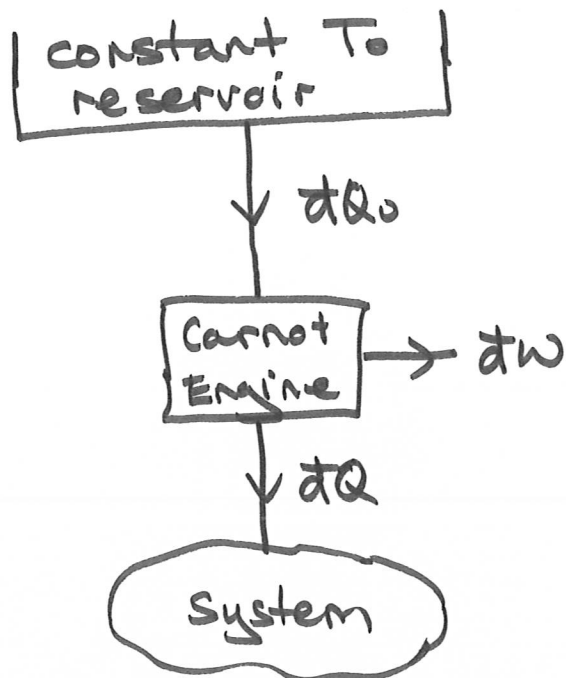


Let's now discuss Clausius' great discovery using Carnot Engine theory.

Consider this set up:



This is a really big hot thing that stays at T_0

A Carnot Engine we can run either as HE or HP

Some system that can absorb or emit heat - we'll do some examples below

One step moves a tiny dQ_0 energy through the HE as shown....

$$\frac{dQ_0}{dQ} = \frac{T_0}{T} \quad \Rightarrow \quad dQ_0 = T_0 \frac{dQ}{T}$$

↑ we assume T is fixed in this tiny step but can change as many steps are done.

Now we do many steps to give the system Q energy.

Then we reverse to HE mode & extract energy from the system to put it back exactly as it was at the beginning.

The HE after any cycle is also back where it was.

Through this loop the heat extracted from the reservoir is

$$Q_0 = \oint dQ_0 = T_0 \oint \frac{dQ}{T}$$

Now without the second law you might wonder whether round this loop you extracted some Q_0 & the CE used it as work....

This is forbidden by the 2nd law though so

$$\oint \frac{dQ}{T} \leq 0 \quad \text{Clausius' Inequality}$$

Let's explore this in more detail:

Reversible Example - if "the system" is reversible

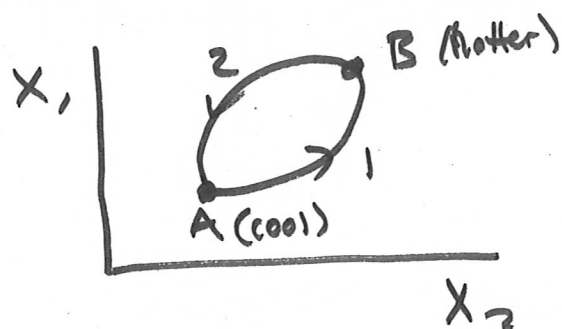
$$\text{we get } \oint \frac{dQ}{T} = 0$$

eg if the system is just an insulated tank of water can reasonably add & subtract small pieces of heat from it reversibly

When run HE store the work in a "battery"
- The whole process in HE mode is exactly reverse of HE mode $\Delta Q_0 = 0$.

$$\oint \frac{dQ_r}{T} = 0.$$

Consider what this means for the system



$$\int_A^B \frac{dQ_r}{T} + \int_B^A \frac{dQ_r}{T} = 0$$

We could also interlink HE & HP modes arbitrarily and take many loop paths back to A! The integral is independent of the path.

This suggests we have found a new function of state, call it S (entropy)

$$S_B - S_A = \int_A^B \frac{dQ_r}{T}$$

$$dS = \frac{dQ_r}{T}$$

(Note this is zero for an adiabatic reversible change where there's no heat exchange).

This expression for dS is only for reversible changes.

