Microcanonical Ensemble

<u>microcanonical ensemble</u> with energy E

all microstates with energy E
have equal probabilities
other microstates have probability 0

thermodynamic variables can be deduced
from a single function of E
and other variables specifying macrostate $(V, N, \ldots)$

$\Omega(E)$ = number of microstates with energy E

probability distribution

$$P_i = \frac{1}{\Omega(E)} \quad \text{if } E_i = E$$

$$= 0 \quad \text{if } E_i \neq E$$

energy averaged over ensemble

$$\langle E \rangle = \sum_i P_i E_i = \sum_{i:E_i=E} \frac{1}{\Omega(E)} E$$

$$= \frac{1}{\Omega(E)} E \underbrace{\sum_{i:E_i=E} 1}_{\Omega(E)} = E$$

information entropy:

$$S_{info} = -\sum_i P_i \log P_i$$

restrict sum to states with nonzero P_i

$$= -\sum_{i:E_i=E}' P_i \log P_i$$

$$= -\sum_{i:E_i=E}' \frac{1}{\Omega(E)} \log \frac{1}{\Omega(E)}$$

$$= -\frac{1}{\Omega(E)} \log \frac{1}{\Omega(E)} \underbrace{\sum_{i:E_i=E}' 1}_{\Omega(E)}$$

$$= -\frac{1}{\cancel{\Omega(E)}} \log \frac{1}{\Omega(E)} \cdot \cancel{\Omega(E)}$$

$$= -\log \frac{1}{\Omega(E)}$$

$$= \log \Omega(E)$$

classical system:

$$\Omega(E) = \int d\omega \; \delta\big(H(p,q) - E\big) \Delta E$$

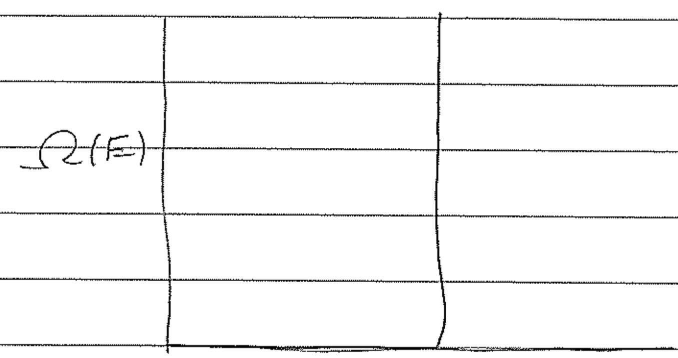
= volume of phase space with energy $H(p,q)$ between $E - \frac{1}{2}\Delta E$ and $E + \frac{1}{2}\Delta E$

for macroscopic system,

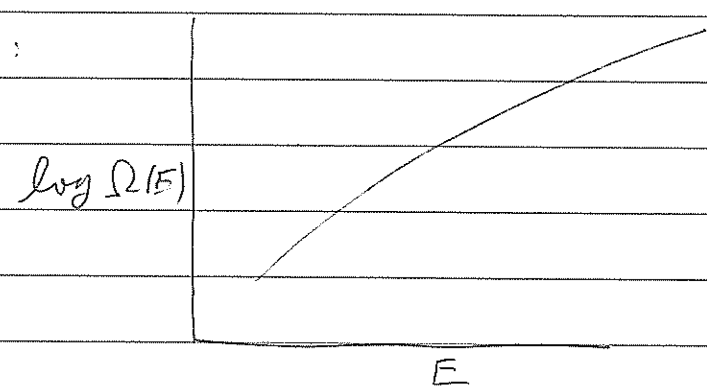
$\Omega(E)$ increases extremely rapidly with E

example of such a function: E^{N_A}, where $N_A = 6\times10^{23}$

graph of $\Omega(E)$:



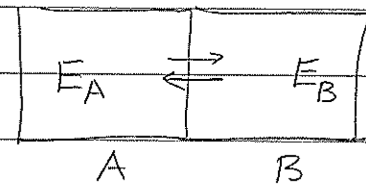
graph of $\log\Omega(E)$:



