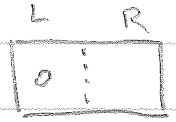
Phys 301 Fall 2020

Lec #2: Second Law

heat flows hot → cold

macroscopic regularity – physical systems evolve to single macroscopic outcome which is overwhelmingly more probable.

Consider: identical particles in a box

(1) 

2 possible states, equally likely

$\left\{ \begin{array}{l} L \\ R \end{array} \right.$

$P_L^{(1)} = 1 \text{ of } 2 = \frac{1}{2}$

(2)

4 possible states:

LL $= 1/4$

LR + RL $= \frac{1}{4} + \frac{1}{4} = \frac{1}{2}$

RR $= 1/4$

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

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

$N = 10^{20}$ $\quad P_L = \left(\frac{1}{2}\right)^{10^{20}} = \frac{1}{10^{3\times10^{19}}}$

10^{20} "large" $\quad$ 1 mole $= 6.022\times10^{23}$ # (things or molecules)

10^{N_A} "Very large"

→ $10^{N_A} N_A = 10^{N_A+1} = 10^{N_A}$ very large numbers have unusual behavior

<u>Probability</u> Consider N tosses of die

$$P_i = \lim_{N \to \infty} \frac{N_i}{N} = \frac{1}{6} \qquad i = 1, \ldots, 6 \text{ sides}$$

$$P(2 \text{ or } 3) = \frac{1}{6} + \frac{1}{6} = \frac{1}{3}$$

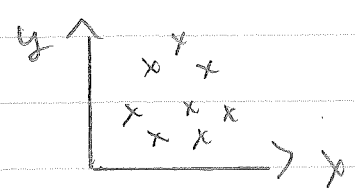
generally, for any m probabilities

$$\boxed{\sum_{i=1}^{m} P_i = 1}$$

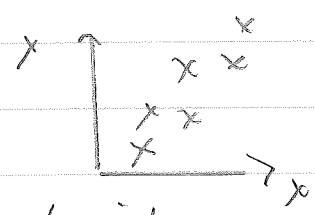
<u>joint</u>: <u>uncorrelated</u>, statistically independent outcomes

$$P_{ab} = P_a P_b$$

Consider pairs of numbers (x, y) scatter plot



uncorrelated



linearly correlated

We are concerned with <u>uncorrelated</u> probabilities

<u>Example</u> Number of ways of arranging 3 distinct objects A, B, C

ABC	cyclic	permutation
ACB	anticyclic	permutation
BCA		
BAC	6 = (3 ways to place first)	
CAB	× (2 ways to place second)	
CBA	× (1 way to place third = 3!	

Generally, # ways to ~~select~~ select N distinct objects = N!

<u>Binomial distribution</u>

Two outcomes with probabilities p, q

$$p + q = 1$$

<u>Physical example</u> – N 2-state paramagnets molecules with weak magnetic moments.

Quantum mechanically have only 2 states aligned (up) or anti-aligned (down) with external magnetic field

$$\vec{B} \uparrow \quad \underbrace{\overset{\vec{\mu}_0}{\uparrow}\ \overset{-\vec{\mu}_0}{\uparrow}\ \downarrow\ \uparrow\ \downarrow \cdots}_{N \text{ magnetic moments in external } \vec{B}}$$

energy $\pm \mu_0 B$

binomial expansion:

$$1 = (p+q)^N = \sum_{m=0}^{N} \underbrace{\binom{N}{m}}_{\text{symbol for "choose } m \text{ out of } N\text{"}} p^m q^{N-m}$$

since order of p's and q's does not matter, divide out equivalent choices

$$\binom{N}{m} = \frac{N!}{m!(N-m)!}$$

$$(p+q)^3 = p^3 + 3pq^2 + 3p^2q + q^3$$

$$m = \quad 3 \qquad 1 \qquad 2 \qquad 0$$

$\therefore 2^3 = 8$ combinations

<u>microstate</u>: (p, q, q)
(q, p, q)
(q, q, p)

