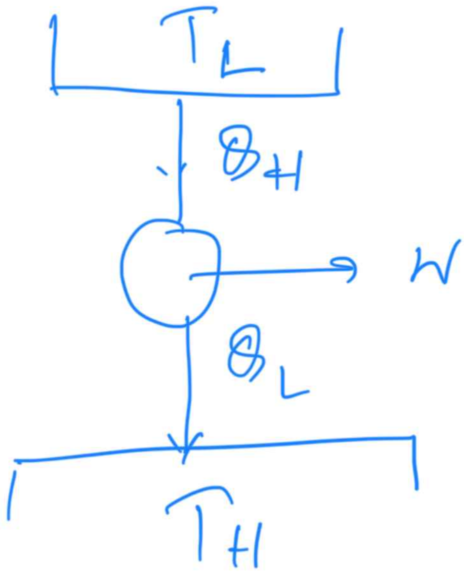
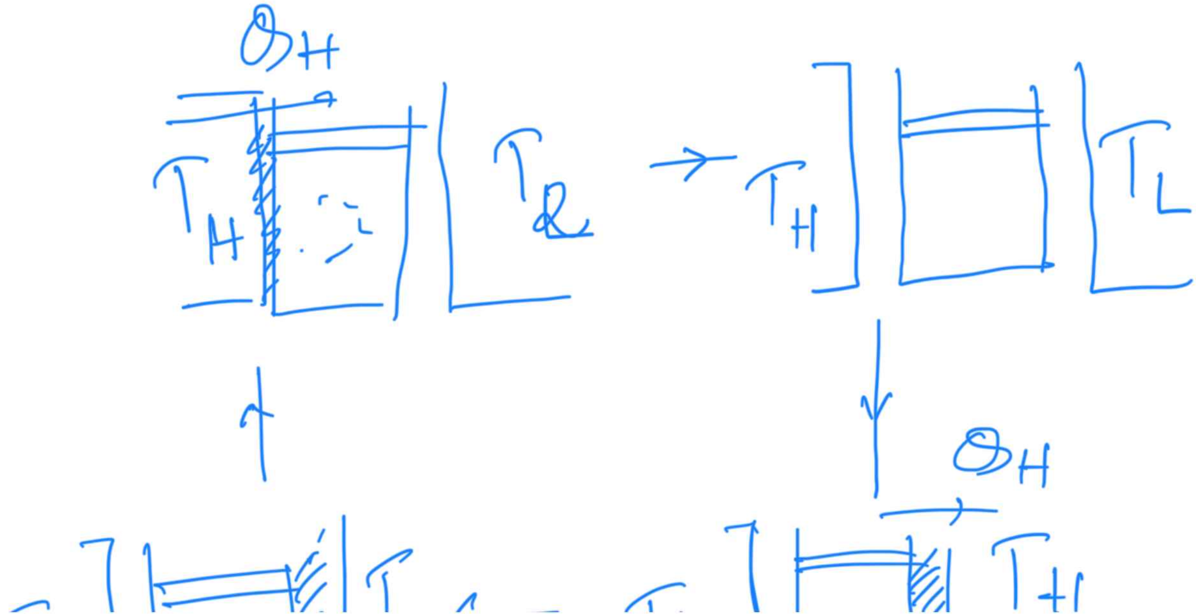
What is equilibrium thermodynamics

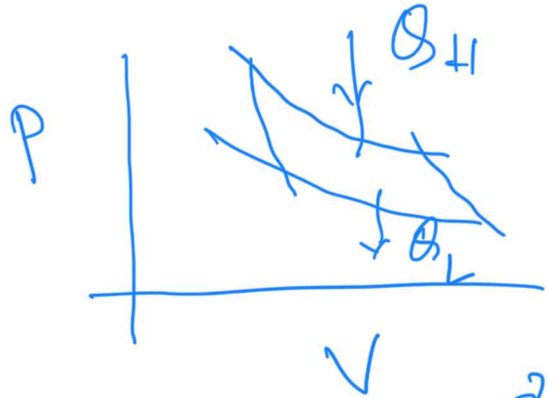
Why statistical Mechanics.

Carnot engine and efficiency.



$$\eta_r = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$





$PV = RT$ $\qquad$ $PV^{\gamma} = RT$

Isothermal expansion $\qquad$ Adiabatic expansion

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H}$$

$$\eta_r = 1 - \frac{T_L}{T_H}$$

$$\eta_{ir} < \eta_r$$

$$1 - \left(\frac{Q_L}{Q_H}\right)_{ir} < 1 - \left(\frac{Q_L}{Q_H}\right)_r \Rightarrow \left(\frac{Q_L}{Q_H}\right)_r < \left(\frac{Q_L}{Q_H}\right)_{ir}$$

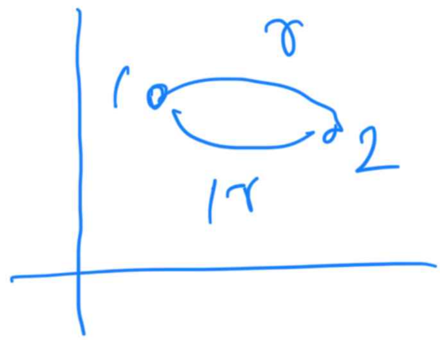
$$\Rightarrow (Q_H) = (Q_H)_{ir}$$

$\Rightarrow (Q_H)_r \quad ($

$\Rightarrow (Q_L)_{Ir} > (Q_L)_r$

$$\left(\frac{Q_L}{T_L}\right)_r = \left(\frac{Q_H}{T_H}\right)_r \Rightarrow -\frac{Q_L}{T_L} + \frac{Q_H}{T_H} > 0$$

