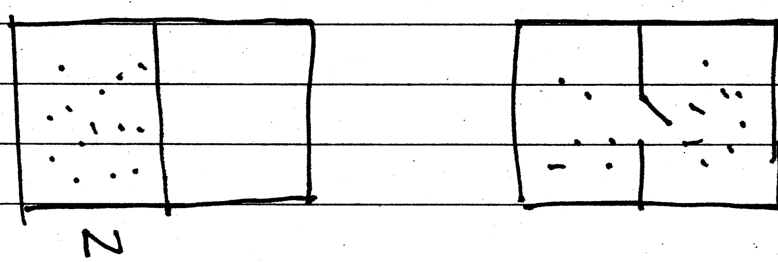
- Interpretation of zeroth Law:

two ~~[illegible]~~ systems @ T_A & T_B brought into contact will lose order and become more disordered until $T_A = T_B$.

<u>2nd Law</u>: An isolated system in equilibrium that has a constraint removed will come to a new equilibrium where the entropy is at least as big as before.

<u>Key</u>: Entropy is <u>not</u> conserved, always bigger or equal to what it was before.

<u>e.g.</u>:



ΔS? $S_1 = N k_B \ln V + \text{const}$; $S_2 = N k_B \ln 2V$

so $\Delta S = S_2 - S_1 = N k_B (\ln 2V - \ln V) = N k_B \ln 2$

> 0

- Could we ever put the molecules back on the LHS? <u>Yes</u>, but we'd have to do work by compressing it → heating it up.
- Thus to create order we must use up mechanical work & turn it into heat.

Open Systems:

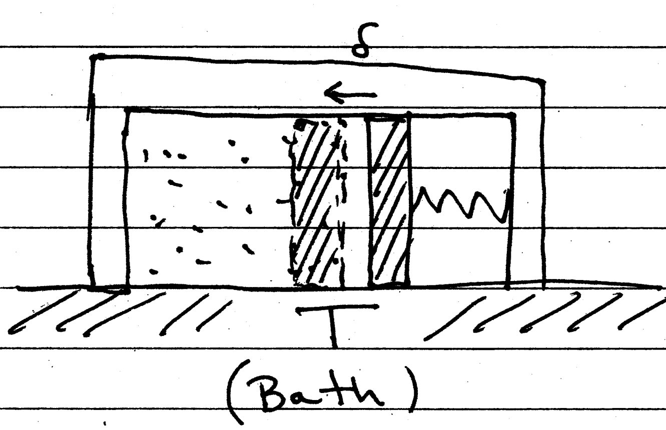
- Previously we said that entropy of a closed system can only increase.

- But we see things (like life) creating order and therefore reducing entropy.

- Resolution: Open systems, are systems in contact with a thermal bath which keeps everything at a constant temperature.

- In an open system, it's possible for some sub-systems to decrease entropy, but the whole system's entropy still goes up.

- Consider a piston in contact with a thermal bath.



- Piston comes into equilibrium with gas — it moves a distance δ.

- What is the change in entropy of gas + spring?

- The volume changed, but gas's energy is still $E = N\left(\frac{3}{2}kT\right)$ since T is fixed.

So

$$\Delta S_a = S_2 - S_1 = \left[N k_B \ln\left(V - \left(\frac{\delta}{L}\right) V \right) \right] - N k_B \ln V$$

$$= N k_B \ln\left(1 - \frac{\delta}{L}\right) \qquad \left(\text{use } \ln(1+\varepsilon) \cong \varepsilon + O(\varepsilon^2)\right)$$

$$\approx -N k_B \frac{\delta}{L}$$

so entropy of gas & spring is < 0 !

- But what about bath?

$$T \Delta S_B = \Delta E_B = -\Delta E_a$$

since the energy lost from the spring must go into the bath.

Total System ΔS: (closed system) $\quad T\Delta S_{tot} = T\Delta S_a + T\Delta S_B$

$$= -\Delta E_a + T\Delta S_a \geqslant 0$$

from 2nd Law

or

$$-(E_f - E_i) + T(S_f - S_i) \geqslant 0$$

$$(E_i - TS_i) - (E_f - TS_f) \geqslant 0$$

or

$$\boxed{E_f - TS_f \leqslant E_i - TS_i}$$

Define: Free energy = $F = E - TS$

- Thus the system of gas + piston will lower its free energy when it comes to equilibrium with the thermal bath.

- No more mechanical work can be extracted out of a system when it is at it's free energy minimum.

- For the gas + piston, the free energy only depends on the position of the piston

$$F(\delta) = E - TS = N\frac{3}{2}k_BT + \frac{1}{2}k\delta^2 - T\left(-Nk_B\frac{\delta}{L}\right)$$