<u>macrostate</u>: physically equivalent
pq^2

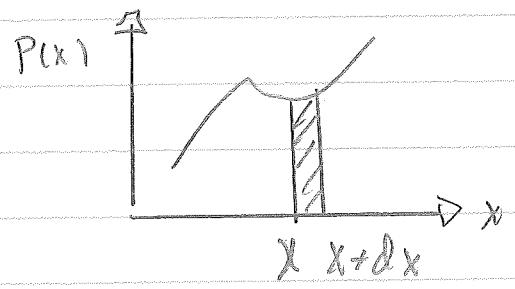
Expectation value, mean or average

Generally with N outcomes x_i having probabilities p_i

$$\bar{x} = \langle x \rangle = \sum_{i=1}^{N} x_i p_i \qquad \text{where } \sum_{i=1}^{N} p_i = 1$$

Can generalize to continuous probabilities

$p(x)$:= probability <u>density</u> function



$p(x)\,dx$ probability for x to be between x, $x+dx$

$$1 = \int_{\text{range}} p(x)\,dx$$

$$\langle x \rangle = \int_{\text{range}} x\,p(x)\,dx$$

average or expectation value of x

<u>Variance</u> (uncertainty)^2

$$(\Delta x)^2 = V(x) = \sum_{i=1}^{N} (x_i - \bar{x})^2 P_i$$

$$= \sum_{i=1}^{N} x_i^2 P_i - 2\bar{x} \underbrace{\sum_{i=1}^{N} x_i P_i}_{\bar{x}} + \bar{x}^2 \underbrace{\sum_{i=1}^{N} P_i}_{1}$$

$$= \langle x^2 \rangle - \langle x \rangle^2$$

$\boxed{\text{Binomial (N paramagnets)}}$ mean magnetic moment $\langle \mu \rangle = \frac{1}{N} \sum \mu_i = \mu_0 \frac{N_{up}}{N} - \mu_0 \frac{N_{down}}{N}$

$$= p\mu_0 - q\mu_0 = (p-q)\mu_0 = (2p-1)\mu_0$$

$$V(\mu) = \langle (\mu - \bar{\mu})^2 \rangle = \langle \mu^2 \rangle - \langle \mu \rangle^2$$ identity

$$= \underbrace{\mu_0^2 p + \mu_0^2 (1-p)}_{\text{first term}} - \underbrace{\left[(2p-1)\mu_0\right]^2}_{\text{second term}}$$

$$= 4\mu_0^2 p(1-p) = 4\mu_0^2 pq$$

$$\Delta\mu = \sqrt{V(\mu)} = 2\mu_0 \sqrt{p(1-p)}$$

<u>Can show</u>: $\langle p \rangle = np$

generally for binomial $V(p) = Np(1-p)$

<u>Gaussian</u> In limit of large N, binomial becomes Gaussian

$$G(x;\mu,\sigma) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2\right]$$

binomial limit $\mu = Np$
$\sigma = \sqrt{Np(1-p)}$

more generally, μ, σ are <u>just parameters</u>

<u>Central limit theorem</u>

If x_i are N independent variables with mean μ and variance σ^2

$$y = \frac{1}{N}\sum_{i=1}^{N} x_i$$

becomes Gaussian $G(y;\mu,\sigma)$

<u>Can Show</u>:

$$\langle x \rangle = \int_{-\infty}^{\infty} x\, G(x;\mu,\sigma) = \mu$$

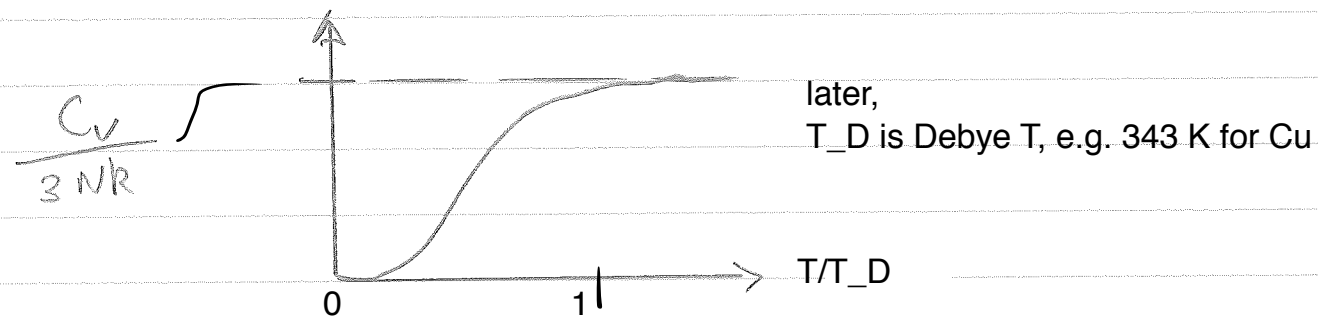
$$V(x) = \int x^2 G(x;\mu,\sigma) = \sigma^2$$