$$\oint \frac{dQ}{T} \le 0$$



$$\int_1^2 \frac{dQ}{T} + \int_2^1 \frac{dQ}{T} \le 0$$

$$S_2 - S_1 + \int_2^1 \frac{dQ}{T} \le 0$$

$$\int_1^2 \frac{dQ}{T} \ge S_2 - S_1 \Rightarrow \int_1^2 \frac{dQ}{T} \ge \Delta S_1 + \Delta S_2$$

irreversible process

Entropy explains the low efficiency for irreversible process

Microscopic explanation for thermodynamic entropy

First law of thermodynamics

$$dQ = dU + dW.$$

$$dS = \frac{1}{T} dU + \frac{1}{T} dW$$

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$$

Microstate and macrostate

Two dice $\{1, 2, 3 \ldots 6\}$

Summation $\{2 \ldots 12\}$ sample

1 — space

Macrostate 2 microstate 1 + 1

3 microstate 1 + 2

2 + 1

4 " 1 + 3

2 + 2

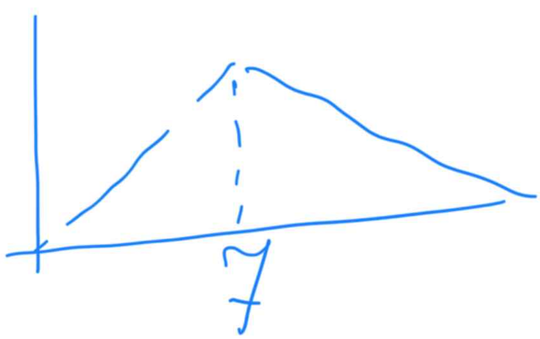
3 + 1

5 " 1 + 4

2 + 3

3 + 2

4 + 1



Most probable microstate = 7

prob of each microstate: $\frac{1}{6} \times \frac{1}{6}$

prob of ...

Coin Toss

probably of ~~n~~ of Heads in N

$$p(n) = {}^N C_n \, p^n (1-p)^{N-n}$$

$$\langle n \rangle = Np$$

$$\langle n^2 \rangle - \langle n \rangle^2 = Np(1-p)$$

Generating function

$$f(z) = \sum_n z^n p(n)$$

$$\langle n \rangle = \left(\frac{\partial f}{\partial z}\right)_{z=1}$$

$$\langle n^2 \rangle - \langle n \rangle = \left(\frac{\partial^2 f}{\partial z^2}\right)_{z=1}$$

For binomial distribution:

$$f(Z) = (Zp+q)^N$$

$$= (Zp+1-p)^N$$

$$\frac{\partial f}{\partial Z} = Np\,(Zp+1-p)^{N-1}$$

$$\langle n \rangle = Np$$

$$\frac{\partial^2 f}{\partial Z^2} = N(N-1)\,p^2\,(Zp+1-p)^{N-2}$$

$$\langle n^2 \rangle - \langle n \rangle = N(N-1)\,p^2$$

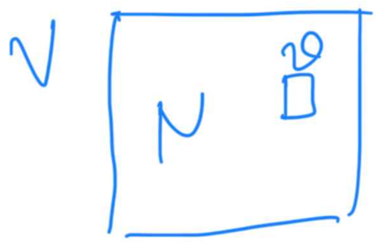
$$\langle n^2 \rangle - \langle n \rangle^2 = -Np^2 + Np$$

$$= Np(1-p)$$

$$\frac{\sigma_n^2}{\langle n^2 \rangle} = \frac{Np(1-p)}{N^2 p^2} = \frac{1}{N}\left(\frac{1-p}{p}\right)$$

$\simeq \frac{1}{\sqrt{N}}, \quad p = \frac{1}{2}$

For a gas in a box of volume V



probability that there are n particles inside v

$$p(n) = {}^{N}C_n \left(\frac{v}{V}\right)^n \left(1 - \frac{v}{V}\right)^{N-n}$$

$$= {}^{N}C_n \left(\frac{\rho v}{N}\right)^n \left(1 - \frac{\rho v}{N}\right)^{N-n} \qquad \boxed{\rho = \frac{N}{V}}$$

$$= {}^{N}C_n \left(\frac{\lambda}{N}\right)^n \left(1 - \frac{\lambda}{N}\right)^{N-n}$$

$N \to \infty$

$$= e^{-\lambda} \frac{\lambda^n}{n!}$$ poisson distribution

Sterling approximation

$$n! = e^{-n} n^{n+\frac{1}{2}} \sqrt{2\pi}$$

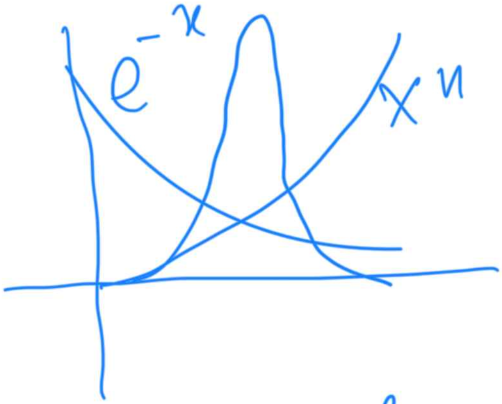
$$p(n) = \frac{e^{-N} N^{N} \frac{1}{\cancel{N^{\pi}}\sqrt{N}}}{e^{-(N-n)} (N-n)^{N-n} \sqrt{\cancel{N}-n}} \frac{\lambda^n}{n!} \left(1-\frac{\lambda}{N}\right)^{N-n}$$

$$= \frac{e^{-N} N^{\cancel{N}-n} \left(1-\frac{\lambda}{N}\right)^{-n} \frac{\lambda^n}{n!}\left(1-\frac{\lambda}{N}\right)^{N}}{e^{-N} (N-n)^{N-n} e^{n}}$$

$$= \frac{\cancel{e^{-N}} N^{\cancel{N}-n} \boxed{\frac{\lambda^n}{n!} e^{-\lambda}}}{\cancel{e^{-N}} N^{\cancel{N}-n} \underbrace{\left(1-\frac{n}{N}\right)^{N-n}}_{\cancel{e^{-n}}} \cancel{e^{n}}}$$

