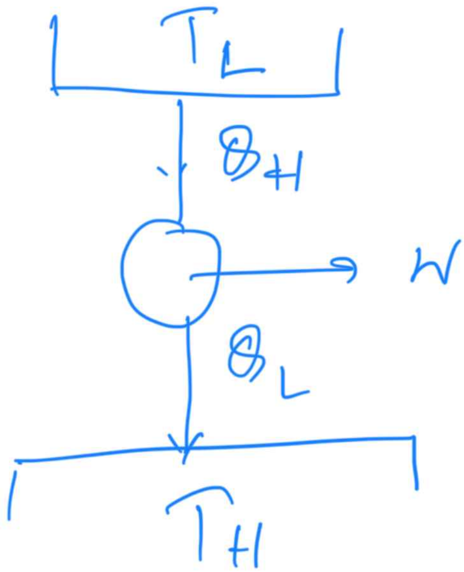
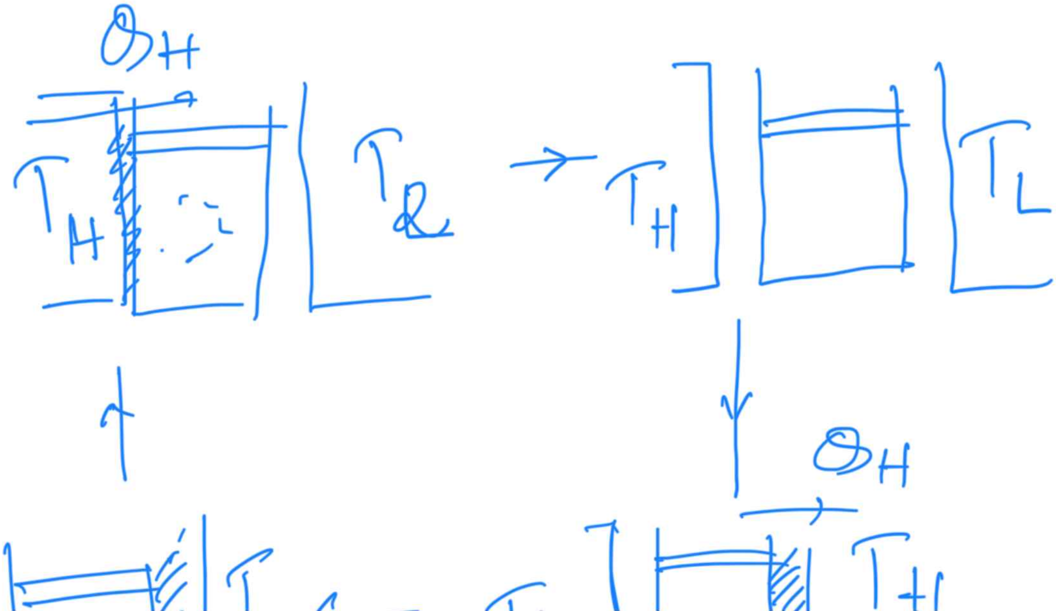
What is equilibrium thermodynamics

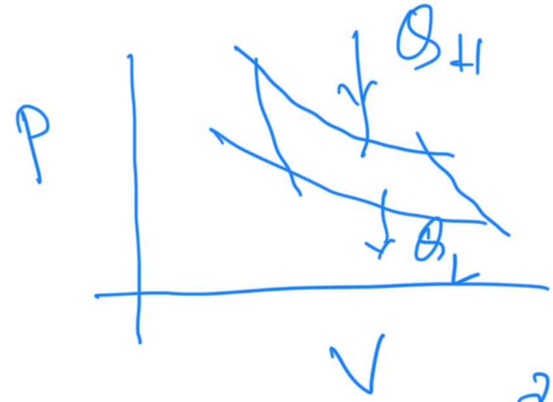
Why statistical Mechanics.

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

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

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

$$\eta_{Ir} < \eta_r$$

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

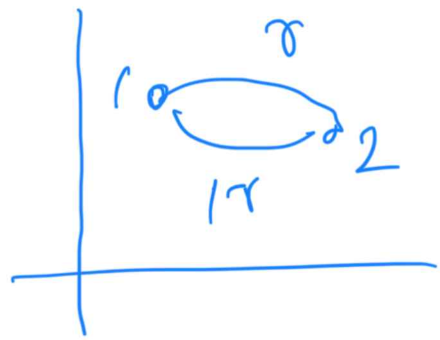
$$\Rightarrow (Q_H) = (Q_H)_{Ir}$$

$\Rightarrow (Q_H)_r$

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

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

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



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

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

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

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

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

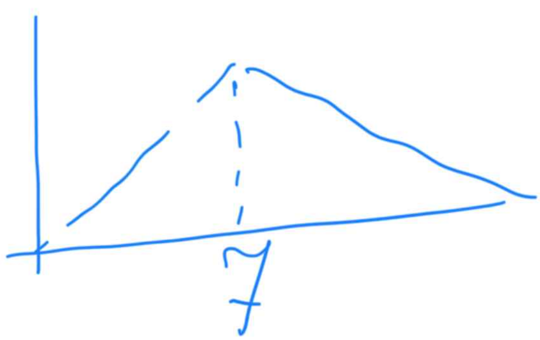
L ~ space

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

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

$$\langle n \rangle = Np$$

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

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:

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

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

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

$$\langle n \rangle = Np$$

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

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

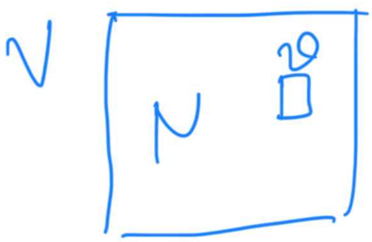
$$\langle n^2 \rangle - \langle n \rangle^2 = -Np^2 + Np$$

$$= Np(1-p)$$

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

$\simeq \frac{1}{N} \quad \frac{1}{2}$

For a gas in a box of volume V



probability that there are n particle 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

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

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

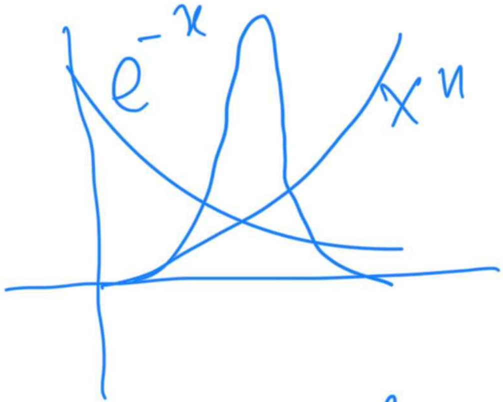
$$= \frac{e^{-N} N^{\cancel{N}-n}}{e^{-N} (N-n)^{N-n} e^{n}} \left(1-\frac{\lambda}{N}\right)^{-n} \frac{\lambda^n}{n!} \left(1-\frac{\lambda}{N}\right)^{N}$$

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

Sterling aproximation

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

$\int_{0}$



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

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

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

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

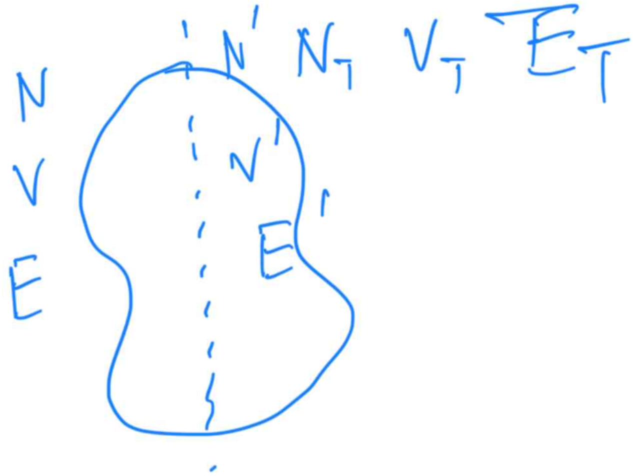
$$f(x) = (n - n\log n) + \frac{(x-n)^2}{n} + \cdots$$

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

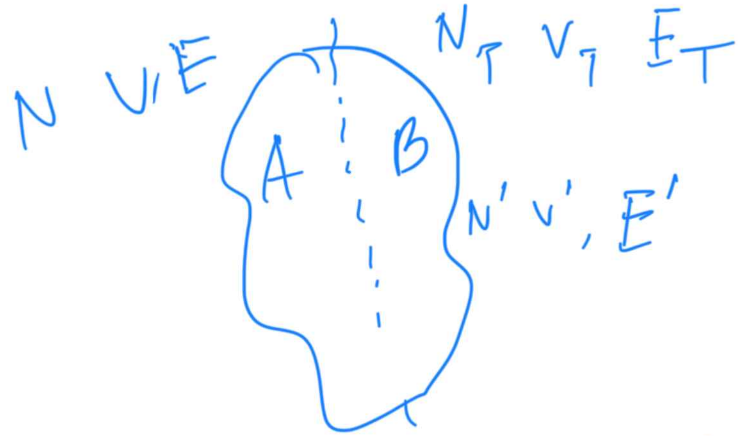
$$= e^{-(n - n\log n)} \sqrt{2\pi n}$$

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

Microcanonical ensemble



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 $E_T = E + E'$

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

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

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

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

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

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

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

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

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 thermodynamic entropy is

Same as the Baltzman entropy.

