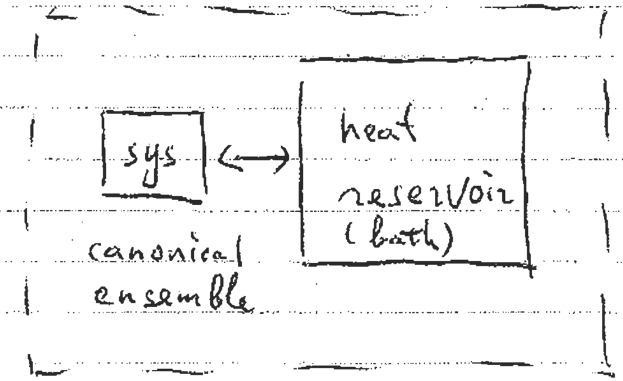
I Canonical ensemble

① 

microcanonical ensemble.

What is the probability for the system to be in a state with energy E_n?

Ideal heat bath: T ind. of energy

From $\dfrac{1}{T} = \dfrac{\partial S(E)}{\partial E}$

$$\Rightarrow \boxed{S_{bath}(E) = \frac{E}{T}}$$

or $\boxed{\text{\# of states } \Gamma_{bath}(E) = e^{E/Tk_B}}$

② Boltzmann distribution

Our system can have many energy levels E_n, $n = 1, 2, \cdots$

Picture of microcanonical ensemble : sys + heat bath

Total energy E_{tot} is fixed (isolated, microcanonical)

# of states when sys is in the n^{th} state

$$= 1 \cdot \Gamma_{bath}(E_{tot} - E_n)$$

$$= e^{(E_{tot} - E_n)/k_B T}$$

$$\boxed{\begin{array}{l}\text{Prob. for the sys be in the } n^{th} \text{ state} \\ \quad \propto e^{-E_n/k_B T}\end{array}}$$

(3) The partition function - the total prob.

$$\boxed{Q(T,V) \equiv \sum_n \underbrace{e^{-E_n/k_B T}}_{\text{ind. prob.}}} \qquad \text{(quantum)}$$

We can rewrite

$$Q = \int dE \underbrace{\sum_n \delta(E - E_n)}_{\equiv \Gamma_{sys}(E) \,=\, \#\text{ of states of sys with energy } E.} e^{-E/k_B T}$$

$$= \int dE \, \Gamma_{sys}(E) \, e^{-E/k_B T}$$

$$= \int dE \, e^{-(E/k_B T) + (S(E)/k_B)}$$

$$= \int dE \underbrace{e^{-\frac{1}{k_B T}(E - S(E)T)}}_{\propto \text{ prob. for sys to have energy } E}$$

Sys. has an energy that maximize

$A = E - S(E)\,T$

max value

$$A_{max} = \bar{E} - S(\bar{E})\,T$$

where $\bar{E}$ satisfies $\underbrace{\frac{1}{T}}_{=\frac{1}{T_{bath}}} = \underbrace{\frac{dS(\bar{E})}{dE}}_{=\frac{1}{T_{sys}}}$

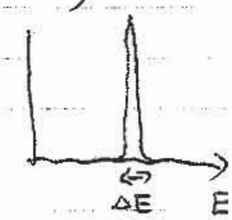
$\bar{E}$ is the energy of sys in equilibrium state $T_{sys} = T_{bath}$

$A = E - ST$ is the Free energy
(Helmholtz energy)

(a) $e^{-\frac{1}{k_B T} A}$ $\propto$ prob. distribution of canonical ensemble.