Sterling approximation

$$n! = \int^{\infty} x^n e^{-x} dx$$



$$I = \int_0^{\infty} e^{-(x - n\log x)}\, dx$$

$$f(x) = x - n\log x$$

$$f'(x) = 1 - \frac{n}{x} \qquad x_0 = n \quad f'(x_0) = 0$$

$$f''(x) = \frac{n}{x^2} \qquad f''(x_0) = \frac{1}{n}$$

$$f(x) = (n - n\log n) + \frac{(x-n)^2}{n} + \cdots$$

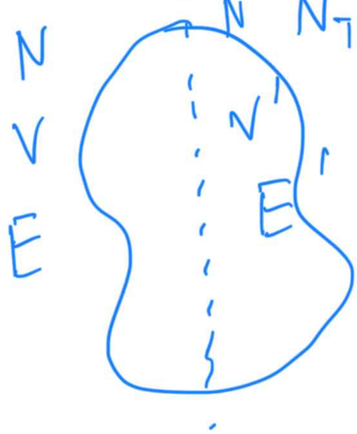
$$I = e^{-(n - n\log n)} \int_{-\infty}^{+\infty} e^{-\frac{(x-n)^2}{n}}\, dx$$

$$= e^{-(n - n\log n)} \sqrt{2\pi n}$$

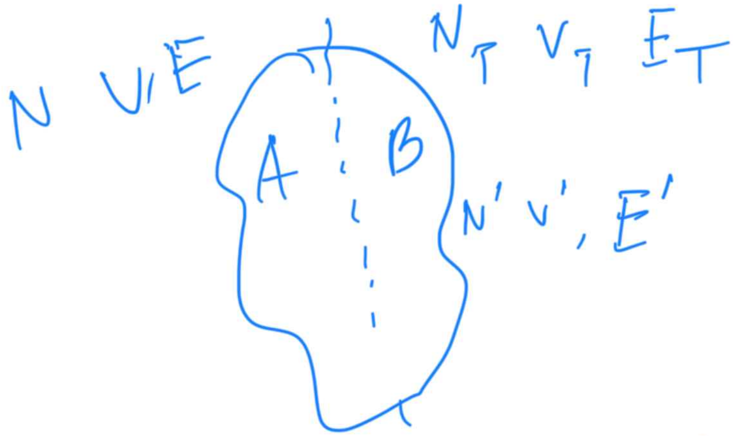
$$n! = e^{-n} \, n^{n+\frac{1}{2}} \sqrt{2\pi}$$

Microcanonical ensemble

$N_T \quad V_T \quad E_T$



Microcanonical ensemble.



# of microstates of the total system such that system A has energy $E = \Omega(E)$

$$p(E) = \frac{\Omega(E)\,\Omega(E')}{\Omega(E_T)}$$

Assuming that the interaction degrees of freedom can be neglected $E_T = E + E'$

$$p(E) = \frac{\Omega(E)\,\Omega(E_T - E)}{\Omega(E_T)}$$

$$\ln p(E) = \ln \Omega(E) + \ln \Omega(E_T - E) + \ln \Omega(E_T)$$

$$\frac{\partial}{\partial E} \ln p(E) = 0$$

$$\Rightarrow \frac{\partial}{\partial E} \ln \Omega(E) = -\frac{\partial}{\partial E} \ln \Omega(E')$$

$$E' = E_T - E \quad \partial E = \partial E'$$

$$\frac{\partial}{\partial E} \ln \Omega(E) = \frac{\partial}{\partial E'} \ln \Omega(E')$$

$$\frac{\partial}{\partial N} \ln \Omega(E, V, N) = \frac{\partial}{\partial N'} \ln \Omega(E', V', N')$$

$$\frac{\partial}{\partial V} \ln \Omega(E, V, N) = \frac{\partial}{\partial V'} \ln \Omega(E', V', N')$$

~~Th~~ First law of thermodynamics

$$dQ = dU + p\,dV$$

From 2nd law $\frac{dQ}{T} = dS$

$$T\,dS = dU + p\,dV$$

$$\Rightarrow \frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V \qquad \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_U$$

If $S = k_B \ln \Omega (E, V, N)$

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \left(\frac{\partial S'}{\partial E'}\right)_{V,N} = \frac{1}{T}$$

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \left(\frac{\partial S'}{\partial V'}\right)_{E'N'} = \frac{P}{T}$$

$$dS = \left(\frac{\partial S}{\partial E}\right) dE + \left(\frac{\partial S}{\partial V}\right) dV$$

$$dS = \frac{1}{T}\,dE + \frac{P}{T}\,dV.$$

So the thermodynamics entropy is

Same as the Boltzman entropy.

Entropy for an Ideal gas. $\mathcal{E} < E$

For one particle $H = \frac{p^2}{2m}$ (no interaction for ideal gas)

phase space volume

$$M = \int_0^R \int_0^P d^3 r \, d^3 p$$

$$p = \sqrt{2m\mathcal{E}}$$

$$M = \frac{4\pi R^3}{3} \times \frac{4\pi p^3}{3}$$

$$= \frac{4\pi}{3} V \cdot (2m)^{1/3} \, \mathcal{E}^{3/2}$$

Number of microstates

$$\frac{4\pi V}{\quad} (2m)^{1/2} \, \mathcal{E}^{3/2}$$

$$\Omega(\mathcal{E} < E) = \frac{\quad}{3h^3}(2m)\quad \mathcal{E}$$

For N particles.

$$\Omega_N(\mathcal{E}) = \Omega(\mathcal{E})^N$$

Entropy $S = K_B \ln \Omega_N(\mathcal{E})$

$$= N K_B \ln \Omega(\mathcal{E})$$

$$= N K_B \ln \frac{4\pi V}{3h^3}(2m)^{1/2}\,\mathcal{E}^{3/2}$$

$$\left(\frac{\partial S}{\partial \mathcal{E}}\right)_V = N K_B \frac{3}{2\mathcal{E}} = \frac{1}{T}$$

$$\Rightarrow \mathcal{E} = \frac{3}{2} N K_B T \qquad U = \frac{3}{2} N K_B T$$

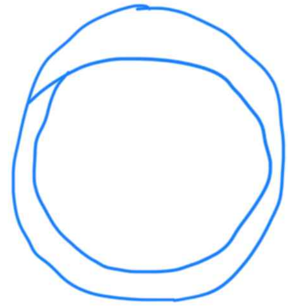
$$\frac{\partial U}{\partial T} = \frac{3}{2} N K_B$$

... ensemble.