<u>Entropy for an ideal gas.</u> $\mathcal{E} < E$

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

phase space volume

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

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

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

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

Number of microstates

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

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

For N particles.

$$\Omega_N(\varepsilon) = \Omega(\varepsilon)^N$$

Entropy $S = K_B \ln \Omega_N(\varepsilon)$

$$= N K_B \ln \Omega(\varepsilon)$$

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

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

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

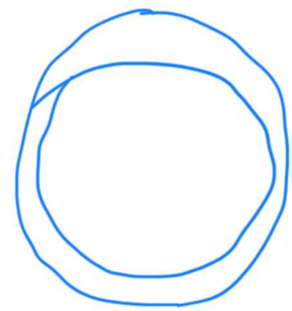
$$\frac{\partial U}{\partial T} = \frac{3}{2} N K_B$$

[illegible] ensemble.

Microcanonical ensemble

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

Volume of an N dimensional sphere



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

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

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

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

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

$$S = k_B \ln \Omega$$

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

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

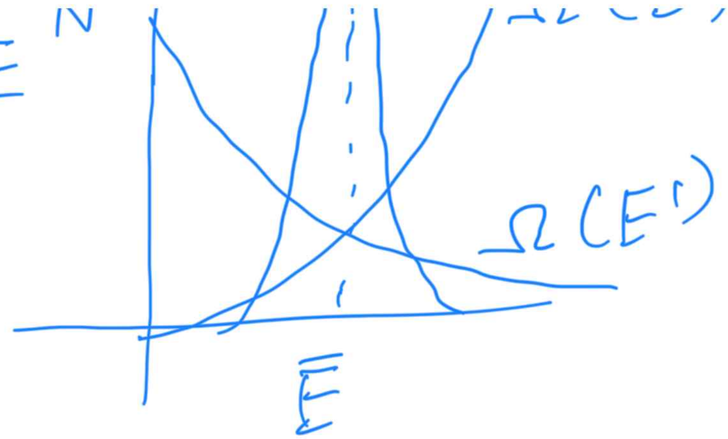
$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{Nk_B}{V} = \frac{P}{T} \qquad \boxed{PV = Nk_B T}$$

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

Distribution for microcanonical ensemble

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

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



$$\ln P(E) = P(\bar{E}) + \frac{\partial \ln P(E)}{\partial E}\bigg|_{\bar{E}} (E-\bar{E})$$

$$+ \frac{1}{2}\frac{\partial^2 \ln P(E)}{\partial E^2}\bigg|_{\bar{E}} (E-\bar{E})^2$$

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

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

<u>Canonical ensemble.</u>

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

(E) ... 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

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

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

∂n_i

$\ln n_i! = n_i \ln n_i - n_i$

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

$$\Rightarrow -\ln n_i - \cancel{\beta}\epsilon_i - \cancel{\alpha} = 0$$

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

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

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

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

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

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

$k_B \beta$

$= U - F$

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

Canonical ensemble

N, V, E $\quad$ N', V', E'

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

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

$$+ \ldots$$

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

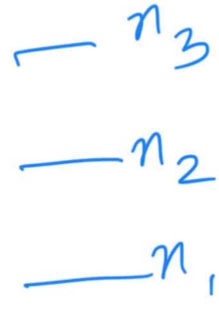
The Gaussian distribution for microcanonical ensemble will become an exponential distribution for canonical ensemble with large energy fluctuation.

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



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

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

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

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

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

maxwell boltzmann distribution

The equation

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

(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 $F = -\frac{1}{\beta} \ln Z \qquad \beta = \frac{1}{k_B T}$

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

$$dF = dU - TdS - SdT$$

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

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

Classical ideal gas (N, V, T)

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

partition function

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

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

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

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

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

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

$$-3NK_BT\ln h\Big]$$

pressure

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{NK_BT}{V} \Rightarrow PV = NK_BT$$

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

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

$$S = \Big[NK_B\ln V + \frac{3}{2}NK_B\ln(2\pi mK_BT) + \frac{3}{2}NK_B - 3NK_B\ln h\Big]$$

$$TS = -F + \frac{3}{2}NK_BT$$

$$U = F + TS = \frac{3}{2}NK_BT$$

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

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

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

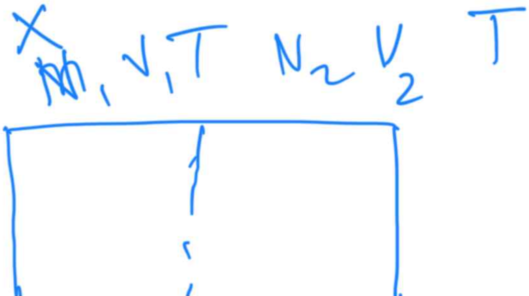
$$\frac{\partial}{\partial \beta} \ln Z = \frac{-\sum \epsilon_i e^{-\beta \epsilon_i}}{Z} = -U$$

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

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

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

Entropy of mixing and Gibbs paradox



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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$S_a - S_b = 0$$

Canonical ensemble.

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

$Z \rightarrow$ partition function.

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

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

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

$$E = pc$$

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

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

$$N!\, h^{3N} \Big[\quad \int_0 \Big]$$

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

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

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

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

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

$$U = 3 N k_B T$$

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

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

$$\ln\left(\frac{eV}{\;}\right) \quad k_B T \ln\left(8\pi (k_B T)^3\right)$$

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

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

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

For adiabatic process

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

$$V T^3 = C$$

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

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

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

by

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

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.

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

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

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

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

$$N!\,(\beta m\omega^2)\quad(\beta\quad)\quad h^{3N}$$

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

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

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

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

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

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

Energy functuation 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 partition function

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

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

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

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

$$- \ln N! - 3N \ln h$$

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

$$= \frac{3N}{2}\cdot\frac{1}{\beta} + \frac{3N}{2}\,\frac{1}{\beta} = \frac{3N}{2}k_BT$$

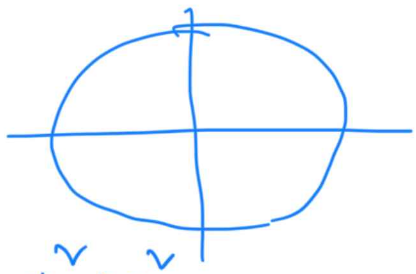
$$+ \frac{3}{2} N k_B T$$

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

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

Microcanonical ensemble

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.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$\hbar\omega << k_BT$

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

$\hbar\omega >> k_BT$

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

$$\simeq Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2 e^{-\hbar\omega/k_BT}$$

$$\simeq 0$$

$$F = -k_BT \ln Z$$

$$\ldots Nk_BT \ln\left(1-e^{-\hbar\omega/k_BT}\right)$$

$= N\hbar\omega + Nk_B T$

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

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

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

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

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

$T \to 0$

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

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

T

Magnetic systems

No interaction only external magnetic field.

$$E = -\mu B \sum \sigma_i$$

$$Z = \sum_{\{\sigma_i\}} e^{-\beta \mu B \sum \sigma_i}$$

$$= \left(\sum_{\sigma_i = \pm 1} e^{-\beta \mu B \sigma_i}\right)\left(\sum e^{-\beta \mu B \sigma_i}\right) \cdots$$

$$= \left(e^{\beta \mu B} + e^{\beta \mu B}\right)^N$$

$$= 2^N \left[\cosh(\beta \mu B)\right]^N$$

$$F = -k_B T \left[N \ln 2 + N \ln[\cosh(\beta \mu B)]\right]$$

$$\ln Z = N\ln 2 + N\ln\cosh(\beta\mu B)$$

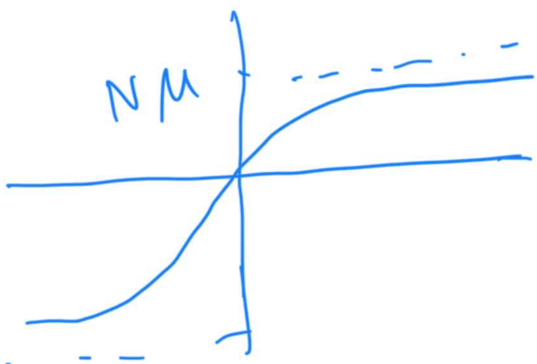
Internal energy

$$U = -\frac{\partial}{\partial\beta}\ln Z = N\mu B\tanh(\beta\mu B)$$

Magnetization

$$M = -\left(\frac{\partial F}{\partial B}\right)_T = N k_B T \beta\mu\tanh(\beta\mu B)$$

$$= N\mu\tanh\left(\frac{\mu B}{k_B T}\right)$$



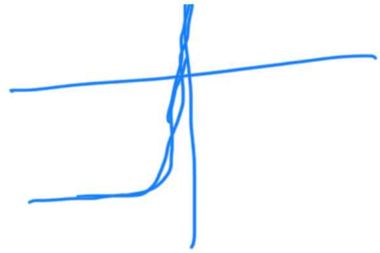
Susceptibility

$$\chi = \left(\frac{\partial M}{\partial B}\right)_T = \frac{N\mu^2}{k_B T}\operatorname{sech}^2\left(\frac{\mu B}{k_B T}\right)$$

