Application of Boltzmann statistics.

Quantum system in Boltzman statistics (not quantum stat. Mech.)

Many quantum system has disrete energy spectrum determined by a quantum number "n". (For example harmonic oscillator $\varepsilon_n = \hbar\omega(n+\frac{1}{2})$ $n=0,1,2\ldots$)

In this case
$$\rho_n = \frac{\exp(-\beta\varepsilon_n)}{Z(T,V,1)}$$

$$Z(T,V,1) = \sum_n \exp(-\beta\varepsilon_n)$$

For system of N non-interacting quantum particles
$$Z = (Z_1)^N \quad \text{or} \quad \underbrace{\frac{1}{N!}}(Z_1)^N$$

still an ad-hoc modification will be clear when one works with quantum SM.

N harmonic oscillators:

$$Z(T,V,1) = \sum_n \exp(-\beta\varepsilon_n) = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})}$$

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

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

$$Z(T,V,N) = \left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right]^{-N}$$

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

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} = \frac{F}{N}$$

$$p = -\left.\frac{\partial F}{\partial V}\right|_{N,T} = 0$$ (no translational motion, no pressure)

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N} = Nk\left[\frac{\beta\hbar\omega}{e^{\beta\hbar\omega}-1} - \ln\left(1 - e^{-\beta\hbar\omega}\right)\right]$$

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

↑ zero point energy.

if we write $U = N\langle\epsilon_n\rangle = N\hbar\omega\left(\frac{1}{2} + \langle n\rangle\right)$

$\Rightarrow$ mean quantum number $\langle n\rangle = \dfrac{1}{e^{\beta\hbar\omega}-1}$

correct even in quantum statistic

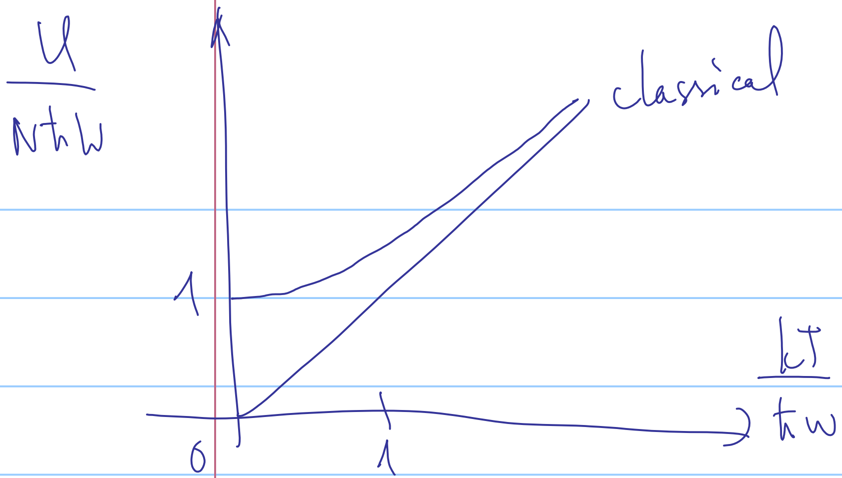
Clearly equipartition theorem doesn't work $(U = NkT)$

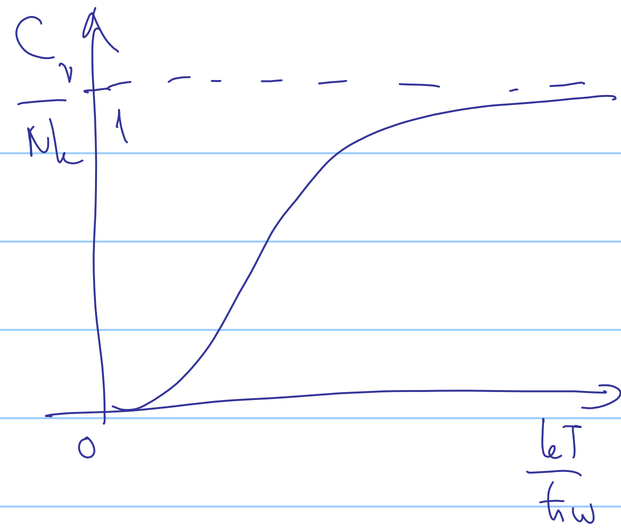
However at large temperature $\beta\hbar\omega \to 0$