"σ" often used to mean $\sqrt{V(x)} = \Delta x$, uncertainty

Einstein Solid (1907)

heat capacity of empirical Dulong-Petit law

dependence of heat capacity on Temperature



classically, C_V solid independent of T.

recall ideal gas

$$U = N \frac{f}{2} kT$$

$$C_V = N \frac{k}{2} k \quad \text{independent of } T.$$

Einstein solid composed of N harmonic oscillators each with $f = 2$. (N/3 atoms)

for kinetic,potenial

Einstein postulated quantized oscillators.

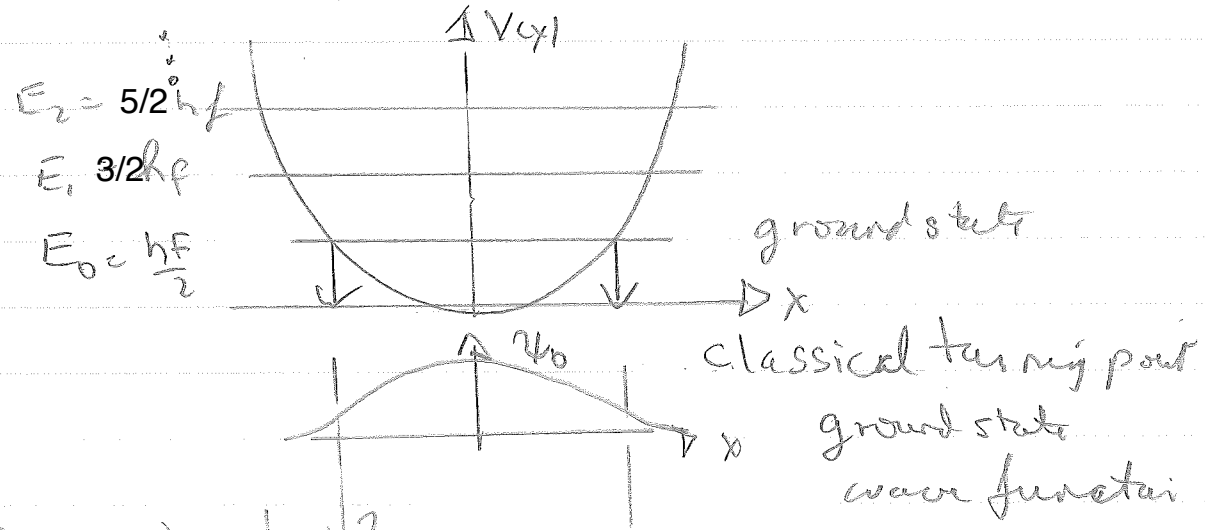
Quantum Oscillator:

harmonic potential $V(x) = \frac{1}{2} m \omega^2 x^2$

$$\omega \equiv 2\pi f$$

$$E = \frac{1}{2} m \dot{x}^2 + \frac{1}{2} m \omega^2 x^2$$

Quantization gives energies $E_n = hf\left(n + \frac{1}{2}\right)$ $n = 0, 1, 2$
with energy difference $\Delta E = hf$



$$P(x, x+\Delta x) = |\psi_0|^2 \Delta x$$

Ground state non-zero energy due to uncertainty principle

$$\Delta x \Delta p_x \geq \frac{\hbar}{2} \qquad \hbar \equiv \frac{h}{2\pi}$$

with $x = \frac{\hbar}{2p}$ minimization gives ground state energy

$$E(p) = \frac{1}{2}\frac{p^2}{2m} + \frac{1}{2} m \omega^2 \left(\frac{\hbar}{2p}\right)^2$$

$$\frac{dE}{dp} = \frac{p}{m} + \frac{m\omega^2}{2}\left(\frac{\hbar}{2}\right)^2 - \frac{2}{p^3}\Bigg|_{p_{min}} = 0$$

$$\frac{p_{min}^2}{m} = \frac{1}{2}\hbar\omega = \frac{1}{2} hf$$

$$m\omega^2 x^2 = m\omega^2 \left(\frac{\hbar^2}{2p_{min}}\right)^2 = \frac{m\omega^2}{4}\hbar^2 \left(\frac{1}{\frac{1}{2}m\hbar\omega}\right)$$

$$= \frac{1}{2}\hbar\omega$$

Giving ground state energy $E_{min} = \frac{1}{2}\hbar\omega$

Multiplicity of Einstein solid macrostate: FI

Einstein Solid: N oscillators, q total units (hf) of energy.