$T \to 0$

$$\frac{N\mu^2}{\ }$$

$B \to 0 \qquad \chi = \frac{\quad}{k_B T}$



$$U = -\mu B \tanh\left(\frac{\mu B}{k_B T}\right)$$

Specific heat $C = \left(\frac{\partial U}{\partial T}\right)_B$

$$= \mu B \cdot \frac{N \mu B}{k_B T^2} \operatorname{sech}^2\left(\frac{\mu B}{k_B T}\right)$$

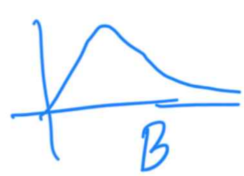
$$= N k_B \left(\frac{\mu B}{k_B T}\right)^2 \operatorname{sech}^2\left(\frac{\mu B}{k_B T}\right)$$

$$= N k_B \left[\frac{(\mu B / k_B T)}{\cosh\left(\frac{\mu B}{k_B T}\right)}\right]^2$$

$B \to \infty$

$$C = N k_B \left[\frac{\mu B}{k_B T} e^{-\mu B / k_B T}\right]^2$$

$\to 0$



$B \to 0 \qquad \left(\mu B\right)^2$

$$C = NK_B\left(\frac{\mu B}{K_BT}\right) \to 0.$$

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

$$F = -K_BT\left[N\ln 2 + N\ln\left[\cosh\left(\frac{\mu B}{K_BT}\right)\right]\right]$$

$$S = K_B\left(\left[N\ln 2 + N\ln\left[\cosh\frac{\mu B}{K_BT}\right]\right)\right.$$

$$+ NK_BT\tanh\left(\frac{\mu B}{K_BT}\right)\frac{\mu B}{K_BT^2}$$

$$= NK_B\ln 2 + NK_B\ln\left(\cosh\frac{\mu B}{K_BT}\right)$$

$$- NK_B\left(\frac{\mu B}{K_BT}\right)\tanh\left(\frac{\mu B}{K_BT}\right)$$

$B \to 0 \quad S \to NK_B\ln 2$

$$NK_B\ln\cosh\left(\frac{\mu B}{K_BT}\right) \to 0$$

$B \to \infty \quad \cosh\left(\frac{\mu B}{K_BT}\right) \sim \frac{1}{2}e^{\mu B/K_BT}$

$$N k_B \left(\frac{\mu B}{k_B T}\right) \tanh \left(\mu B / k_B T\right)$$

$$\approx N k_B \left(\frac{\mu B}{k_B T}\right) \frac{e^{\mu B / k_B T} - e^{-\mu B / k_B T}}{}$$

$$S \to 0$$

<u>Classical case.</u>

$$E = -\mu B \cos\theta.$$

$$Z = \sum e^{\beta \mu B \cos\theta}$$

$$= 4\pi \int_0^{2\pi} \sin\theta \; e^{\beta \mu B \cos\theta} d\theta.$$

$$\beta \mu B \cos\theta = x$$

$$\beta \mu B \sin\theta d\theta = dx$$

$$= \frac{4\pi}{\beta \mu B} \int_{-\beta \mu B}^{\beta \mu B} e^{x} dx$$

$$= \frac{4\pi}{\beta\mu B} \sinh(\beta\mu B)$$

$$F = -k_B T\left[-\ln(\beta\mu B) + \ln\sinh(\beta\mu B)\right]$$

$$M = -\left(\frac{\partial F}{\partial B}\right) = k_B T\left[-\beta\mu\frac{1}{\beta\mu B} + \beta\mu\coth(\beta\mu B)\right]$$

$$= \mu\left[\coth x - \frac{1}{x}\right]$$

$x = \beta\mu B$ as $B \to 0$ $x \to 0$

$$M = \mu\left[\frac{1}{x} + \frac{x}{3} + x^3 \ldots - \frac{1}{x}\right]$$

$$\simeq \mu\frac{x}{3} = \mu\beta\mu B = \frac{\mu^2 B}{k_B T}$$

Magnetic system with interaction.

1 d ising model.

$$E = -J\sum \sigma_i\sigma_j$$

$$Z = e^{\beta J \sum \sigma_i \cdot \sigma_j}$$

$$\sigma_i \cdot \sigma_j$$

Nearest neighbour interation

$$E = -J \sum \sigma_i \, \sigma_{i+1}$$

$$Z = \sum_{\{\sigma_i\}} e^{\beta J \sum \sigma_i \, \sigma_{i+1}}$$

$$\sigma_i \, \sigma_{i+1} = m_i$$

$$Z = \sum_{\{\sigma_i\}} e^{\beta J \sum m_i}$$

$$= \left(e^{\beta J} + e^{-\beta J}\right)^N$$

$$= 2^N (\cosh(\beta J))$$

$$\ln Z = N \ln 2 + N \ln(\cosh(\beta J))$$

$$\frac{\partial}{\partial \beta} \ln Z = N J \tanh(\beta J)$$

$$\frac{\partial}{\partial \beta J} = N \tanh(\beta J)$$

$$\langle \sigma_i \sigma_{i+1} \rangle = \tanh(\beta J)$$

$$\langle \sigma_i \sigma_{i+r} \rangle = \langle \sigma_i \sigma_{i+1}^2 \sigma_{i+2}^2 \cdots \sigma_{i+r} \rangle$$

$$= \langle \sigma_i \sigma_{i+1} \rangle \langle \sigma_{i+1} \sigma_{i+2} \rangle \cdots \langle \sigma_{i+r-1} \sigma_{i+r} \rangle$$

$$= [\tanh(\beta J)]^r = \left[\frac{1}{\tanh(\beta J)}\right]^{-r}$$

$$= e^{-r(-\log(\tanh \beta J))} = e^{-r/\xi}$$

$$\xi = -\frac{1}{\log \tanh(\beta J)}$$

$$\beta \to \infty \qquad \xi \to \infty$$

Short range interaction leads to long range correlation

Magnetism with interaction

$$\mathcal{H} = -J\sum \sigma_i \sigma_j - B\sum \sigma_i$$

decoupling Hamiltonian using Mean Field Theory

$$\sigma_i - \langle \sigma_i \rangle = \delta\sigma_i$$

$$m = \frac{1}{N}\sum \langle \sigma_i \rangle$$

$$\sigma_i \sigma_j = \left(\langle \sigma_i \rangle + \delta\sigma_i\right)\left(\langle \sigma_j \rangle + \delta\sigma_j\right)$$

$$= \langle \sigma_i \rangle \langle \sigma_j \rangle + \langle \sigma_j \rangle \delta s_i + \langle \sigma_i \rangle \delta\sigma_j + \delta\sigma_i \cdot \delta\sigma_j$$