$$U \simeq \ldots = NkT.$$

this is because for small T, only $n = 0$ or 1 contributes to Z, $U \simeq \frac{N\hbar\omega}{2}$, for large T many n contributes to Z $\sum_n \to \int dn$ discreteness doesn't show up anymore

Side note: calculate $\langle\epsilon_n\rangle = \frac{1}{Z}\sum_n \hbar\omega\left(n+\frac{1}{2}\right)e^{-\beta\epsilon_n}$





$C_v = C_p = Nk$ for classical

$$C_v = \frac{\partial U}{\partial T}\bigg|_{N,V} = Nk(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$$

gap system

$\beta\hbar\omega \to 0$, large T $\qquad C_v \to Nk$

$\beta\hbar\omega \to \infty$, small T $\qquad C_v \to e^{-\beta\hbar\omega}$ exponential

it's very difficult to excite an oscillators

A microcanonical perspective.

$$E_\ell = \hbar\omega\left(\ell + \frac{N}{2}\right).$$

a microstate is a distint wave of putting ℓ quanta of energy $\hbar\omega$ on N harmonic oscillator.

$$\circ \,|\, \circ \;\; \circ \,||\, \circ \;\; \circ \;\; \circ \;\; \circ \;\; \circ \,|\, \cdots \,|\, \circ$$

$\leftarrow$ quanta

$\uparrow$ $N-1$ lines

if lines & balls are the same species, there are exactly $((N-1)+\ell)!$ ways to arrange them. but the balls are indistinguishable, lines are distinguishable

So the # of ways is

$$\Omega(E) = \frac{(N-1+l)!}{l!\,(N-1)!}$$

$$S = k(l+N)\ln(l+N) - kl\ln l - Nk\ln N$$

$S(E,V,N)$: $\quad l = \frac{E}{\hbar\omega} - \frac{N}{2}$

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{V,N} = \frac{k}{\hbar\omega}\ln\frac{E+\frac{N\hbar\omega}{2}}{E-\frac{N\hbar\omega}{2}}$$

$$E = \frac{N}{2}\hbar\omega\,\frac{e^{\beta\hbar\omega}+1}{e^{\beta\hbar\omega}-1}$$ same as in canonical,

Gibbs canonical and grand canonical ensemble

If external heat bath not only maintain temperature T but also generalized force $\vec{F}$ on the system, the probability of a microstate of the combined system is

$$\propto \exp\left(-\beta H + \beta\vec{F}\vec{x}\right).$$

normalization $\Rightarrow$

$$\rho = \frac{e^{-\beta H + \beta\vec{F}\cdot\vec{x}}}{\underbrace{\sum e^{-\beta H + \beta\vec{F}\vec{x}}}_{Z(T,\vec{F},N)}}$$ Gibbs partition function

Paramagnetism:

many substances has permanent magnetic moment $\vec{\mu}$.

if subject to magnetic field $\vec{H}$, they try to align to lower the energy $-\vec{\mu}\cdot\vec{H}$. thermal motion destroyes perfect alignment. what is total moment at a given temperature?