Find δ which minimizes F. $\frac{dF}{d\delta} = 0$

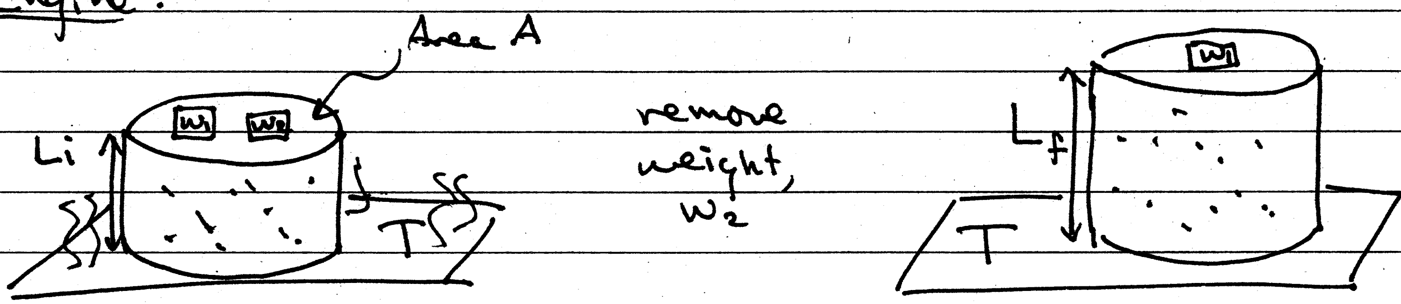
- So the gas is pushing back on the spring. This is entropic force.

$$\boxed{f_a = -\frac{dF}{dL}}$$

- So if F is not in a minimum, it will push or pull on an external load with a force = to f_a.

- So the system can do work.
- Rewriting. $|\Delta F| = |f \cdot \Delta L| \equiv$ work done
- So the most work that a system can do is equal (or less than) the free energy change.
- In practice, the work done, $w < \Delta F$.

Engine:



- $\Delta F = -N k_B T \ln \dfrac{L_f}{L_i}$

- Final pressure: $p_f = \dfrac{N k_B T}{\underset{\displaystyle L_f \cdot A}{\overset{\shortparallel}{V}}}$ or $p_f L_f = \dfrac{N k_B T}{A}$

also $p_f = \dfrac{w_1}{A}$ $\leftarrow$ weight balanced.

- Work done by gas: $w_1 (L_f - L_i) = N k_B T X$

where $X = \dfrac{(L_f - L_i)}{L_f}$

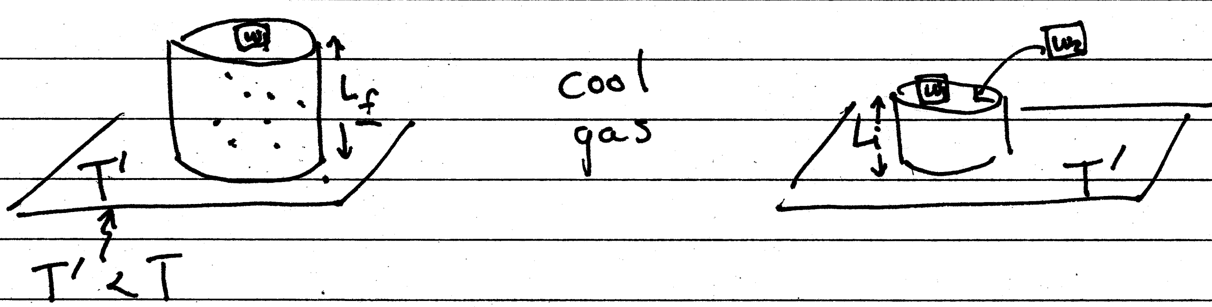
Compare ΔF to work done:

$$|\Delta F| = -Nk_BT\ln(1-X) \quad \text{c.f.} \quad Nk_BTX$$

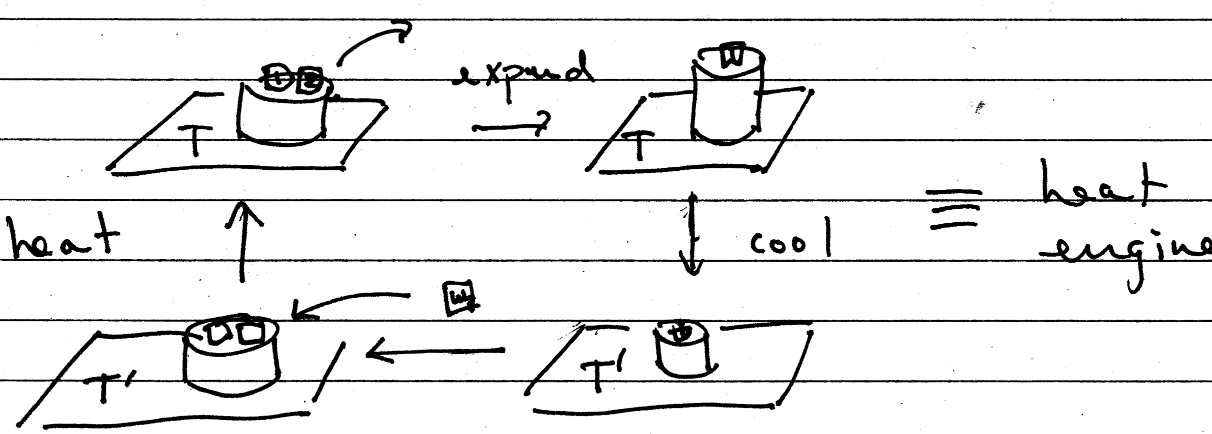
$$X < \ln(1-X) \quad \text{for} \quad 0<X<1$$

so work done is less than $|\Delta F|$. Good.

Finish the cycle:



- Now you've reset the engine, put back onto higher bath, T, remove w_2 & do work



- The engine converts thermal energy into work but some of the world's order is drained on every cycle. Eventually $T' = T$ (long time)