Small fluctuation $\delta\sigma_i \delta\sigma_j = 0$

$$\sigma_i \sigma_j \simeq \langle \sigma_i \rangle \langle \sigma_j \rangle + \langle \sigma_j \rangle \left(\sigma_i - \langle \sigma_i \rangle\right)$$

$$+\langle\sigma_i\rangle\left(\sigma_j-\langle\sigma_j\rangle\right)$$

$$=\langle\sigma_j\rangle\sigma_i+\langle\sigma_i\rangle\sigma_j-\langle\sigma_i\rangle\langle\sigma_j\rangle$$

$$\langle\sigma_i\rangle = m \quad \langle\sigma_j\rangle = m$$

$$\sigma_i\sigma_j = m\left(\sigma_i+\sigma_j\right)-m^2$$

Hamiltonian

$$\mathcal{H} = -Jm\sum_{\langle ij\rangle}\left(\sigma_i+\sigma_j-m\right)$$

$$-B\sum\sigma_i$$

$$= -Jm\sum_{\langle ij\rangle}\left(2\sigma_i-m\right)-B\sum\sigma_i$$

$$= -\frac{Jmq}{2}\sum_{i=1}^{N}\left(2\sigma_i-m\right)-B\sum_{i=1}^{N}\sigma_i$$

$$= \frac{NqJm^2}{2}-\mu\overbrace{\left(B+qJm\right)}^{B_{eff}}\sum\sigma_i$$

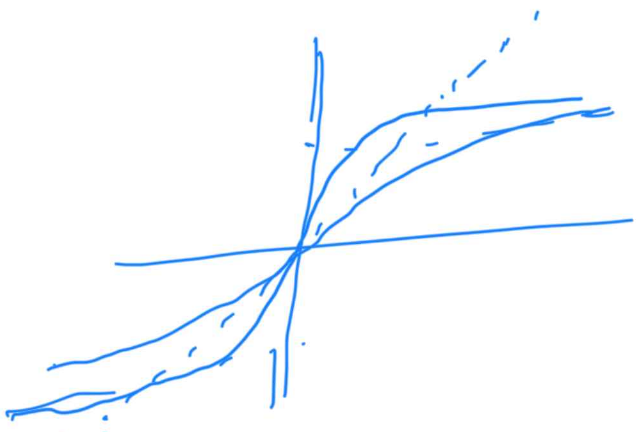
$$Z = e^{-\beta N q J m^2/2}\left[2\cosh(\beta\mu B_{eff})\right]$$

$$M = N\mu \tanh(\beta\mu B_{eff})$$

$$m = \tanh\left[\beta(B + qJm)\right]$$

$B \to 0$

$$m = \tanh(\beta q J m)$$



For small m $\quad m = \beta q J m$

For $\beta q J < 1$ one solution

$\beta q J > 1$ three solutions

$q_c J$

$$\Rightarrow \quad \frac{qJ}{k_B T_c} = 1 \qquad T_c = \frac{qJ}{k_B}$$

$$\Rightarrow \quad m = \tanh\left(\frac{T_c}{T} m\right)$$

magnetization close to T_c

$$\tanh(x) = x - \frac{x^3}{3} + \dots$$

$$\Rightarrow \quad m = \frac{T_c}{T} m - \frac{1}{3}\left(\frac{T_c}{T} m\right)^3$$

$$m\left[\left(\frac{T_c}{T} - 1\right) - \frac{1}{3}\left(\frac{T_c}{T}\right)^3 m^2\right] = 0$$

$T \to T_c^-$

$$m = 0$$

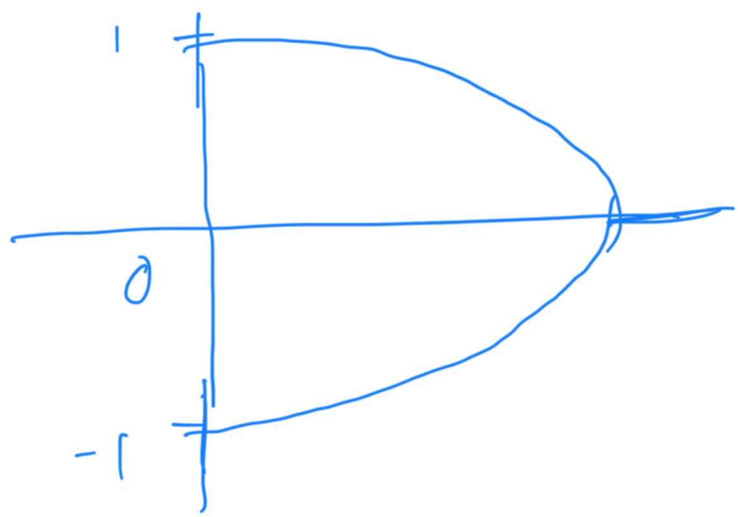
$$m = \pm\sqrt{3\,\frac{\left(\frac{T_c}{T} - 1\right)}{(T_c/T)^3}}$$

$$= \pm\sqrt{3\left(\frac{T}{T_c}\right)^2\left(\frac{T_c - T}{T_c}\right)}$$

$T > T_c \quad m = 0$

$T < T_c$

$$m = 3 \frac{T}{T_c} \frac{(T_c - T)^{1/2}}{T_c^{1/2}} \sim t^{1/2}$$



m changes continuously

Susceptibility χ

$$\chi : \frac{\partial m}{\partial H} \Big|_{B=0}$$

$$m = \tanh\left(\frac{T_c}{T} m + \beta H \right)$$

$$\frac{\partial m}{\partial H} = \beta\, \operatorname{sech}^2\left(\frac{T_c}{T} m + \beta H\right)$$

$$+ \frac{T_c}{T} \frac{\partial m}{\partial H} \operatorname{sech}^2\left(\frac{T_c}{T} m + \beta H\right)$$

$$\chi_T(T, H) = \frac{\left(\beta + \frac{T_c}{T} \chi_T\right)}{\cosh^2\left(\frac{T_c}{T} m + \beta H\right)}$$

$$\chi_T \cosh^2\left(\frac{T_c}{T} m\right) = \beta + \frac{T_c}{T} \chi_T$$

$$\chi_T = \frac{\beta}{\cosh^2\left(\frac{T_c}{T} m\right) - \frac{T_c}{T}}$$

$T \to T_c^+$

$$\chi_T = \frac{\beta}{1 - \frac{T_c}{T}}$$

$$= \frac{1}{K_B (T - T_c)}$$

$T \to T_c^-$

$$\beta$$

$$\psi_T = \frac{}{\left(1+\frac{1}{2}\left(\frac{T_c}{T}\right)^2 m^2\right)^2 - \frac{T_c}{T}}$$

$$= \frac{\beta}{1+\left(\frac{T_c}{T}\right)^2 m^2 - \frac{T_c}{T}}$$

$$= \frac{\beta}{1+\left(\frac{T_c}{T}\right)^2 3\left(\frac{T}{T_c}\right)^2\left(1-\frac{T}{T_c}\right) - \frac{T_c}{T}}$$

$$= \frac{\beta}{\left(1-\frac{T_c}{T}\right)+3\left(1-\frac{T}{T_c}\right)}$$

$$= \frac{\beta}{\frac{T-T_c}{T} - 3\,\frac{T-T_c}{T_c}}$$

$$= \frac{\beta}{\left(\frac{1}{T}-\frac{3}{T_c}\right)(T-T_c)}$$

$$= \frac{1}{k_B\left(1 - 3\frac{T}{T_c}\right)(T - T_c)}$$

$T < T_c$

$$\psi = \frac{1}{2k_B(T_c - T)}$$

Free energy F

$$Z = e^{-\beta q N J m^2/2}\left[2\cosh\left(\frac{T_c}{T} m\right)\right]^N$$

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

$$= \frac{q N J m^2}{2} - N k_B T \ln 2$$

$$- N k_B T \ln \cosh\left(\frac{T_c}{T} m\right)$$

$q N J m^2 \quad \ldots$

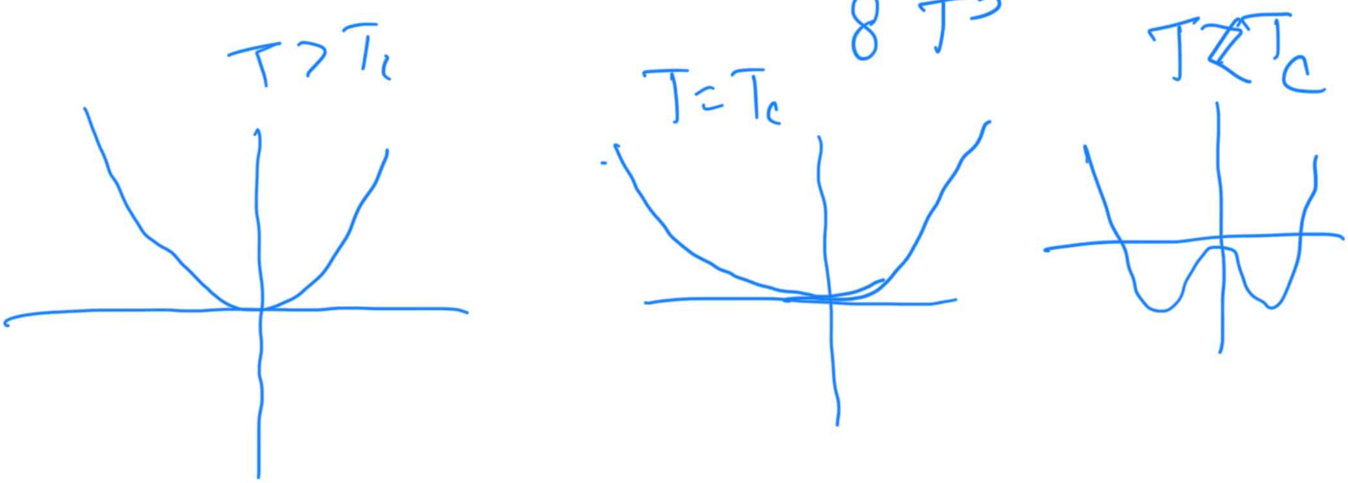
$$= \frac{[illegible]}{2} - N k_B T \ln 2$$