Microcanonical ense

Volume of phase space with energy E and $E + dE$

Volume of an N dimensional sphere



$$V_n(R) = \frac{\pi^{n/2} R^n}{\Gamma\left(\frac{n}{2}+1\right)}$$

$$\Omega(E) = \frac{V^N}{h^{3N}} \frac{\pi^{N/2} \, p^{3N}}{\Gamma\left(\frac{N}{2}+1\right)}$$

$$= \frac{V^N}{h^{3N}} \frac{\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}+1\right)} (2m)^{3N/2} E^{3N/2}$$

$$\Omega(E \to E+\Delta E) = \frac{V^N}{h^{3N}} \frac{\pi^{3N/2} (2m)^{3N/2}}{\Gamma\left(\frac{3N}{2}+1\right)} \times \frac{3N}{2} E^{3N/2-1}$$

$N \quad 3N/2 \quad \pi^{3N/2} (2m)^{3N/2}$

$$= V\, C\, E \qquad C = \frac{\quad}{h^{3N}\,\Gamma\left(\frac{3N}{2}+1\right)}$$

$$S = k_B \ln \Omega$$

$$= k_B \left[N \ln V + \frac{3N}{2} \ln E + \ln K \right]$$

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{3Nk_B}{2E} = \frac{1}{T} \Rightarrow \boxed{E = \frac{3}{2} N k_B T}$$

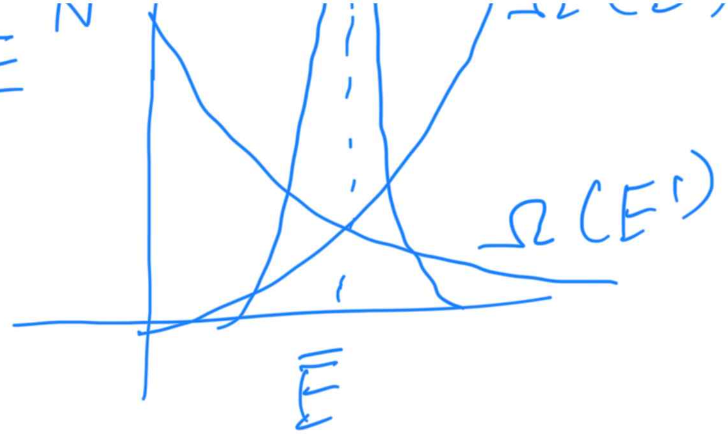
$$\left(\frac{\partial S}{\partial V}\right)_{E,V} = \frac{Nk_B}{V} = \frac{P}{T} \quad \boxed{PV = Nk_B T}$$

Specific heat $c_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} N k_B$

distribution for microcanonical ensemble

$$p(E) = \frac{\Omega(E)\,\Omega(E')}{\Omega(E_T)}$$

$\Omega(E) \sim E^N$



$$\ln P(E) = p(\bar{E}) + \left.\frac{\partial \ln P(E)}{\partial E}\right|_{\bar{E}} (E-\bar{E}) + \frac{1}{2}\left.\frac{\partial^2 \ln P(E)}{\partial E^2}\right|_{\bar{E}} (E-\bar{E})^2$$

$$= P(\bar{E}) - \frac{1}{2}\kappa (E-\bar{E})^2$$

$$p(E) = C\, e^{-\frac{1}{2}\kappa (E-\bar{E})^2}$$

Canonical ensemble.

NVE A B

Number of microstate of the system such that A has energy E

$$\Omega(E) =$$

$$P(E) = \frac{\Omega(E')}{\Omega(E_T)}$$

$$\ln P(E) = \ln \Omega(E_T - E) + \ln \Omega(E_T)$$

$$\ln P(E) = \ln P(E_T) - \frac{\partial}{\partial E} \ln P(E)\Big|_{E_T} \varepsilon$$

$$P(E) \simeq C e^{-\beta \varepsilon}$$

$$\beta(\varepsilon) = \frac{\partial}{\partial E} \ln(P(E))\Big|_{E_T} = \frac{1}{T}$$

heat bath temperature T

Canonical ensemble at mean

total number

energy $\langle E \rangle$ and ...

of particle fixed

n_3 No of ways N

n_2 particle can be

n_1 distributed among M states

$$W = \frac{N!}{n_1!\, n_2!\, n_3! \cdots n_M!}$$

$$\frac{1}{N}\sum_i n_i \epsilon_i = E \qquad \sum n_i = N.$$

Entropy $S = k_B \ln W$

Maximize entropy with the constraints

$$\frac{\partial}{\partial n_i}\left[\ln W - \alpha \sum n_i \epsilon_i - \beta \sum n_i\right] = 0$$

$$-\frac{\partial}{\partial n_i} \ln n_i! - \cancel{\beta}\, \epsilon_i - \cancel{\alpha} = 0$$