$\log\Omega(E)$ increases roughly like $\log E$

two macroscopic system A and B
in thermal contact
but otherwise isolated

energies: E_A and E_B



thermal contact: can exchange energy

otherwise isolated $\Longrightarrow$ total energy $E_A + E_B$ is conserved

number of microstates

for A: $\Omega_A(E_A)$

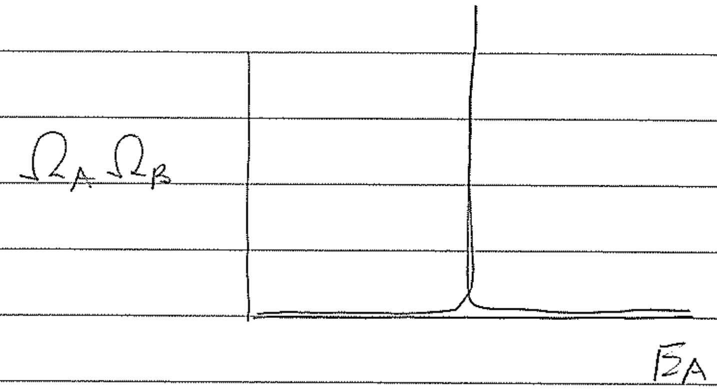
for B: $\Omega_B(E_B)$

for A and B: $\Omega_A(E_A) \times \Omega_B(E_B)$

microcanonical ensemble with total energy E

all microstates with $E_A + E_B = E$
are equally likely

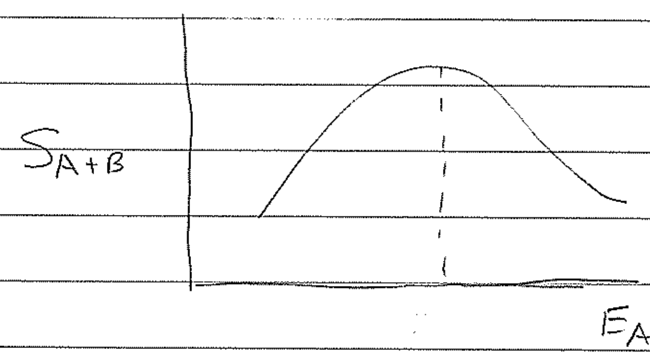
$$\Omega_{A+B}(E, E_A) = \Omega_A(E_A) \cdot \Omega_B(E - E_A)$$



energy E_A is overwhelmingly likely
to be extremely near
the value that maximizes $\Omega_A(E_A)\,\Omega_B(E-E_A)$

information entropy

$$S_{A+B}(E, E_A) = S_A(E_A) + S_B(E-E_A)$$



energy E_A is overwhelmingly likely
to be extremely near
the value that maximizes total entropy

maximize total entropy:

$$\frac{d}{dE_A}\left(S_A(E_A)+S_B(E-E_A)\right)=0$$

$$\frac{dS_A}{dE_A}(E_A)+\frac{dS_B}{dE_B}(E-E_A)\cdot\frac{d}{dE_A}(E-E_A)=0$$

$$\frac{dS_A}{\partial E_A}(E_A)-\frac{dS_B}{dE_B}(E-E_A)=0$$

equilibrium condition: $\boxed{\frac{\partial S_A}{\partial E_A}=\frac{\partial S_B}{\partial E_B}}$

from thermodynamics: $\boxed{T_A=T_B}$

$\Longrightarrow$ $\frac{\partial S}{\partial E}$ must be determined by temperature T

fundamental thermodynamic relation

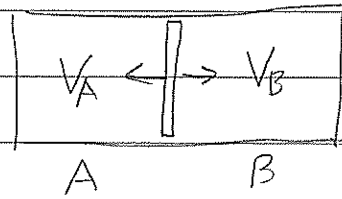
$$dE=TdS-PdV+\cdots$$

$$\Longrightarrow T=\left(\frac{\partial E}{\partial S}\right)_{V,\ldots}$$

If information entropy and thermodynamic entropy can be identified, then

$$\left(\frac{\partial S}{\partial E}\right)_{V,\ldots}=\frac{1}{T}$$

Two macroscopic systems A and B
that can exchange volume with $V = V_A + V_B$ fixed



equilibrium condition: $\boxed{\dfrac{\partial S_A}{\partial V_A} = \dfrac{\partial S_B}{\partial V_B}}$

mechanics: $P_A = P_B$ at equilibrium

$\Longrightarrow$ $\dfrac{\partial S}{\partial V}$ must be determined by pressure P

thermodynamics: $dE = TdS - PdV + \ldots$

$$\Longrightarrow P = T\left(\frac{\partial S}{\partial V}\right)_{E,\ldots}$$

if information entropy and thermodynamic entropy
can be identified then

$$\left(\frac{\partial S}{\partial V}\right)_{E,\ldots} = \frac{P}{T}$$