$$- N k_B T \ln\left(1 + \frac{1}{2}\left(\frac{T_c}{T} m\right)^2\right)$$

$$= \frac{1}{2} N k_B T_c m^2 - N k_B T \ln 2$$

$$- N k_B T \left[\frac{1}{2}\left(\frac{T_c}{T} m\right)^2 - \frac{1}{8}\left(\frac{T_c m}{T}\right)^4 + \dots \right]$$

$$= -N k_B T \ln 2 + \frac{N k_B T_c}{2T}(T - T_c) m^2 + \frac{N k_B T_c^4}{8 T^3} m^4$$



$$F = -b + a m^2 + b m^4$$

Exact solution for 1-d ising model

$$E = -J\sum \sigma_i \sigma_{i+1} - B\sum \sigma_i$$

$$Z = \sum_{\{\sigma_i\}} e^{\beta J \sum \sigma_i \sigma_{i+1} - \beta B \sum \sigma_i}$$

$$= \sum_{\{\sigma_1 \sigma_2 \ldots \sigma_N\}} e^{\beta J\, \sigma_1 \sigma_2 - \beta B \sigma_1}\, e^{\beta J\, \sigma_2 \sigma_3 - \beta B \sigma_2} \ldots\ldots$$

$$= \sum_{\sigma_1} \sum_{\sigma_2} e^{\beta E(\sigma_1 \sigma_2)}\, e^{\beta E(\sigma_1, \sigma_3)}$$

$$= \sum_{\sigma_1} \sum_{\sigma_3} \sum_{\sigma_2} T_{\sigma_1 \sigma_2} T_{\sigma_2 \sigma_3} T_{\sigma_3 \sigma_4}$$

$$= \sum T_{\sigma_1 \sigma_2} T_{\sigma_2 \sigma_3} T_{\sigma_3 \sigma_1} = \mathrm{Tr}\,(T^N)$$

$$T = \begin{pmatrix} e^{+\beta(J+B)} & e^{-\beta J} \\ e^{-\beta J} & e^{+\beta(J-B)} \end{pmatrix}$$

$$\left(e^{\beta(J+B)} - \lambda\right)\left(e^{\beta(J-B)} - \lambda\right) - e^{-2\beta J} = 0$$

$$\lambda^2 - \left[e^{\beta(J+B)} + e^{\beta(J-B)}\right]\lambda - e^{-2\beta J} = 0$$

$$\lambda^2 - 2e^{\beta J}\cosh(\beta B)\lambda + e^{2\beta J} - e^{-2\beta J} = 0$$

$$\lambda = e^{\beta J}\cosh(\beta B) \pm \left(e^{2\beta J}\cosh^2\beta B - e^{2\beta J} + e^{-2\beta J}\right)^{1/2}$$

$$= e^{\beta J}\cosh(\beta B) \pm \left(2^{2\beta J}\sin^2\beta J + e^{-2\beta J}\right)^{1/2}$$

$$F = -k_B T \ln \lambda_1$$

$$M = \frac{\partial F}{\partial B}\bigg|_{B=0} = \frac{k_B T}{\lambda_1}\frac{\partial \lambda_1}{\partial B}$$

$$= \frac{k_B T}{\lambda_1}\left[\beta e^{\beta J}\sinh(\beta B) + \frac{\beta e^{2\beta J}\sinh(\beta B)\cosh(\beta B)}{\left[e^{2\beta J}\sinh^2(\beta B) + e^{-2\beta J}\right)^{1/2}}\right]$$

$$= \frac{1}{\lambda_1} e^{\beta J}\sinh(\beta B)\left[1 + \frac{e^{\beta J}\cosh(\beta B)}{\left(e^{2\beta J}\sinh^2(\beta B) + e^{-2\beta J}\right)^{1/2}}\right]$$

$$M = \frac{e^{\beta J}\sinh(\beta B)}{\left[e^{2\beta J}\sinh^2(\beta B) + e^{-2\beta J}\right]^{1/2}}$$

~~as~~ $\beta \to \infty$

$$M = \frac{e^{\beta(J+B)}}{\quad}$$

e

$$\frac{\partial M}{\partial B} = \frac{e^{\beta J}\cosh(\beta B)}{\left(e^{2\beta J}\sinh^2(\beta B) + e^{-2\beta J}\right)^{3/2}}$$

$$\simeq e^{2\beta J} \qquad B \to 0$$

Quantum Statistics

1) Onset of quantum statistics

For classical ideal gas

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

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

Thermal de broglie wavelength

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

Density $n = \frac{N}{V} \sim L^{-3}$

$n\lambda^3 \gg 1$ Quantum regime

$n\lambda^3 \ll 1$ classical regime

When $n\lambda^3 = 1$

$$\Rightarrow \frac{n h^3}{(2\pi m k_B T)^{3/2}} = 1$$

$$n^2 h^6 = (2\pi m k_B T)^3$$

$$T = \frac{n^{2/3} h^2}{2\pi m k_B}$$

Example

(a) H_2 : $n = 2 \times 10^{19}/\text{c.c.}$

$$\Rightarrow T_0 = 5 \times 10^{-2}\,K$$

(b) ^4He : $n \simeq 10^{22}/\text{c.c.}$

$$T_0 \simeq 2K$$

(c) Electrons in a metal

$$n = 10^{22}/\text{c.c.}$$

$$T_0 \simeq 10^4\,K$$

Parity of wave function

$$[H, P] = 0$$

$$\hat{P}\, \underbrace{\psi(r_1, r_2)} = p\,\psi(r_2, r_1)$$

Hamiltonian
eigenfunction

Indistinguishability

$$|\psi(r_1, r_2)|^2 = |\psi(r_2, r_1)|^2$$

$$\psi(r_1, r_2) = \pm \psi(r_1, r_2)$$

$$\psi(r_1, r_2) = A\left[\phi_1(r_1)\,\phi_2(r_2) \pm \phi_1(r_2)\,\phi_2(r_1)\right]$$

$$\langle \psi(r_1, r_2) | \psi^*(r_1, r_2) \rangle = 1$$

$$A^2 \langle \phi_1(r_1)\,\phi(r_2) - \phi_1(r_2)\,\phi_2(r_1) | (\phi_1(r_1)\,\phi_2(r_2) \pm \phi_1(r_2)\,\phi_2(r_1)) \rangle$$

$$A^2 \Big[\langle \phi_1(r_1)\,\phi_2(r_2) | \phi_1(r_1)\,\phi_2(r_2) \rangle$$

$$+ \langle \phi_1(r_1)\,\phi_2(r_1) | \phi_1(r_2)\,\phi_2(r_1) \rangle$$

$$+\left(\phi_1(r_2)\,\phi_2(r_1)\ \ldots\right)$$

$$A = \frac{1}{\sqrt{2}}$$

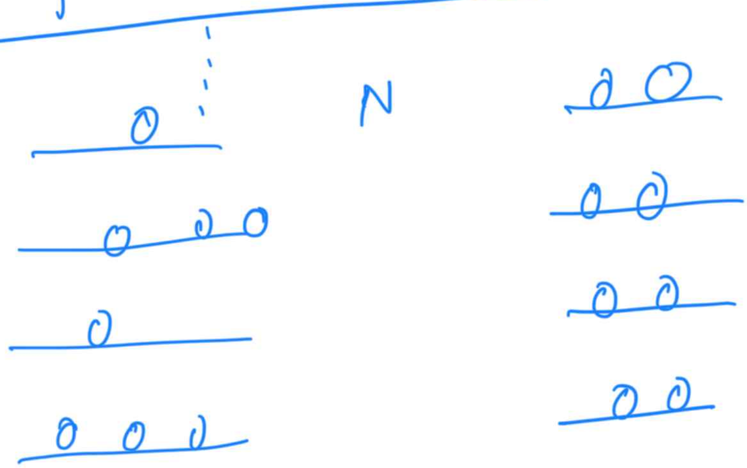
For two particles

$$\psi(r_1, r_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(r_1) & \phi_2(r_1) \\ \phi_1(r_2) & \phi_2(r_2) \end{vmatrix}$$

For N particles

$$\psi(r_1, r_2, \ldots, r_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(r_1) & \ldots & \phi_N(r_1) \\ \vdots & & \\ \phi_1(r_N) & \ldots & \phi_N(r_N) \end{vmatrix}$$

Boson particles spin 1



energy

g_i degeneracy for ϵ_i and ...