∂n_i

$$\ln n_i! \approx n_i \ln n_i - n_i$$

$$\frac{\partial}{\partial n_i} \ln n_i! = \ln n_i - 1 + 1 = \ln n_i$$

$$\Rightarrow -\ln n_i - \beta \epsilon_i - \alpha = 0$$

$$n_i = e^{-\beta \epsilon_i - \alpha} = \frac{1}{Z} e^{-\beta \epsilon_i}$$

$$Z = \sum e^{-\beta \epsilon_i} = e^{-\beta(\epsilon_i - F)}$$

Free energy $F = \frac{1}{\beta} \log Z$

$$U = \langle E \rangle = \frac{\sum \epsilon_i e^{-\beta \epsilon_i}}{Z} =$$

$$S = -k_B \sum_i p_i \log p_i = \left(\sum_i + \beta \epsilon_i p_i - \ln Z \right) k_B$$

$$\underline{S} = \sum \epsilon_i p_i - \frac{1}{\beta} \ln Z$$

$k_B\beta$

$$= U - F$$

$$F = U - \frac{S}{k_B\beta} = U - TS \quad \Big| \quad \beta = \frac{1}{k_B T}$$

Canonical ensemble

The number of microstate of the total system such that system A has energy E $\Omega(E)$

$$p(E) = \frac{\Omega(E')}{\Omega(E_T)}$$ since the system A has no influence on B

$$\ln p(E) = \ln \Omega(E_T - E) - \ln \Omega(E_T)$$

$E << E_T \qquad E = \varepsilon$

Expanding around E_T

$$\ln p(E) = \ln p(E_T) - \frac{\partial}{\partial E} \ln p(E) \Big|_{E_T} \varepsilon$$

$$+ \cdots$$

$$\Rightarrow \quad \phi(E) \sim c\, e^{-\beta E} \qquad \beta = \frac{\partial}{\partial E} \ln \phi(E) \Big|_{E_T}$$

The Gaussian distribution for microcanonical ensemble will became an exponential distribution for canonical ensemble with large energy fluctuation.

Number of microstates

For discrete energy states

N number of particles in volume V in contact with a heat bath at temperature T

Number of ways N particles can be arranged in M energy states

$$\Omega = \frac{N!}{n_1!\, n_2!\, n_3! \cdots n_M!}$$

— n_3

— n_2

— n_1

Average energy $\langle E \rangle = \sum n_i \epsilon_i$

Total number of particles $N = \sum n_i$

Maximize entropy $S = \ln \Omega$ with the two constraints

Maximize $L = \ln \Omega - \beta \sum n_i \epsilon_i - \alpha \sum n_i$

$$L = \ln N! - \sum_i \ln n_i! - \beta \sum n_i \epsilon_i - \alpha \sum n_i$$

Using stirling approximation

$$L = -\sum_i (n_i \ln n_i + n_i) - \beta \sum n_i \epsilon_i - \alpha \sum n_i - \ln N!$$

$$\frac{\partial L}{\partial n_i} = -\ln n_i - \beta \epsilon_i - \alpha = 0$$

$$\Rightarrow n_i = e^{-\beta \epsilon_i - \alpha}$$

The Maxwell-Boltzmann distribution

The equ...

$$p_i = \frac{e^{-\beta \epsilon_i}}{Z} \qquad Z = \sum_{\{n_i\}} e^{-\beta \epsilon_i}$$

(partition function)

$$\Rightarrow \quad S = -k_B \sum p_i \ln p_i$$

$$U = \sum p_i \epsilon_i$$

$$S = \left(\sum_i p_i \beta \epsilon_i + \ln Z\right) k_B$$

$$, \frac{S}{\beta} = \left(U + \frac{1}{\beta} \ln Z\right) k_B$$

Free energy $\quad F = -\frac{1}{\beta} \ln Z \qquad \beta = \frac{1}{k_B T}$

$$F = U - TS \qquad F = -k_B T \ln Z$$

$$dF = dU - T\,dS - S\,dT$$

$$dF = -p\,dV - S\,dT \qquad [T\,dS = dU + p\,dV]$$

$$\Rightarrow \quad S = -\left(\frac{\partial F}{\partial T}\right)_V \qquad p = -\left(\frac{\partial F}{\partial V}\right)_T$$

Classical ideal gas (N, V, T)

Hamiltonian $= \sum_i \frac{p_i^2}{2m}$

partition function

$$Z = \frac{1}{h^{3N}} \int d^{3N}r \, d^{3N}p \, e^{-\sum \frac{p_i^2}{2m}}$$

$$= \frac{V^N}{h^{3N}} \left[\int_{-\infty}^{+\infty} dp \, e^{-\beta p^2/2m} \right]^{3N}$$

$$= \frac{V^N}{h^{3N}} \left(2\pi \frac{m}{\beta} \right)^{3N/2} = \frac{V^N}{h^{3N}} (2\pi m k_B T)^{3N/2}$$

$$F = -k_B T \ln Z$$

$$= -k_B T \left[N \ln V + \frac{3N}{2} \ln (2\pi m k_B T) - 3N \ln h \right]$$

$$= -\left[N k_B T \ln V + \frac{3}{2} N k_B T \ln (2\pi m k_B T) \right.$$

$$- 3 N K_B T \ln h]$$

pressure

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{N K_B T}{V} \Rightarrow pV = N K_B T$$

$$F = U - TS \qquad U = F + TS$$

Entropy $S = -\left(\frac{\partial F}{\partial T}\right)_V$

$$S = \Big[N K_B \ln V + \frac{3}{2} N K_B \ln (2\pi m K_B T) + \frac{3}{2} N K_B - 3 N K_B \ln h\Big]$$

$$TS = -F + \frac{3}{2} N K_B T$$

$$U = F + TS = \frac{3}{2} N K_B T$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} N K_B$$