$$E = -\sum_{i=1}^{N} \vec{\mu}_i \cdot \vec{H}$$

$$Z = \int d\Omega_1 \dots \int d\Omega_N \exp\left(\sum \beta \mu H \cos\theta_i\right)$$

$$= \left[Z(T,H,1)\right]^N$$

where
$$Z(T,H,1) = \int d\Omega \exp\left(\beta\mu H \cos\theta\right)$$

$d\Omega = 2\pi \sin\theta \, d\theta .$

$$z(T,H,1) = 2\pi \int_{-1}^{1} dx \, \exp\{\beta\mu H x\} = 4\pi \frac{\sinh(\beta\mu H)}{\beta\mu H}$$

$$\langle\vec{\mu}\rangle = \frac{1}{z} \int \mu \cdot \begin{pmatrix} \sin\theta\cos\varphi \\ \sin\theta\sin\varphi \\ \cos\theta \end{pmatrix} e^{\beta\mu H\cos\theta} \sin\theta \, d\theta \, d\varphi$$

$$\mu_x = \mu_y = 0$$

$$\mu_z = \frac{\mu}{z} \int \cos\theta \, e^{\beta\mu H\cos\theta} \sin\theta \, d\theta \, . \, 2\pi$$

$$= \frac{2\pi\mu}{z} \int_{-1}^{1} dx \, . \, x \, e^{\beta\mu H x}$$

$$= \frac{2\pi\mu}{z} \frac{\partial}{\partial(\beta\mu H)} \underbrace{\int_{-1}^{1} dx \, e^{\beta\mu H x}}_{2\sinh(\beta\mu H)/\beta\mu H}$$

$$= \frac{2\pi\mu}{4\pi\sinh(\beta\mu H)} \beta\mu H \left[\frac{2\cosh(\beta\mu H)}{\beta\mu H} + 2\sinh(\beta\mu H)\left(-\frac{1}{(\beta\mu H)^2}\right)\right]$$

$$= \mu \left[\coth(\beta\mu H) - \frac{1}{\beta\mu H} \right]$$

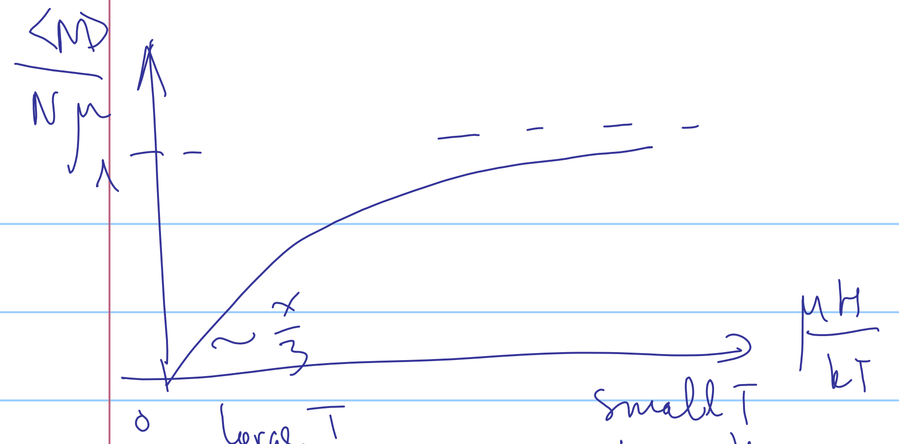
We can also use thermodynamics to derive $\langle\mu\rangle$

$$G = -kT \ln Z = -NkT \ln z(T,H,1)$$

$(T,H,1)$

$\uparrow$ generalized force

$$\langle\vec{M}\rangle = -\frac{\partial G}{\partial H} = \ldots = N\langle\mu\rangle$$



Curie's law

zero field susceptibility: $\chi = \lim_{x \to 0} \frac{\partial \langle \vec{M} \rangle}{\partial H} = \frac{N\mu^2}{kT} = \frac{C}{T}$

$$S(T,H,N) = -\frac{\partial G}{\partial T}\Big|_{H,N} = Nk \ln\left\{4\pi \frac{\sinh(\beta\mu H)}{\beta\mu H}\right\}$$

$$- \frac{N\mu H}{T} \underbrace{\left\{\coth(\beta\mu H) - \frac{1}{\beta\mu H}\right\}}_{L(x)}$$