Number of ways $W = \prod_i \frac{(n_i + g_i - 1)!}{n_i! \, (g_i - 1)!}$

$S = \ln W =$

Minimise S with constraint

$$\sum n_i \epsilon_i = E \qquad \sum n_i = N$$

$$\ell = \sum_i \ln \frac{(n_i + g_i - 1)!}{n_i! \, (g_i - 1)!} - \beta \sum n_i \epsilon_i - \alpha \sum n_i$$

$$= \sum_i \Big[(n_i + g_i - 1) \ln (n_i + g_i - 1) - (n_i + g_i - 1) \Big]$$

$$- \sum n_i \ln n_i + \sum n_i - \sum_i (g_i - 1) \ln (g_i - 1)$$

$$+ \sum (g_i - 1) - \beta \sum n_i \epsilon_i$$

$$- \alpha \sum n_i$$

$$\frac{\partial l}{\partial n_i} = \ln(n_i + g_i - 1) + 1 - (\ln n_i + 1) - \beta \epsilon_i - \alpha = 0$$

$$\ln \frac{n_i + g_i - 1}{n_i} = \beta \epsilon_i + \alpha$$

$$\ln\left(1 + \frac{g_i}{n_i}\right) = \beta \epsilon_i + \alpha$$

$$1 + \frac{g_i}{n_i} = e^{\beta \epsilon_i + \alpha}$$

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

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

Fermion obeys pauli's exclusion principle

$$W = \prod_i \frac{g_i!}{n_i!\,(g_i - n_i)!}$$

$$l = \sum_i \ln g_i! - \ln n_i! - \ln (g_i - n_i)!$$

$$\beta \sum n_i \epsilon_i \quad -\alpha \sum n_i$$

$$= \sum_i g_i \ln g_i - n_i \ln n_i - (g_i - n_i) \ln (g_i - n_i)$$

$$- \beta \sum n_i \epsilon_i \quad - \alpha \sum n_i$$

$$\frac{\partial l}{\partial n_i} = -\ln n_i + \ln (g_i - n_i) - \beta \epsilon_i - \alpha$$

$$= 0$$

$$\ln \frac{g_i - n_i}{n_i} = \beta \epsilon_i + \alpha$$

$$\left(\frac{g_i}{n_i} - 1 \right) = e^{\beta \epsilon_i + \alpha}$$

$$\frac{g_i}{n_i} = e^{\beta \epsilon_i + \alpha} + 1$$

$$n_i = \frac{g_i}{e^{\beta \epsilon_i + \alpha} + 1}$$

$$n_i = \frac{g_i}{e^{\beta \epsilon_i + \alpha} \mp 1} \qquad \begin{matrix} - \text{ Boson} \\ + \text{ Fermion} \end{matrix}$$

Electron inside a box

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} = E\psi$$

$$\psi = A \sin kx \qquad k^2 = \frac{2mE}{\hbar^2}$$

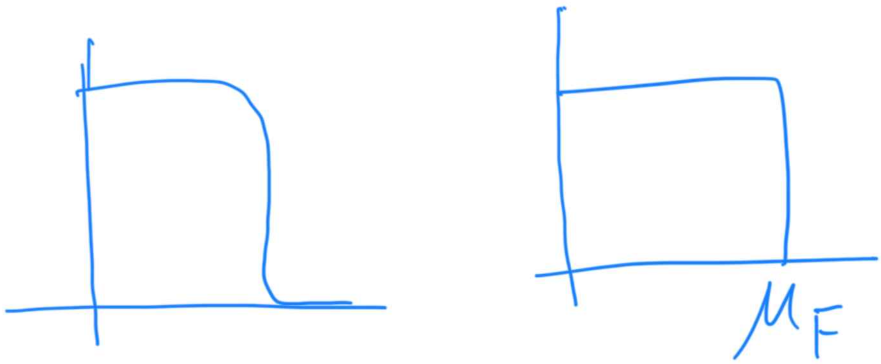
$$ka = n\pi \implies k = \frac{n\pi}{a}$$

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \pi^2}{2ma^2} n^2$$

In three dimension

$$E = \frac{\hbar^2 \pi^2}{2ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$F(E)$



$\beta = \infty$

$\alpha = -\beta\mu$

$$F(E) = \frac{1}{e^{\beta(E-\mu)} + 1} \qquad \beta \to \infty$$

Electron gas in metals

$$\langle n_i \rangle = \frac{g_i}{e^{\beta(\epsilon_i - \mu)} + 1}$$

$$N = \sum_i \langle n_i \rangle \qquad E = \sum_i \langle n_i \rangle \epsilon_i$$

$$N = \int_0^{\infty} g(\epsilon)\, F(\epsilon)\, d\epsilon$$

$$E = \int_0^{\infty} \epsilon\, g(\epsilon)\, F(\epsilon)\, d\epsilon$$

At $t = 0$ $\quad \int_0^{k_F} g(k)\, dk = N$

$$g(k)\, dK = \frac{8\ V}{\pi^2} K^2\, dK.$$

$$\Rightarrow \frac{8V}{\pi^2} \frac{K_F^3}{3} = N \qquad K_F = \left(\frac{3\pi^2}{8} n\right)^{1/3}$$

$$\epsilon_F = \frac{\hbar^2 K^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{3\pi^2}{8} n\right)^{2/3}$$

density of states in ϵ

$$g(k)\,dk = \frac{8V}{\pi^2}\,\frac{2m}{\hbar^2}\sqrt{\frac{2m}{\hbar^2}}\,\epsilon^{1/2}d\epsilon \qquad k^2 = \frac{2m\epsilon}{\hbar^2}$$

$$k\,dk = \frac{2m\,d\epsilon}{\hbar^2}$$

$$= \frac{8V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\epsilon^{1/2}\,d\epsilon$$

$$\epsilon_F^{3/2} = \left(\frac{\hbar^2}{2m}\right)^{3/2}\frac{3\pi^2}{8}\,\frac{N}{V}$$

$$\boxed{g(\epsilon)\,d\epsilon = \frac{3N}{2\epsilon_F^{3/2}}\,\epsilon^{1/2}\,d\epsilon.}$$

$$N = \int_0^\infty g(\epsilon)\,F(\epsilon)\,d\epsilon. \qquad E = \int_0^\infty \epsilon\, g(\epsilon)\,F(\epsilon)\,d\epsilon$$

$$I = \int_0^\infty \phi(\epsilon)\,F(\epsilon)\,d\epsilon.$$

def's $\quad \phi(\epsilon) = \frac{d\Psi}{d\epsilon} \Rightarrow \Psi(\epsilon) = \int_0^\epsilon \phi(\epsilon')\,d\epsilon'$

$$I = \cancel{\Psi(\epsilon)F(\epsilon)\Big|_0^\infty}^{\,0} - \int_0^\infty \Psi(\epsilon)\,F'(\epsilon)\,d\epsilon$$

$\beta(\epsilon-\mu)$

$$F(\epsilon) = \frac{1}{e^{\beta(\epsilon-\mu)}+1} \qquad F'(\epsilon) = \frac{-\beta e^{\beta(\epsilon-\mu)}}{\left(e^{\beta(\epsilon-\mu)}+1\right)^2}$$

$$\int_0^\infty \Psi(\epsilon)\, F'(\epsilon)\, d\epsilon = \sum_m \int \frac{1}{m!} \left.\frac{\partial^m \Psi}{\partial \epsilon^m}\right|_{\epsilon=\mu} (\epsilon-\mu)^m F'(\epsilon)\, d\epsilon$$

$$= \sum \frac{1}{m!} \left.\frac{\partial^m \Psi}{\partial \epsilon^m}\right|_{\epsilon=\mu} \int_0^\infty (\epsilon-\mu)^m F'(\epsilon)\, d\epsilon$$

$$-(\epsilon-\mu)^m \frac{\beta e^{\beta(\epsilon-\mu)}}{\left(e^{\beta(\epsilon-\mu)}+1\right)^2} \qquad \beta(\epsilon-\mu) = x.$$

$$\int \phi(\epsilon)\, F(\epsilon)\, d\epsilon = \frac{1}{m!} \left.\frac{\partial^m \Psi}{\partial \epsilon^m}\right|_{\epsilon=\mu} \frac{1}{\beta^m} \frac{x^m\, dx}{\left(e^{x/2}+e^{-x/2}\right)^2}$$

$$\phi(\epsilon) = g(\epsilon) = \frac{3}{2} \frac{N}{\epsilon_F^{3/2}} \epsilon^{1/2}$$

$$\Psi(\epsilon) = \int_0^\epsilon \phi(\epsilon')\, d\epsilon' = \frac{3N}{\epsilon_F^{3/2}} \epsilon^{3/2}.$$