The average energy U can also be calculated by differentiating $\ln Z$

$$\ln Z = \ln \sum_{\{n_i\}} e^{-\beta \epsilon_i}$$

$$\frac{\partial}{\partial \beta} \ln Z = \frac{-\sum \epsilon_i e^{-\beta \epsilon_i}}{Z} = -U$$

$$Z = \frac{V^N}{h^{3N}} \left(\frac{2\pi m}{\beta}\right)^{3N/2}$$

$$\ln Z = N \ln V + \frac{3N}{2} \ln\left(\frac{2\pi m}{\beta}\right) - 3N \ln h$$

$$\frac{\partial}{\partial \beta} \ln Z = \frac{3N\beta}{2\, 2\pi m} \cdot \left(-\frac{2\pi m}{\beta^2}\right) = -\frac{3}{2} N \frac{1}{\beta} = \frac{3}{2} N k_B T$$

Entropy of mixing and Gibbs paradox

N_1, V_1, T N_2, V_2, T

Before mixing

$$S_1 = N_1 K_B \ln V_1 + \frac{3}{2} N_1 K_B \ln(2\pi m K_B T) + \frac{3}{2} N_1 K_B - 3 N_1 K_B \ln h$$

$$S_2 = N_2 K_B \ln V_2 + \frac{3}{2} N_2 K_B \ln(2\pi m K_B T) + \frac{3}{2} N_2 K_B - 3 N_2 K_B \ln h$$

$S_b = S_1 + S_2$

After mixing

$$S_a = (N_1 + N_2) K_B \ln(V_1 + V_2) + \frac{3}{2}(N_1 + N_2) \ln(2\pi m K_B T) + \frac{3}{2}(N_1 + N_2) K_B - 3(N_1 + N_2) K_B \ln h$$

$$S_a - S_b = (N_1 + N_2) K_B \ln(V_1 + V_2) - N_1 K_B \ln V_1 - N_2 K_B \ln V_2$$

$$V_1 = V_2 = V \qquad N_1 = N_2 = N$$

$$S_a - S_b = 2 N k_B \ln 2V - 2 N k_B \ln V$$

$$S_a - S_b = 2 N k_B \ln 2$$

<u>Resolution:</u>

particles are identical

$$Z = \frac{1}{h^{3N} N!} \int d^{3N} r \int d^{3N} p \; e^{-\sum p_i^2/2m}$$

$$= \frac{1}{N!} \frac{V^N}{h^{3N}} \left(2\pi m k_B T\right)^{3N/2}$$

$$N! \simeq e^{-N} N^{N+\frac{1}{2}} \sqrt{2\pi}$$

$$Z = \left(\frac{e V}{N}\right)^N \frac{1}{h^{3N}} \left(2\pi m k_B T\right)^{3N/2}.$$

$$F = -k_B T \ln Z$$

$$= -k_B T \left[N \ln\left(\frac{eV}{N}\right) + \frac{3N}{2} \ln\left(2\pi m k_B T\right) - 3N \ln h \right]$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = N k_B \ln\left(\frac{eV}{N}\right) + \frac{3Nk_B}{2} \ln\left(2\pi m k_B T\right) + \frac{3N k_B}{2} - 3N k_B \ln h$$

Entropy of mixing

After mixing

$$S = (N_1 + N_2) \ln \frac{e(V_1+V_2)}{N_1+N_2} + \frac{3(N_1+N_2)}{2} \ln(2\pi m k_B T) + \frac{3(N_1+N_2)}{2} k_B - \frac{3(N_1+N_2)}{2} k_B \ln h$$

before mixing

$$S = N_1 \ln\left(\frac{eV_1}{N_1}\right) + N_2 \ln\left(\frac{eV_2}{N_2}\right)$$

$$S_b = N_1 \ln\left(\frac{\quad}{N_1}\right) \ldots \left(\frac{\quad}{N_2}\right)$$

$$+ \frac{3(N_1+N_2)}{2} \ln\left(2\pi m k_B T\right)$$

$$+ \frac{3(N_1+N_2)}{2} k_B - 3(N_1+N_2) k_B \ln h$$

$$S_a - S_b = (N_1+N_2) \ln \frac{e(V_1+V_2)}{N_1+N_2}$$

$$- N_1 \ln \frac{eV_1}{N_1} - N_2 \ln\left(\frac{eV_2}{N_2}\right)$$

$$N_1 = N_2 = N \qquad V_1 = V_2 = V$$

$$S_a - S_b = 0$$

Canonical ensemble.

The probability of occupying a state with energy E $p(E) = \frac{e^{-\beta E}}{Z}$

$Z \rightarrow$ partition function.

Free energy $F = -k_B T \ln Z$ $\quad \beta = \frac{1}{k_B T}$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \qquad p = -\left(\frac{\partial F}{\partial V}\right)_T$$

Classical ideal gas

$$Z = \frac{V^N}{h^{3N}}\left(2\pi m k_B T\right)^{3N/2}$$

$$F = -k_B T\left[N\ln V + \frac{3N}{2}\ln(2\pi m k_B T) - 3N\ln h\right]$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{N k_B T}{V}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = N k_B \ln V + \frac{3}{2} N k_B \ln(2\pi k_B m T)$$

$$+ \frac{3}{2} N K_B - 3 N K_B \ln h$$

For adiabatic expansion $S = C$

$$\Rightarrow N K_B \ln \left[V T^{3/2} \right] = C$$

$$\Rightarrow V T^{3/2} = C \qquad p = \frac{N K_B T}{V}$$

$$T = \frac{pV}{N K_B}$$

$$\Rightarrow V \left(\frac{p V}{N K_B} \right)^{3/2} = C$$

$$p^{3/2} V^{5/2} = C \Rightarrow p V^{5/3} = K$$

$$\gamma = 5/3$$

For monoatomic gas

An ideal gas with relativistic particle

$$E = pc$$

$$Z = \frac{1}{h^{3N} N!} \int d^{3N} r \int d^{3N} p \, e^{-\beta p c}$$

$$= \frac{V^N}{\ldots h^{3N}} \left[4\pi \int^{\infty} p^2 e^{-\beta p c} \, dp \right]^N$$