first osc. e=1hf, 2nd e=3hf, 3rd 0…

Multiplicity of macrostate (see "stars & bars" proof in text) 0 1 0 0 0 1 1 0 0 0 & so on

q dots
$N-1$ bars

$$\Omega(N,q) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!\,(N-1)!}$$

Consider Two in thermal contact
N_A, q_A and N_B, q_B with $q = q_A + q_B$ fixed

Multiplicity of Macrostate

$$\Omega_{tot} = \Omega_A(N_A, q_A)\,\Omega_B(N_B, q_B)$$

for isolated system in thermal equilibrium
fundamental assumption of stat. mech. —
each microstate equally probable

In thermal equilibrium, system evolves to most probable state.

Most probable

Suppose $N_A = N_B = N$

most probable state is $q_A = q_B = \frac{q}{2}$

Sterling approximation

$$N! \cong N^N e^{-N} \sqrt{2\pi N}$$

Euler

$$\Omega_{max} = \left(\frac{e}{N}\right)^{2N} \left(\frac{q}{2}\right)^{2N} \qquad \text{eq 2.23}$$

Gaussian fluctuations about maximum:

Distribution is Gaussian (unnormalized) in difference from $q/2$: $q_A = \frac{q}{2} + x$

$q_B = \frac{q}{2} - x$

$$\Omega(x) = \Omega_{max}\, e^{-N\left(\frac{2x}{q}\right)^2} \qquad \text{eq. 2.27}$$

Compare to $e^{-\frac{1}{2}\left(\frac{x}{\sigma}\right)^2}$

$$\frac{1}{\sigma^2} = \frac{4N}{q^2}, \quad \sigma = \frac{q}{2\sqrt{N}}$$

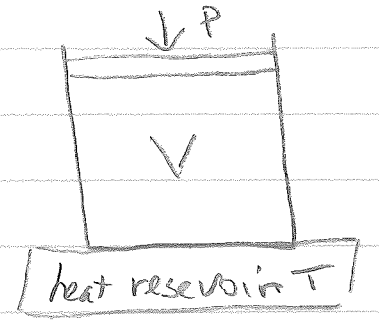
"width" $\equiv 2\sigma = \frac{q}{\sqrt{N}}$

exceedingly narrow for $N \sim N_A$

Entropy of ideal Gas N molecules, Volume V

$\Omega \propto V^N$ this is all we need for this result

Constant pressure expansion at constant temp T
Slow, "Quasi-static" expansion so T = const.



$$\frac{\Omega_f}{\Omega_i} = \frac{\Omega(V+\Delta V)}{\Omega(V)} = \left(\frac{V+\Delta V}{V}\right)^N = \left(1+\frac{\Delta V}{V}\right)^N$$

at constant T, $\Delta U = W + Q = 0$

$$Q = -W = P\Delta V = NkT\left(\frac{\Delta V}{V}\right)$$

$$\ln\left(\frac{\Omega_f}{\Omega_i}\right) = N\underbrace{\ln\left(1+\frac{\Delta V}{V}\right)}_{\text{Taylor } \ln(1)+x+\cdots} \approx N\left(\frac{\Delta V}{V}\right)$$

$$\ln\left(\frac{\Omega_f}{\Omega_i}\right) = N\left(\frac{Q}{NkT}\right) = \frac{Q}{kT}$$

$$\boxed{\Delta S = k\ln(\ \ )\quad \text{entropy}}$$

const P,T expansion of ideal gas, $\Delta S = \frac{Q}{T} = Nk\ln\left(\frac{V_f}{V_i}\right)$