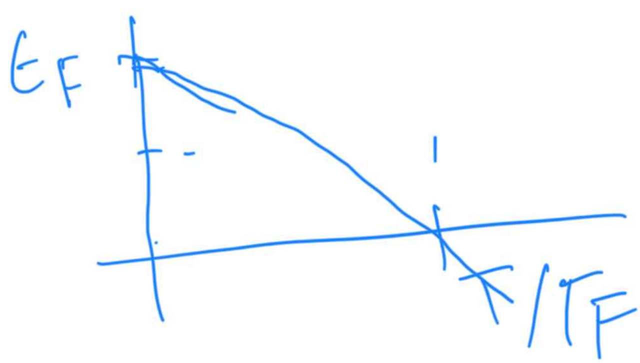
$$N = \int_{-\infty}^{+\infty} \frac{e^x}{(e^x+1)^2}\, dx = \frac{\pi^2}{6}$$

$$N = \psi(\epsilon)\Big|_0^{\mu} + \frac{1}{2} \frac{\partial^2 \psi}{\partial \epsilon^2}\Big|_{\epsilon=\mu} \beta^{-m} \int_{-\infty}^{+\infty} \frac{x^2 e^x}{(e^x+1)^2} dx$$

$$= 3N \left(\frac{\mu}{\epsilon_F}\right)^{3/2} + \frac{1}{2}\,\frac{3}{4}\,\frac{N}{\epsilon_F^{3/2}\mu^{1/2}} \frac{\pi^2}{6}$$

$$\mu = \epsilon_F \left(1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\mu}\right)^2\right)$$

$$= \epsilon_F \left(1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\epsilon_F}\right)^2\right)$$



For energy

$$\int \cdots \quad \frac{1}{\;} \frac{\partial^2 \psi}{\;}\Big| \beta^{-m} \int \frac{x^m e^x}{(e^x+1)^2} dx$$

$$\int \phi(\epsilon) F(\epsilon) d\epsilon = \sum \frac{1}{m!} \frac{\partial^2}{\partial\epsilon^2}\Big|_{\epsilon=\mu}$$

$$\psi(\epsilon) = \int_0^{\epsilon} \phi(\epsilon')\, d\epsilon'$$

$$\phi(\epsilon) = \epsilon g(\epsilon) = \frac{3}{2} \frac{N}{\epsilon_F^{3/2}} \epsilon^{3/2}.$$

$$\psi(\epsilon) = \frac{3}{5} \frac{N}{\epsilon_F^{3/2}} \epsilon^{5/2}.$$

$$E = \psi(\epsilon)\big|_{\mu} + \frac{3}{4} \frac{N}{\epsilon_F^{3/2}} \mu^{1/2} \cdot b.$$

$$= \frac{3}{5} \frac{N}{\epsilon_F^{3/2}} \mu^{5/2} + \beta^2 \frac{3Nb}{4\epsilon_F^{3/2}} \mu^{1/2}$$

$$\mu = \epsilon_F \left(1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\epsilon_F}\right)^2\right)$$

$$\boxed{E = \frac{3}{5} N \epsilon_F \left(1 + \frac{5}{12}\pi^2 \left(\frac{k_B T}{\epsilon_F}\right)^2\right)}$$

$$C_V = \frac{dE}{dT} = \frac{3}{5} N \epsilon_F \frac{2 k_B^2 T}{\epsilon_F^2} \pi^2$$

$$= \frac{3\pi}{5} N k_B \left(\frac{k_B T}{\epsilon_F} \right)$$

Vibration of solids

$$\mathcal{H} = \sum \frac{p_i^2}{2m} + V(\vec{r}_1, r_2 \dots r_N)$$

$$= \sum_i \frac{p_i^2}{2m} + \sum_{r_i, r_j} \frac{\partial^2 V}{\partial r_i \, \partial r_j} \vec{r}_i \cdot \vec{r}_j$$

3N normal modes.

From equipartition theorem at equilibrium

$U = 3N(k_B T) = 3N k_B T$

Specific heat $C_V = 3R$

Einstein's approximation - all normal modes have same frequency and energies are quantised

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

$$= \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$

$$-\ln Z = N\left(\frac{1}{2}\beta\hbar\omega + \ln\left(1 - e^{-\beta\hbar\omega}\right)\right)$$

$$U = -\frac{\partial}{\partial\beta}\ln Z = \frac{1}{2}N\hbar\omega + \frac{\hbar\omega e^{-\beta\hbar\omega}}{\left(1 - e^{-\beta\hbar\omega}\right)}$$

$$C_V = \frac{\partial U}{\partial T} = -\frac{\partial U}{\partial\beta}\frac{1}{k_B T^2}$$

$$= \hbar\omega\left[\frac{-\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} - \frac{e^{-2\beta\hbar\omega}\hbar\omega}{\left(1 - e^{-\beta\hbar\omega}\right)^2}\right]$$

$$= N\hbar^2\omega^2 e^{-\beta\hbar\omega} \left[1 - e^{-\beta\hbar\omega} + e^{-\beta\hbar\omega}\right]$$

$$\frac{\ }{k_B T\left(1-e^{-\beta\hbar\omega}\right)^2}\left[\ \ \right]$$

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

$T \to \infty$

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

$$\simeq N k_B \quad \text{Dulong' Petits law}$$

$$T \to 0 \quad C_V = N k_B \left(\frac{\hbar\omega}{k_B T}\right) e^{-\hbar\omega/k_B T} \to 0$$

Deby's theory.

~~The~~ All the ω's are possible

calculate density of states in the

... with periodic

n space ... .

boundary condition

$$Z = \prod_{\omega_j=1}^{3N} \sum e^{-\beta(n+\frac{1}{2})\hbar\omega_j}$$

$$= \prod_{\omega_j=1}^{3N} \frac{e^{-\frac{1}{2}\beta\hbar\omega_j}}{1-e^{-\beta\hbar\omega_j}}$$

$$-\ln Z = \sum_{\omega_j=1}^{3N} \frac{1}{2}\beta\hbar\omega_j + \ln\left(1-e^{-\beta\hbar\omega_j}\right)$$

$$U = -\frac{\partial}{\partial\beta}\ln Z = \sum_{\omega_j} \frac{3}{2}\hbar\omega_j + \frac{3\hbar\omega_j}{e^{\beta\hbar\omega_j}-1}$$

$$\frac{\partial U}{} = \frac{1}{} \frac{\partial U}{}$$

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

$$= \sum_{\omega_j} + \frac{1}{k_B T^2} \frac{3\,\hbar\omega_j \cdot \hbar\omega_j}{\left(e^{\beta\hbar\omega_j} - 1\right)^2}$$

$$= \sum_{\omega_j} 3 \cdot k_B \left(\frac{\hbar\omega_j}{k_B T}\right)^2 \frac{1}{\left(e^{\beta\hbar\omega_j} - 1\right)^2}$$

$$= 3 \quad k_B \left(\frac{\hbar}{k_B T}\right)^2 \int_0^{\omega_D} \frac{\omega^2 g(\omega)\, d\omega}{\left(e^{\beta\hbar\omega} - 1\right)^2}$$

density of states in K-space

$$g(K)\, dK = \frac{4\pi K^2\, dK}{(2\pi/L)^3}$$

$$= \frac{V K^2\, dK}{2\pi^2}$$

$$\omega = cK$$

$$g(\omega)\,d\omega = \frac{V\,\omega^2\,d\omega}{2c^3\pi^2}$$

$$\int_0^{\omega_D} g(\omega)\,d\omega = 3N$$

$$\Rightarrow \frac{V}{2c^3\pi^2}\,\frac{\omega_D^3}{3} = 3N$$

$$g(\omega)\,d\omega = \frac{9N}{\omega_D^3}\,\omega^2$$

$$C_V = 3\,k_B\left(\frac{\hbar}{k_B T}\right)^2 \frac{9N}{\omega_D^3}\int_0^{\omega_D} \frac{\omega^4\,d\omega}{\left(e^{\beta\hbar\omega}-1\right)^2}$$

$$\beta\hbar\omega = x \qquad \frac{\hbar\omega_D}{k_B T} = x_D \qquad T_D = \frac{\hbar\omega_D}{k_B}$$

$$d\omega = \frac{dx}{\beta\hbar}$$

$$C_V = 3N k_B\left(\frac{\hbar}{\ldots}\right)^2 \frac{9N}{\ldots^3}\int\left(\frac{1}{\beta\hbar}\right)^5 \frac{x^4\,dx}{(e^x\ldots)^2}$$

$$C_V = 9 N k_B \left(k_B T / \omega_D \right) \int_0^{x_D} \frac{\quad}{(e^x - 1)}$$

$$= 3 \cdot k_B \left(\frac{\hbar}{k_B T} \right)^2 \frac{9N}{\omega_D^3} \left(\frac{k_B T}{\hbar} \right)^5 \int_0 \frac{x^4 \, dx}{(e^x - 1)^2}$$

$$= 27 N k_B \left(\frac{k_B T}{\hbar \omega_D} \right)^3 \int_0^{T_D/T} \frac{x^4 \, dx}{(e^x - 1)^2}$$