Non-Reversible Case

Let's make path 1 non-reversible, Clausius' inequality still applies

$$\oint \frac{dQ}{T} = \int_{\text{path 1}}^B \frac{dQ}{T} + \int_B^A \frac{dQ_R}{T} \leq 0$$

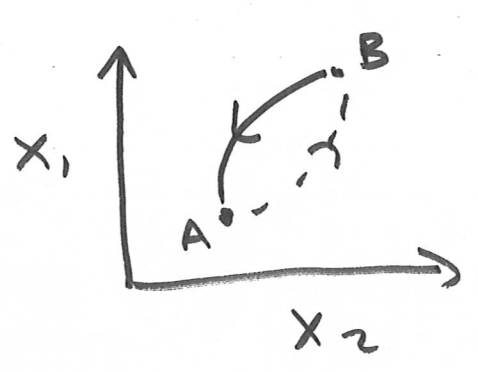
$S_B - S_A = -\Delta S$

$$\Rightarrow dS \geq \int_A^B \frac{dQ}{T}$$

or $dQ \leq T dS$

It helps to consider an example. Let's make system the water tank + tiny bubbles of unreacted mixed H_2 & O_2 !

Absorption of dQ can trigger $2H_2 + O_2 \rightarrow 2H_2O$ emitting energy into the water in addition to dQ



We get to B for less input dQ .

Now we have to HP phase the same amount to return system to A. Q_0 is negative - more energy from system than into it.

↳ and more W for HP!

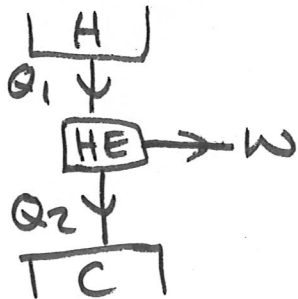
If you want to restore the bubble too it's much worse! EG an imp in a closet with a HE emerges & does work to rebuild the bubble... dumping even more energy into the water!

Clausius' Proposed 2nd Law: entropy always rises ($S \geq 0$)
in any process

What is entropy?

Thermodynamically this is a hard question... but let's look at examples... they suggest entropy measures growth of disorder as one approaches a thermalized state from which work can't be extracted.

① Heat Engines



$$\Delta S = \frac{Q_2}{T_2} - \frac{Q_1}{T_1}$$

↑ heat is removed

For a reversible Carnot engine

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \Rightarrow \Delta S = 0$$

If it's less efficient then more of Q_1 is lost as heat Q_2 & the result is positive.

ΔS measures the loss of ability to extract work.

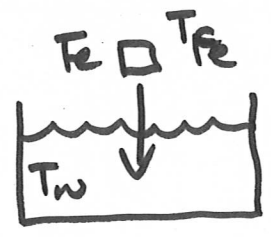
③ Phase Change

$$Q = mL \quad \text{eg melting}$$

$$\text{So } \Delta S = \frac{mL}{T_m}$$

Here the temperature doesn't change but the rise in disorder is clear (solid melts). This is ΔS for the water - if the change is reversible both for water & environment net ΔS might be zero.

④ Cooling In Water



We need to compute ΔS as both iron & water.

Assume the water gains energy but basically at fixed T_w

$$Q_{\text{iron losses}} = M_{Fe} C_{Fe} (T_{Fe} - T_w)$$

$$\Rightarrow \Delta S_{\text{water}} = \frac{M_{Fe} C_{Fe} (T_{Fe} - T_w)}{T_w}$$

For the iron the change in S depends on its temperature that changes continually

$$\delta S_{Fe} = M_{Fe} C_{Fe} \frac{\delta T}{T}$$

(here we assume small changes are reversible)

$$\Delta S_{Fe} = \int_{T_{Fe}}^{T_w} M_{Fe} C_{Fe} \frac{dT}{T}$$

$$= - M_{Fe} C_{Fe} \ln \frac{T_{Fe}}{T_w}$$

$$\Delta S_{TOT} = M_{Fe} C_{Fe} \left[\frac{T_{Fe} - T_w}{T_w} - \ln \frac{T_{Fe}}{T_w} \right]$$

- If $T_{Fe} = T_w$ both terms are zero
- $T_{Fe} > T_w$ then ΔS is positive

Here we interpret the entropy rise as measuring the irreversibility of the process.

④ Isothermal Gas Expansion

Heat absorbed = work done by gas

$$dQ_R = T dS = P dV$$

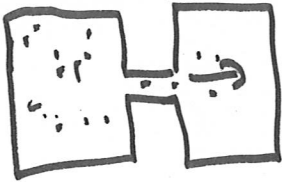
$$\Delta S_{gas} = \int_{V_1}^{V_2} \frac{P dV}{T} \quad PV = n_m RT$$

$$= \int_{V_1}^{V_2} n_m R \frac{dV}{V}$$

$$= n_m R \ln \frac{V_2}{V_1}$$

$\Delta S_{univ} = 0$ if the surroundings change is reversible ... else true.