$N!\, h^{3N}$

$\beta p c = x \qquad \beta c\, dp = dx$

$$= \frac{V^N}{N!\, h^{3N}} \left[4\pi \int \left(\frac{x}{\beta c}\right)^2 e^{-x} \frac{dx}{\beta c} \right]^N$$

$$= \frac{V^N}{N!\, h^{3N}} \left[\frac{8\pi}{(\beta c)^3} \right]^N$$

$$\ln Z = N \ln e\frac{V}{N} + N \ln\left(\frac{8\pi}{(\beta c)^3}\right) - 3N \ln h$$

$$\frac{\partial}{\partial \beta} \ln Z = -N \frac{\beta c}{8\pi} \frac{8\pi}{\beta^2 c} = -\frac{3N}{\beta}$$

$$U = 3 N k_B T$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3 N k_B$$

$$F = -k_B T \ln Z$$

$$\ldots \ln\left(\frac{e V}{\ldots}\right) \ldots T \ln\left(8\pi (k_B T)^3 \ldots\right)$$

$$= -\left[N k_B T \ln\left(\frac{eV}{N}\right) + N k_B T \ln\left(\frac{8\pi}{c^3}(k_B T)^3\right) - 3 N k_B T \ln h \right]$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{N k_B T}{V}$$

$$S = -\left(\frac{\partial F}{\partial T}\right) = N k_B \ln\left(\frac{eV}{N}\right) + N k_B \ln\left(\frac{8\pi}{c^3}(k_B T)^3\right) + 3 N k_B - 3 N k_B \ln h$$

For adiabatic process

$$\Rightarrow N k_B \ln\left[\frac{e}{N} \cdot \frac{8\pi}{c^3} k_B^3 \, V T^3\right] = c$$

$$V T^3 = C$$

$$p = \frac{N k_B T}{V} \qquad U = 3 N k_B T$$

$$= \frac{u}{3} \qquad u = \frac{U}{V}$$

$$T^3 \propto \frac{1}{V} \sim a^{-1}$$

b V

$$T = \frac{pV}{N k_B}$$

For adiabatic expansion

$$\Rightarrow V \frac{p^3 V^3}{N^3 k^3} = C$$

$$p^3 V^4 = C \Rightarrow p V^{4/3} = K$$

adiabatic expansion coefficient $\gamma = 4/3$

Canonical partition function for harmonic oscillator.

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

$$Z = \frac{1}{N!} \frac{1}{h^{3N}} \int d^{3N} r \, d^{3N} p \, e^{-\beta \left(p^2/2m + \frac{1}{2} m \omega^2 x^2 \right)}$$

$$= \frac{1}{h^{3N} N!} \left[\int_{-\infty}^{+\infty} e^{-\frac{\beta}{2} m \omega^2 x^2} dx \right]^{3N} \left[\int_{-\infty}^{+\infty} e^{-\beta p^2/2m} dp \right]^{3N}$$

$$= \frac{1}{N!} \left(\frac{2\pi}{\ldots} \right)^{3N/2} \left(\frac{2\pi m}{\ldots} \right)^{3N/2} \frac{1}{h^{3N}}$$

$$\ln Z = \frac{3N}{2}\ln\left(\frac{2\pi}{\beta m\omega^2}\right) + \frac{3N}{2}\ln\left(\frac{2\pi m}{\beta}\right) - \left[N\ln N - N\right] - 3N\ln h$$

$$\frac{\partial}{\partial\beta}\ln Z = -\left[\frac{3N}{2}\cdot\frac{1}{\beta} + \frac{3N}{2}\cdot\frac{1}{\beta}\right]$$

$$U = \frac{3N}{2}k_B T + \frac{3N}{2}k_B T$$

$$F = -\frac{3Nk_BT}{2}\ln\left(\frac{2\pi}{m\omega^2}k_BT\right) - \frac{3}{2}Nk_BT\ln\left(2\pi m k_BT\right) - k_BT\left[N\ln N - N\right] - 3N\ln h$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = 0$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{3Nk_B}{2}\ln\left(\frac{2\pi k_BT}{m\omega^2}\right) + \frac{3}{2}Nk_BT + \frac{3}{2}Nk_B\ln\left(\frac{2\pi}{m}k_BT\right) + \frac{3}{2}Nk_BT - 3Nk_B\ln h.$$

Energy fluctuation in canonical ensemble:

$$\langle E\rangle = \frac{\sum \varepsilon_i e^{-\beta\epsilon_i}}{Z}$$

$$= -\frac{\partial}{\partial\beta}\ln Z$$

$$\frac{\partial}{\partial\beta}\langle E\rangle = -\frac{\sum_i \varepsilon_i^2 e^{-\beta\epsilon_i}}{Z} - \frac{\sum \varepsilon_i e^{-\beta\epsilon_i}}{Z^2}\frac{\partial Z}{\partial\beta}$$

$$= -\langle E^2\rangle - \sum_i \varepsilon_i e^{-\beta\epsilon_i}\frac{1}{Z}\frac{\partial}{\partial\beta}\ln Z$$

$$= -\langle E^2\rangle + \langle E\rangle^2$$

$$\langle E^2\rangle - \langle E\rangle^2 = -\frac{\partial}{\partial\beta}\langle E\rangle = k_B T^2\frac{\partial\langle E\rangle}{\partial T}$$

$$\langle\Delta E^2\rangle = k_B T^2 c_V.$$

Classical simple Oscillator

Canonical partion function

$$Z = \frac{1}{N!}\frac{1}{h^{3N}}\int d^{3N}x \, d^{3N}p \, e^{-\beta\left(p^2/2m + \frac{1}{2}m\omega^2 x^2\right)}$$