Bose-Einstein Condensation

The occupancy for Boson:

$$n_\epsilon = \frac{g_\epsilon}{e^{\beta(\epsilon-\mu)} - 1}$$

chemical potential $\mu < 0$ as

$n_\epsilon > 0$ as $\beta \to \infty$

For $\epsilon = 0$

$$N_0 = \frac{1}{e^{-\beta\mu} - 1}$$

$$\Rightarrow e^{-\beta\mu} = \frac{1}{N_0} + 1 \Rightarrow \mu = -\frac{k_B T}{N_0}$$

$\therefore \mu < 0$ as $\beta \to \infty$

For $\epsilon > 0$

$$N_{ex} = \int^{\infty} \frac{g(\epsilon)\, d\epsilon}{e^{\beta(\epsilon-\mu)}}$$

$$\int_0 \frac{}{e^{(\ldots)}-1}$$

ideal

Density of states for a Boson gas

$$g(K)\,dK = \frac{4V}{\pi^2} K^2 dK$$

$$\epsilon = \frac{\hbar^2 K^2}{2m} \Rightarrow g(\epsilon)d\epsilon = \frac{4V}{\pi^2}\frac{m}{\hbar^2}\sqrt{\frac{\hbar^2}{2m}}\,\epsilon^{1/2}d\epsilon$$

$$d\epsilon = \frac{\hbar^2}{m} K\,dK \qquad = \frac{2V}{\pi^2}\left(\frac{2m}{\hbar^2}\right)^{1/2}\epsilon^{1/2}d\epsilon$$

In thermodynamic limit

For $\mu = 0$ the minimum temperature

$$N = \frac{2V}{\pi^2}\left(\frac{2m}{\hbar^2}\right)^{1/2}\int_0^\infty \frac{\epsilon^{1/2}d\epsilon}{e^{\beta\epsilon}-1}$$

$$= \frac{2V}{\pi^2}\left(\frac{2m}{\hbar^2}\right)^{1/2}\left(\frac{1}{\beta}\right)^{3/2}\int_0^\infty \frac{x^{1/2}dx}{e^x-1}$$

$\beta\epsilon = x$

$$N = \frac{2V}{\pi^2}\sqrt{\frac{2m}{\hbar^2}}\left(K_B T_c\right)^{3/2}\xi\left(\frac{3}{2}\right)$$

$$\xi(\cancel{x}) = \int^\infty \frac{x^{\cancel{x}-1}dx}{x}$$

Reeman zeta function

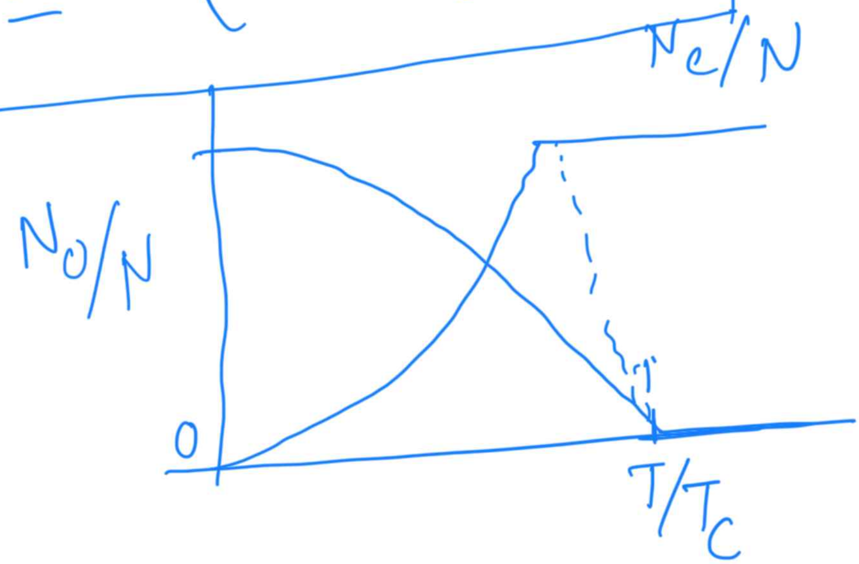
$$\int_0 \frac{}{e^x - 1}$$

$$\frac{2V}{\pi^2}\sqrt{\frac{2m}{\hbar^2}} = \frac{N}{(k_B T_c)^{3/2}\,\zeta(3/2)}$$

$$N_e = \frac{1}{\zeta(3/2)}\frac{2V}{\pi^2}\sqrt{\frac{2m}{\hbar^2}}\,(k_B T)^{3/2}\int_0^\infty \frac{x^{1/2}\,dx}{e^x - 1}$$

$$= \frac{N}{(k_B T_c)^{3/2}}(k_B T)^{3/2} = N\left(\frac{T}{T_c}\right)^{3/2}$$

$$\boxed{\frac{N_0}{N} = \left(1 - \left(T/T_c\right)^{3/2}\right)}$$



dependence of μ on T

$$N_0 \quad = \quad 1 - \left(\frac{T}{T_c}\right)^{3/2}$$

$$\overline{N} - \quad \left(\frac{T}{T_c}\right)$$

From occupancy at temperature $T < T_c$

$$N_0 = \frac{1}{e^{-\beta\mu} - 1}$$

$$e^{-\beta\mu} = \frac{1}{N_0} + 1$$

$$-\beta\mu = \ln \frac{N_0 + 1}{N_0} \simeq \ln\left(\frac{N+1}{N}\right)$$

$$\boxed{\mu = -k_B T \ln\left(1 + \frac{1}{N}\right)}$$

Energy and specific heat

$$E = \int_0^\infty \frac{\epsilon\, g(\epsilon)\, d\epsilon}{e^{\beta(\epsilon-\mu)} - 1}$$

$$= \frac{1}{\zeta(3/2)} \frac{N}{(k_B T_c)^{3/2}} \int^\infty \frac{\epsilon^{3/2}\, d\epsilon}{e^{\beta(\epsilon-\mu)} - 1}$$

at low T, $\mu \to 0$

$$= \frac{1}{\zeta(3/2)} \frac{N}{(K_B T_c)^{3/2}} \frac{1}{\beta^{5/2}} \int_0^\infty \frac{x^{3/2}\, dx}{e^x - 1}$$

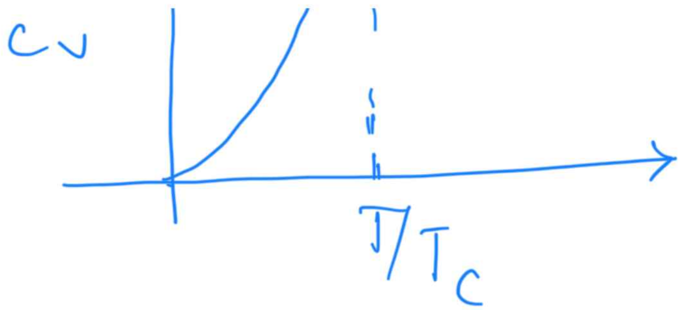
$$= \frac{N (K_B T)^{5/2}}{(K_B T_c)^{3/2}} \frac{\zeta(5/2)}{\zeta(3/2)}$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{5}{2} N K_B \frac{\zeta(5/2)}{\zeta(3/2)} \left(\frac{T}{T_c}\right)^{3/2}$$

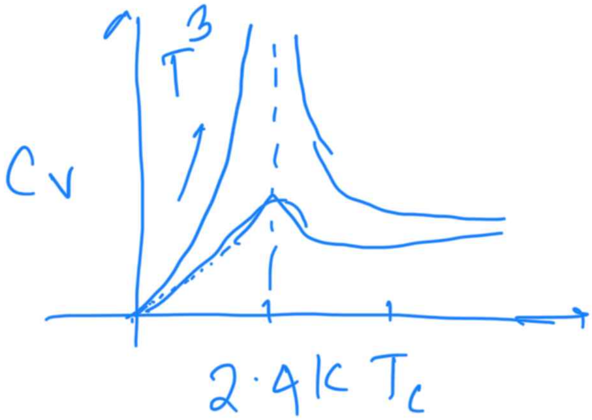
$$\simeq 1.96\, N K_B \left(\frac{T}{T_c}\right)^{3/2}$$

For large T, the gas behaves as classical ideal gas

$$C_V = \frac{3}{2} N K_B$$



For liquid helium He^4 experimental observation $T_c \sim 3.3\,K$



Importance of phonon modes.