(E) JOULE EXPANSION



Here the gas is isolated from the surroundings... and the process is not reversible.

$$dQ = 0, T = \text{const}$$

We can't use $\Delta S = \frac{dQ_{\text{R}}}{T}$ to compute the change.

However, we can compute ΔS for the gas by finding an alternative reversible route from initial \rightarrow final state. Entropy is a function of state!

Eg isothermal expansion from $V_1 \rightarrow V_2$. T fixed
 $\Rightarrow \Delta U = 0$.

$$\Delta S_{\text{gas}} = nR \ln V_2/V_1$$

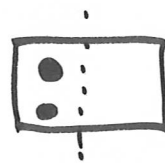
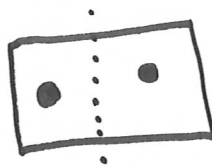
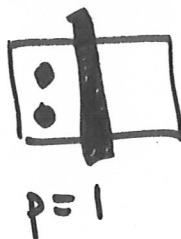
The entropy increase when $V_2 > V_1$ reflects evolution from unlikely \rightarrow likely state.

The Joule Expansion is the hint as to what entropy is at a microscopic level...

Clausius Proposed 2nd Law: entropy always increases.

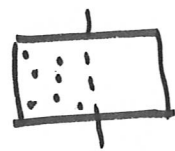
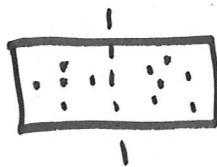
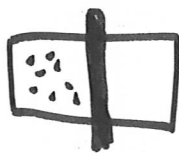
Statistical Interpretation

2 pt Joule expansion



$$p = \frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$$

N pt Joule expansion



$$p = \left(\frac{1}{2}\right)^N$$

2^N is rather large $= 10^{\log 2^N}$
 $= 10^{N \log 2}$
 $= 10^{0.3 N}$

For air at stp $N = 10^{25} \text{ m}^{-3}$

$$2^N \approx 10^{10^{25}} !$$

The age of the Universe is only 10^{17} seconds...
so there's no chance of you ever seeing such a state. Totally irreversible.

Microstate Counting

Another approach is to ask how many "states" exist for each configuration

eq 10 pts

number is

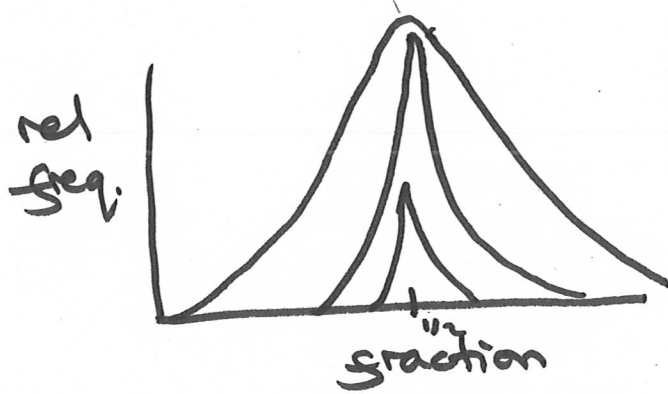
$$\frac{N!}{n!(N-n)!}$$

total number of choices for N

$$\frac{\text{total choices in } n \times \text{total choices in } (N-n)}{\text{total choices in } N}$$

R	L	#
0	10	1
1	9	10
2	8	45
3	7	120
4	6	210
5	5	252

One finds



As N grows becomes very peaked.

So we're going to interpret entropy as something that is larger for a state with higher number of ways of creating: "multiplicity" ω

To find the matching formula go back to the Joule expansion

$$\frac{\omega_2}{\omega_1} = \left(\frac{V_2}{V_1}\right)^N$$

If you double V each of N pts gets 2x as many ω

$$\ln \frac{\omega_2}{\omega_1} = N \ln \frac{V_2}{V_1}$$

Our thermodynamic result was $S = nR \ln V_2/V_1$

So we get

$$S = k \ln W$$

Boltzmann's
Entropy Formula

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check: $\Delta S = k \ln \frac{W_2}{W_1}$

$$= kN \ln \frac{V_2}{V_1}$$
$$= n_m N_A k \ln \frac{V_2}{V_1}$$
$$= n_m R \ln \frac{V_2}{V_1} \quad \checkmark$$