Sys. wants to minimize the free energy
(which mean to reach equilibrium state)

(b) $e^{-\frac{1}{k_B T} A}$ is sharply peaked



As a result

$$Q = \int dE\, e^{-\frac{1}{k_B T} A}$$

$$\sim e^{-\frac{1}{k_B T} A_{min}}$$

A_{min}: free energy of equilibrium state.

$$\boxed{A = -k_B T \ln Q}$$

Compare with microcanonial ensemble

micro canonical

Prob. : $\Gamma(E) = e^{S/k_B}$ $\qquad$ $\Gamma(E)\, e^{-\frac{E}{k_BT}} = e^{-\frac{(E-ST)}{k_BT}}$

$$= e^{-A/k_BT}$$

(4) Thermodynamical relation & quantities

Let $\tilde{A}(E,T) = E - S(E)\,T$

Free energy is obtained by minimize $\tilde{A}$ respect to E:

$$A(T) = \tilde{A}(\bar{E}(T),T)\,, \qquad \left.\frac{\partial \tilde{A}(E,T)}{\partial E}\right|_{E=\bar{E}} = 0$$

(a) Entropy: Calculate

$$\frac{\partial A(T)}{\partial T} = \underbrace{\left.\frac{\partial \tilde{A}}{\partial E}\right|_{E=\bar{E}}}_{=0} \frac{\partial \bar{E}(T)}{\partial T} + \left.\frac{\partial \tilde{A}}{\partial T}\right|_{E=\bar{E}}$$

$$\boxed{\frac{\partial A}{\partial T} = -S}$$

specific heat:

$$\frac{\text{Heat}}{\partial T} = \boxed{T\frac{dS}{dT} = C}$$

(b) Energy: $\bar{E} = A + S(E)\,T$

$$= A - T\frac{\partial}{\partial T}A$$

Second way $\quad \bar{E} = \langle E \rangle_{average} = \sum_n E_n e^{-\beta E_n} \Big/ \sum_n e^{-\beta E_n}$

$$= -\frac{\partial}{\partial \beta}\ln Q = \left(k_B T^2 \frac{\partial}{\partial T}\right)\frac{-1}{k_BT}A$$

$$= A - T\frac{\partial}{\partial T}A$$

(5) Energy cost of information

Flexible chain:

$$\text{Length} = \underset{R}{(+1)} + \underset{R}{(+1)} + \underset{L}{(-1)} + \underset{R}{(+1)} + \underset{R}{(+1)}$$

$$= N_R - N_L$$

No internal energy.

Total number of states $= 2^N$ $\quad (N = N_R + N_L)$

number of states w/ $N_R - N_L = 0$

$$= C_N^{N/2} = \frac{N!}{(N/2)!}$$

Total entropy $\quad S_{tot} = k_B \ln 2^N = N k_B \ln 2$

Entropy with Length $= 0$ $\quad S_0 = k_B \ln C_N^{N/2}$

$$\approx k_B \; N \ln N - 2\left(\tfrac{N}{2}\right)\ln\left(\tfrac{N}{2}\right)$$

$$= N k_B \ln 2 \doteq S_{tot}$$

Entropy with Length $= N$ $\quad S_1 = k_B \ln 1 = 0$

Energy required to stretch the chain from Length $= 0$ to Length $= N$?

No internal energy $\Rightarrow$ No energy cost X

chain entropy ↓ heat bath entropy ↑

ΔS for the heat bath $= N k_B \ln 2$.

Entropy of heat bath $S_{bath} = \dfrac{E_{bath}}{T}$

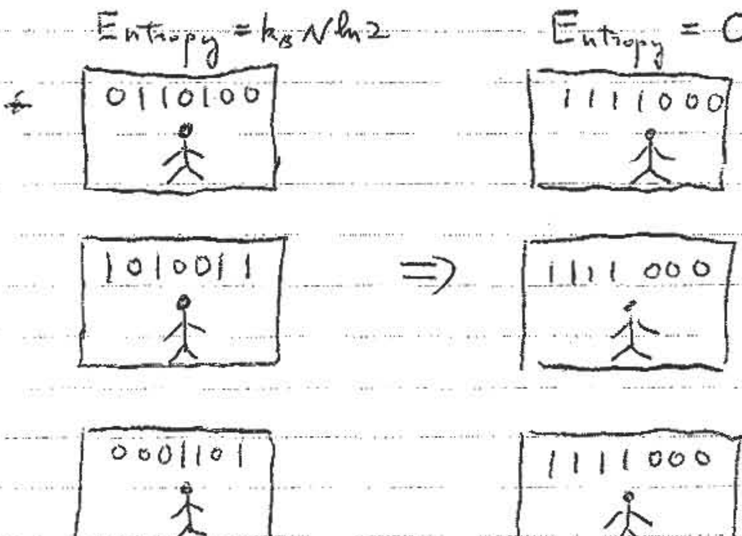
$S_{bath} \uparrow$ can only be achieved through $E_{bath} \uparrow$