Q.M. Entropy of ideal gas

Q.M. particle in box Appendix A

Wave amplitude $\psi_N(x)$ (generally complex)
& energy quantum number

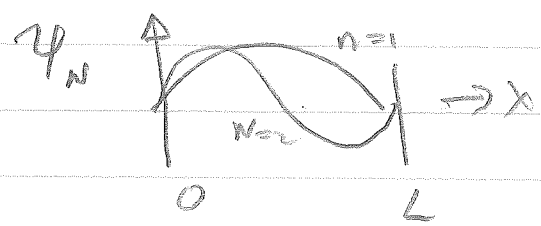
Prob. $|\psi_N(x)|^2 dx$ $\int_0^L |\psi_N(x)|^2 dx$

box of length L: $0 < x < L$

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

wave number $k_N = \frac{n\pi}{L} = \frac{2\pi}{\lambda_N}$

wave length $\lambda_N = \frac{2L}{N}$ $N = 1, 2, 3,$



waves must fit in box

momentum $P_n = \hbar k_N = \frac{h}{2\pi}\left(\frac{2\pi}{\lambda_N}\right) = \frac{h}{\lambda_N} = \frac{hN}{2L}$

$$E_n = \frac{1}{2m} P_N^2 = \frac{1}{2m}\left(\frac{h}{\lambda_N}\right)^2 = \frac{h^2 n^2}{8mL^2}$$

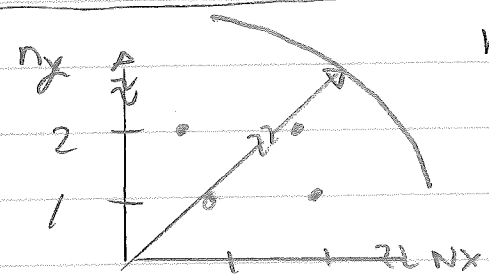
Ground state $\Delta x \Delta p \approx L\left(\frac{h}{2L}\right) = \frac{h}{2}$

In 3 dim. box $L^3 = V$

$$E(n_x, n_y, n_z) = \frac{|\vec{p}|^2}{2m} = \frac{1}{2m}\left(\frac{h}{2L}\right)(n_x^2 + n_y^2 + n_z^2)$$

Const state with total E

$$n = \sqrt{n_x^2 + n_y^2 + n_z^2}$$



$$p_i = \left(\frac{h}{2L}\right) n_i \qquad i = x, y, z$$

states for single particle with large E, in

$$\Omega_1 = \int_{n_x, n_y, n_z > 0} dn_x\, dn_y\, dn_z = \int_{-\infty}^{\infty} \left(\frac{1}{8}\right)\left(\frac{2L}{h}\right)^3 d^3p$$

↑ one octant only

$$= \frac{L^3}{h^3}\int d^3p = \frac{V}{h^3}\int d^3p$$

note the relation of this to the uncertainty principle.
QM implies quantized phase space volume.

Change variables from p to $E = \frac{p^2}{2m}$

$$d^3p = 4\pi p^2 dp = 4\pi (2mE) \frac{dE}{\left|\frac{dE}{dp}\right|} = 4\pi m \sqrt{2mE}\, dE$$

$$\frac{dE}{dp} = \frac{p}{m} = \frac{\sqrt{2mE}}{m}$$

Integral over <u>all</u> of phase space

single particle

$$\Omega_1 = \frac{V}{h^3}\int_0^E 4\pi m\sqrt{2mE}\, dE = 4\pi\sqrt{2m^3}\left(\frac{2}{3}\right)E^{3/2}\frac{V}{h^3}$$

Constraint $E = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) = \text{Const}$

gives area of surface of radius $\sqrt{2mE}$ in phase space,

$$\sum_p{}' = \frac{d\Omega_1}{dE}\Delta E = 4\pi m(2mE)^{1/2}\frac{V}{h^3}\Delta E = \frac{V}{h^3}\frac{3}{2}\left[4\pi\sqrt{2m^3}\,\frac{2}{3}E^{3/2}\right]\left(\frac{\Delta E}{E}\right)$$

$$= \left(\frac{3}{2}\right)\Omega_1\left(\frac{\Delta E}{E}\right) = g_1(E)\,\Delta E$$

density of states

$\Delta E \sim$ fluctuations in energy

eq. 2.40

Schroeder calculate $\sum_p^N$ explicitly :