$$= \frac{1}{N!}\frac{1}{h^{3N}}\left[\int d^3x \, e^{-\frac{\beta}{2}m\omega^2 x^2}\right]^{3N} \left[\int d^3p \, e^{-\beta p^2/2m}\right]^{3N}.$$

$$= \frac{1}{N!}\frac{1}{h^{3N}}\left(\frac{2\pi m}{\beta}\right)^{3N/2}\left(\frac{2\pi}{m\omega^2\beta}\right)^{3N/2}.$$

$$\ln Z = 3N/2 \ln\left(\frac{2\pi m}{\beta}\right) + \frac{3N}{2}\ln\left(\frac{2\pi}{m\omega^2\beta}\right) - \ln N! - 3N\ln h$$

$$\langle E\rangle = -\frac{\partial}{\partial\beta}(\ln Z)$$

$$= \frac{3N}{2}\cdot\frac{1}{\beta} + \frac{3N}{2}\frac{1}{\beta} = \frac{3N}{2}k_B T$$

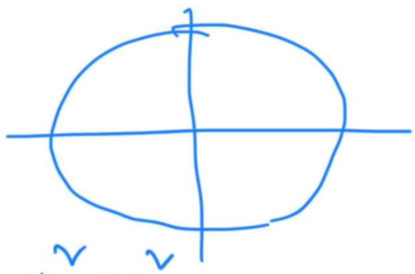
$+\frac{3}{2} N k_B T$

$$F = -k_B T \ln Z$$

$$\left(\frac{\partial F}{\partial V}\right)_T = p = 0$$

<u>Microcanonical ensemble</u>

In one dimension



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

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

Area of phase space $= \pi \sqrt{2mE \cdot \frac{2E}{m\omega^2}}$

$$= \frac{2\pi E}{\omega}$$

For N oscillators.

$$\Omega = \frac{1}{h^N}\left(\frac{2\pi E}{\omega}\right)^N = \frac{1}{N}\left(\frac{E}{\hbar\omega}\right)^N$$

$$h^N \left(\omega \right)$$

For energy E and $E+\Delta$

$$\Omega_N(E, E+\Delta) = \frac{1}{(N-1)!} \frac{E^{N-1}}{\hbar\omega^{N-1}} \left(\frac{\Delta}{\hbar\omega}\right)$$

$$\simeq \frac{1}{N!} \left(\frac{E}{\hbar\omega}\right)^N \left(\frac{\Delta}{\hbar\omega}\right)$$

$$S = k_B \ln \Omega_N$$

$$= -k_B \ln N! + N \ln\left(\frac{E}{\hbar\omega}\right) + \ln\left(\frac{\Delta}{\hbar\omega}\right)$$

$$\frac{\partial S}{\partial E} = \frac{N}{E} = \frac{1}{k_B T} \qquad E = N k_B T$$

Quantum case for the oscillator

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

$$Z_1 = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega}$$

$$e^{-\beta\hbar\omega}.$$

$$= \frac{\quad}{1 - e^{-\beta\hbar\omega}}$$

$$Z_N = \frac{e^{-\beta N\hbar\omega}}{\left(1 - e^{-\beta\hbar\omega}\right)^N}$$

$$\ln Z_N = -N\hbar\omega\beta - N\ln\left(1 - e^{-\beta\hbar\omega}\right)$$

$$U = -\frac{\partial}{\partial\beta}\ln Z_N = \frac{N\hbar\omega\, e^{-\beta\hbar\omega}}{\left(1 - e^{-\beta\hbar\omega}\right)} + N\hbar\omega$$

$$= N\hbar\omega + N\hbar\omega\,\frac{e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$

$$= N\hbar\omega\,\frac{1}{e^{\hbar\omega/k_BT} - 1} + N\hbar\omega$$

$$\frac{\partial U}{\partial T} = \frac{-N\hbar\omega \cdot\cdot\, e^{\hbar\omega/k_BT}}{\left(e^{\hbar\omega/k_BT} - 1\right)^2} \times \frac{(-\hbar\omega)}{k_B}\frac{1}{T^2}$$

$$= \frac{N\left(\frac{\hbar\omega}{k_B T}\right) e^{\hbar\omega/k_B T} k_B}{\left(e^{\hbar\omega/k_B T} - 1\right)^2}$$

$\hbar\omega \ll k_B T$

$$= N k_B \left(1 + \frac{\hbar\omega}{k_B T}\right) = N k_B + \frac{N\hbar\omega}{T}$$

$\hbar\omega \gg k_B T$

$$\frac{\partial U}{\partial T} = N k_B \frac{\left(\frac{\hbar\omega}{k_B T}\right)^2 e^{\hbar\omega/k_B T}}{\left(e^{\hbar\omega/k_B T} - 1\right)^2}$$

$$\simeq N k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 e^{-\hbar\omega/k_B T}$$

$$\simeq 0$$

$$F = -k_B T \ln Z$$

$$\ldots N k_B T \ln\left(1 - e^{-\hbar\omega/k_B T}\right)$$

$= N\hbar\omega + Nk_B T$

$$S = -\frac{\partial F}{\partial T} = k_B \ln Z + k_B T$$

$$= Nk_B \ln\left(1 - e^{-\hbar\omega/k_B T}\right)$$

$$- Nk_B T \frac{e^{-\hbar\omega/k_B T}}{1 - e^{-\hbar\omega/k_B T}} \times \frac{(-\hbar\omega)}{k_B T^2}$$

$$= Nk_B \ln\left(1 - e^{-\hbar\omega/k_B T}\right)$$

$$+ \frac{N\hbar\omega}{T} \frac{e^{-\hbar\omega/k_B T}}{1 - e^{-\hbar\omega/k_B T}}$$

$T \to 0$

$$S = \frac{N\hbar\omega}{T} \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

$$\sim N\hbar\omega \frac{e^{-\hbar\omega/k_B T}}{} \simeq 0$$

T