$$\Delta E_{bath} = T \Delta S = k_B T N \ln 2$$

= energy cost to stretch the chain

$$= A_{final} - A_{init} = (-S_{final} T) - (-S_{init} T) = \Delta S\, T$$

What about information



To encode one bit of information, we need $k_B T \ln 2$ amount of energy

Total entropy can only increase

* Ideal memory chip:

to program 1 G bytes of RAM at room temperature we need energy $= k_B T (\ln 2) \times 8 \times 10^9$

$= 2.3 \times 10^{-4}$ erg

* Ideal bus: 1 G bits / second

power $= 3 \times 10^{-5}$ erg/s $= 3 \times 10^{-12}$ Watt

Computer ~ 100 Watt

How to measure the amount of information

information = Const. − entropy $\times k_B^{-1}$

		information	entropy/k_B
0 50%	1 50%	0	$\ln 2$
0 100%	1 0%	$\ln 2$	0

$$\boxed{\text{information} = \underbrace{\ln \Gamma}_{\#\text{ of states}} - \sum \underbrace{P_i}_{\text{prob. for state "i"}} \ln \frac{1}{P_i}}$$

information = 0 if $P_i = \frac{1}{\Gamma}$

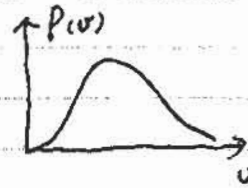
information = $\ln \Gamma$ if only one $P_i = 1$

⑥ Maxwell distribution and equipartition of energy.

Prob. to find $\vec{p}$ in volum $d^3\vec{p}$: $\boxed{C e^{-\beta \vec{p}^2/2m} d^3\vec{p}}$

Prob. to find v between v and $v+dv$: $\boxed{\tilde{C} e^{-\beta \frac{mv^2}{2}} v^2 dv}$

Maxwell distribution



Kinetic energy of x-motion

$$\left\langle \frac{p_x^2}{2m} \right\rangle = \frac{\int d^3\vec{p}\ \frac{p_x^2}{2m} e^{-\beta \vec{p}^2/2m}}{\int d^3\vec{p}\ e^{-\beta \vec{p}^2/2m}}$$

$$= \frac{\int dp_x\ \frac{p_x^2}{2m} e^{-\beta p_x^2/2m}}{\int dp_x\ e^{-\beta p_x^2/2m}} \qquad \int dx\, e^{-x^2} = \sqrt{\pi}$$

$$= -\frac{d}{d\beta} \ln \underbrace{\int dp_x\ e^{-\beta p_x^2/2m}}_{= \sqrt{\pi}\sqrt{\frac{2m}{\beta}}}$$

$$= \frac{1}{2}\frac{1}{\beta} = \frac{k_B T}{2}$$

$$\left\langle \frac{p_x^2}{2m} \right\rangle = \left\langle \frac{p_y^2}{2m} \right\rangle = \left\langle \frac{p_z^2}{2m} \right\rangle = \frac{k_B T}{2}$$

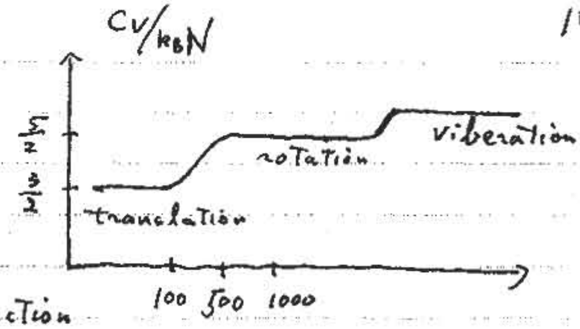
$$= \left\langle \frac{p_x^2}{2m'} \right\rangle \longleftarrow$$ For a mixture of particles of mass m and m'