Gibb's Entropy Formula

$$S = -k \sum_{\text{states}} p_i \ln p_i$$

\uparrow prob of being in state

EG | If assume have N equally likely states

then $p_i = 1/N$

$$S = -k \sum_{i=1}^N \frac{1}{N} \ln \left(\frac{1}{N} \right)$$

$$= \frac{k}{N} \ln N \sum_{i=1}^N 1$$

$$= k \ln N \quad \text{agrees with Boltzmann}$$

EG) For a gas $p_i \sim e^{-E_i/kT}$

If we make a reversible change ~~states~~ ^{particles} just move between the available states

$$dS = -k \sum_i (dp_i \ln p_i + dp_i)$$

$$F = p \ln p$$
$$\frac{dF}{dp} = \ln p + 1$$

sum of probability equals 1 before & after

$$\Rightarrow \sum_i \delta p_i = 0$$

$$= -k \sum_i dp_i \ln p_i$$

$$= \frac{1}{T} \sum_i dp_i E_i$$

$$= \frac{1}{T} \sum_i [d(p_i E_i) - dE_i p_i]$$

this is the change in the average energy

$$dU$$

this is the average value of the energy change of the system ~~doing~~ done on it.

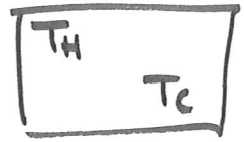
$$= \frac{1}{T} (dU - dW)$$

$$= \frac{dQ}{T}$$

agrees with Clausius.

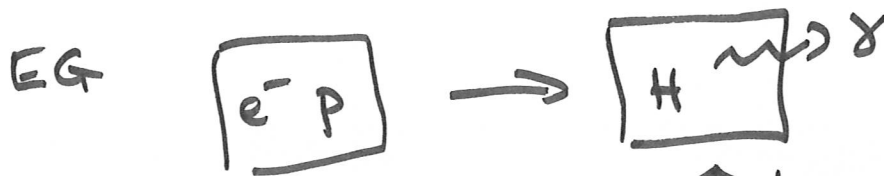
COSMOLOGY

If the Universe were an ideal gas
Then heat engines can do work until
thermalized. "heat death"



S rises until thermalized.

Interactions eg gravity make this more complex



↑ long term more
ordered states
are more likely
Higher ω .

The highest microstate in gravity is believed
to be collapse to a BH (still research!)

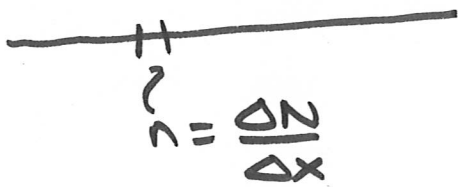
Thus Universe started looking like a uniform
thermalized ideal gas but the collapses to
galaxies, stars etc increasing entropy.

↳ "emergent"
This generates an arrow of time even
when fundamental interactions are $t \rightarrow -t$
invariant.

We do not yet understand the initial conditions
though!

A Heuristic Derivation of Gibbs Form For A 1d Gas 65

Consider a 1D gas with density variations. There will be diffusion



Fick's Law: $\frac{dN}{dt} = -D \frac{dn}{dx}$

\downarrow current in opposite direction to gradient

$\Rightarrow \frac{dn}{dt} = +D \frac{d^2n}{dx^2}$

\downarrow current reduces n
 \uparrow dimensions $M^2 = 1$

We want to find a quantity (entropy) that grows while $|dn/dx| \neq 0$. A guess

$\frac{dS}{dt}$ ← dimensionless

$$= \int dx \left(\frac{dn}{dx} \right)^2 \frac{D}{n}$$

we sum over all x so our is a global quantity

to make the S fits out dimensions

Now $\frac{d}{dx} \left[(1 + \ln n) \frac{dn}{dx} \right] = \frac{1}{n} \left(\frac{dn}{dx} \right)^2 + (1 + \ln n) \frac{d^2n}{dx^2}$

$$\Rightarrow \frac{dS}{dt} = (1 + \ln n) \frac{dn}{dx} \Big|_{-\infty}^{\infty} - D \int dx (1 + \ln n) \frac{d^2n}{dx^2}$$

\uparrow data at $\pm\infty$ shouldn't expect what happens in middle... or chose $dn/dx = 0$ there....

$$\frac{ds}{dt} = - \int dx (1 + \ln n) \frac{dn}{dt}$$

using Diffusion
equation

$$= - \int dx \frac{d}{dt} (n \ln n)$$

Now we treat density as \propto to prob for a particle & we have

$$S \sim - \sum_i p_i \ln p_i$$