3d-1 ≈ 3d
d=3N

compare to volume of d-hypersphere

$$\Omega_N = f(N)\,\frac{V^N}{h^{3N}}\,[mU]^{3N/2}$$

$$= \frac{1}{N!}\left[\frac{V}{h^3}(2\pi mU)^{3/2}\right]^N \frac{1}{\left(\frac{3N}{2}\right)!}$$

atoms are indistinguishable

Approximate for large N

with $N! = N^N e^{-N}$

$$\left(\frac{3N}{2}\right)! = \left(\frac{3N}{2}\right)^{3N/2} e^{-3N/2}$$

$$\Omega_N = N^{-N} e^{N} e^{3N/2} \left[\frac{V}{h^3}\left(2\pi m U \left(\frac{2}{3N}\right)\right)^{3/2}\right]^N$$

$$\ln \Omega_N = N \ln N \left[\frac{V}{h^3}\left(\frac{4\pi}{3} m \frac{U}{N}\right)^{3/2}\right]$$

$$-N\ln N + N + \underbrace{3N/2}_{5N/2}$$

(1912) <u>Sackur-Tetrode</u>

$$\ln \Omega_N = N \ln \left[\frac{V}{N h^3}\left(\frac{4\pi}{3} m \left(\frac{U}{N}\right)\right)^{3/2}\right] + \frac{5}{2}N$$

from $n \ln n$ from $n!$

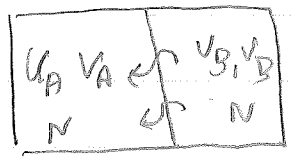
factors $\frac{V}{N}, \frac{U}{N}$ don't change if you divide system in half.

$\boxed{\text{Indistinguishability solves Gibbs paradox (1874)}}$

<u>note</u> becomes invalid at low temperature.
validity only if $[\ ] \gg 1$

entropy S (like energy U) is an extensive quantity,
double the size n double entropy

Interacting Gas exchange heat, molecules



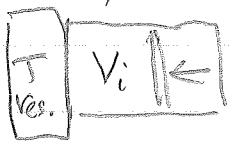
$$\Omega_{TOT} = \Omega_A \Omega_B = |f(N)|^2 (V_A V_B)^N (U_A U_B)^{3N/2}$$

similar to Einstein solid $(q_A q_B)^N$ so fluctuations in energy difference about Ω_{max} $(U_A = U_B)$ are Gaussian

$$\sigma = \frac{1}{2} \frac{U_{TOT}}{\sqrt{\frac{3N}{2}}} \propto \frac{1}{\sqrt{N}}$$

Expansion of gas

recall, quasi-static isothermal expansion



$\Delta U = 0$

$$Q = -W = \int_{V_i}^{V_f} p\,dV = NkT \ln\left(\frac{V_f}{V_i}\right)$$

s

$$\Delta S = Q/T$$

Free expansion $\Delta U = 0$

punctured barrier

$Q = 0$, $W = 0$ but

ΔS is the same,

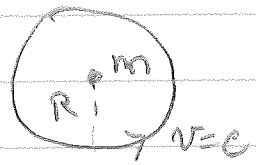
$$\Delta S = NkT \ln\left(\frac{V_f}{V_i}\right)$$

$$\boxed{\text{irreversible process } \Delta S > 0}$$

S is a state variable: value independent of thermodynamic path (history). Can choose any path to evaluate.

Ex 2.42 Entropy of black hole

event horizon (Schwartzchild radius)
related to mass. dimensional argument



$$\frac{v^2}{R} = \frac{Gm}{R^2}$$

$$R = \frac{Gm}{c^2}$$

expect $S \sim NR$ where N = # particle
count particle with minimum energy $\lambda \sim R$ (photons)

$$E = \frac{hc}{\lambda} \approx \frac{hc}{R}$$

$$N = \frac{mc^2}{\left(\frac{hc}{R}\right)} = \frac{mRc^2}{hc} = \frac{Gm^2}{hc}$$

$$S = (8\pi^2)\, k\left(\frac{Gm^2}{hc}\right)$$

↑ Hawking calculation

$$\frac{S_{B.H.}}{k} \sim 10^{77}$$ one solar mass

$$\frac{S_{sun}}{k} \sim 10^{57}$$

black hole has enormous entropy.