Total energy $E = \frac{N k_B T}{2} \times 3$

heat capacity : $C_V = \frac{\partial E}{\partial T} = \frac{3}{2} N k_B$

mixed gas $C_V = \frac{3}{2} k_B (N_1 + N_2 \cdots)$

But for H_2



Rotation around z-direction

$$E_m = \frac{L_z^2}{2I} =: E_0 m^2 \qquad m = 0, \pm 1, \pm 2 \cdots$$

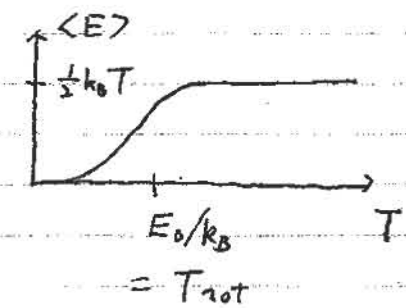
average energy $\langle E \rangle = \dfrac{\sum E_m e^{-\beta E_m}}{\sum_m e^{-\beta E_m}}$

if $E_0 \beta \ll 1$:

$$\langle E \rangle = \frac{\int dm \; \frac{1}{2} E_0 m^2 e^{-\beta E_0 m^2}}{\int dm \; e^{-\beta E_0 m^2}} = \frac{1}{2} k_B T$$

if $E_0 \beta \gg 1$:

$$\langle E \rangle =: E_0 e^{-E_0/k_B T}$$



	T_{rot}	T_{vib}
H_2	85.4	6100
N_2	2.86	3340
O_2	2.07	2230

$\uparrow$ for air $C_V \simeq \frac{7}{2} k_B (N_{O_2} + N_{N_2})$
at room temperature

(7) Free energy of classical ideal gas

partition function

$$Q(T,V) = \int \frac{d^{3N}p \; d^{3N}q}{N! \; h^{3N}} \, e^{-\beta(p_1^2 + \cdots + p_N^2)/2m}$$

$$\boxed{\beta = \frac{1}{k_B T}}$$

$$= \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N$$

$$\int \frac{dp}{h} e^{-\beta p^2/2m} = \frac{1}{\lambda}$$

$$\lambda = \sqrt{2\pi \hbar^2 / mkT}$$

$$\sim \hbar / \sqrt{mkT} = \frac{\hbar}{\sqrt{2mK}}$$

K: average kinetic energy

$$\boxed{\begin{aligned} A(V,T) &= -k_B T \ln Q \\ &= N k_B T \left[\ln(n\lambda^3) - 1 \right] \end{aligned}}$$

Entropy

$$\boxed{S = -\left(\frac{\partial A}{\partial T}\right)_V = N k_B \left(\frac{5}{2} + \ln \frac{v}{\lambda^3} \right)} \qquad v = \frac{V}{N}$$

$\frac{v}{\lambda^3}$ = # of states per particles

$$\left.\frac{\partial A}{\partial V}\right|_T = -kT \frac{\frac{\partial}{\partial V} Q}{Q}$$

$$= -kT \frac{\sum_n -\beta \frac{\partial E_n}{\partial V} e^{-\beta E_n}}{\sum_n e^{-\beta E_n}}$$

$$= \frac{\sum_n \frac{dE_n}{dV} e^{-\beta E_n}}{\sum_n e^{-\beta E_n}}$$

$= -\langle P \rangle$ ← average pressure.

$\frac{dE_n}{dV}$: change of energy for isolated system. $-\frac{dE_n}{dV}$ = pressure for the n^{th} state

$$A(V,T) = N k_B T \left[\ln\left(\frac{N\lambda^3}{V}\right) - 1 \right]$$

$$P = -\frac{\partial A}{\partial V}\bigg|_{T,N} = N k_B T / V$$ equ. of state.