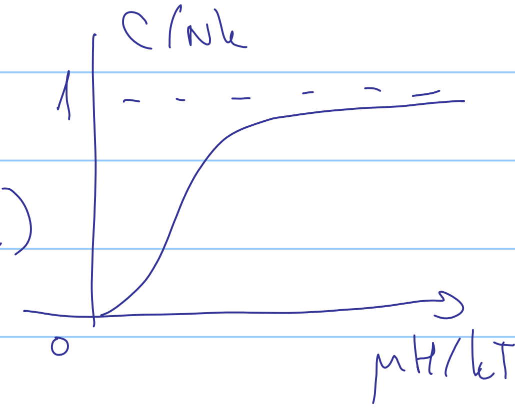
Helmholtz

$$\mathcal{H}(T,H,N) = G + TS = -\langle \vec{M} \rangle \cdot \vec{H}$$

Specific heat at constant $\vec{H}$

$$C_H = \frac{\partial \mathcal{H}}{\partial T}\Big|_{H,N} = \frac{\partial}{\partial x}\left(-N\mu H L(x)\right)\frac{\partial x}{\partial T}$$

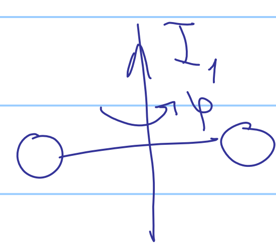
$$= \frac{Nk}{H}\left[1 - \frac{x^2}{\sinh^2 x}\right]$$



at high T $C \to 0$ (bound system)

no magnetic dipoles contribution to specific heat at high T.

Gas with internal degrees of freedom:



$$H = \underset{\text{trans}}{H}(\vec{R}, \vec{P}) + H_{rot}(\varphi_i, p_{\phi_i}) \qquad p_\theta = I_1 \dot{\theta}$$

$$= \sum \frac{p_i^2}{2m} + \frac{1}{2} \frac{p_{\phi_i}^2}{I_1 \sin^2\theta} + \frac{p_\theta^2}{2I_1} \qquad p_\phi = I_1 \dot{\varphi} \sin^2\theta$$

$$z_1 = \frac{1}{h^3} \int d^3\vec{R} \int d^3\vec{p} \cdot \frac{1}{h^2} \int d\phi \int dp_\phi \, e^{-\frac{\beta p_i^2}{2m} - \frac{\beta p_{\phi_i}^2}{2I_1 \sin^2\theta}} \int d\theta \int dp_\theta \, e^{-\beta p_\theta^2 /}$$

$$= \underbrace{Z_{trans}}_{V\left(\frac{2\pi M k T}{h^2}\right)^{3/2}} \cdot Z_{rotation}$$

π indistinguishable atoms

$$z_{rot} = \frac{1}{h^2} \int_0^{\pi} d\phi_i \int dp_{\phi_i} \, e^{-\left(\frac{\beta p_{\phi_i}^2}{2I_1 \sin^2\theta}\right)} \int_0^{\pi} d\theta \underbrace{\int dp_\theta \, e^{-\frac{\beta p_\theta^2}{2I_1}}}_{\sqrt{\pi} \cdot \sqrt{\frac{2I_1}{\beta}}}$$

$$= \frac{1}{h^2} \cdot \pi \sqrt{\frac{2\pi I_1}{\beta}} \underbrace{\int_0^{\pi} d\theta}_{-\cos\theta\big|_0^{\pi} = +2} \underbrace{\int dp_\phi \, e^{-\frac{\beta p_\phi^2}{2I_1 \sin^2\theta}}}_{\sqrt{\frac{2\pi I_1 \sin\theta}{\beta}}}$$

$$= \frac{2\pi}{h^2} \frac{2\pi I_1}{\beta} = \frac{I_1 k T}{\hbar^2}$$

$$F_{rot} = -NkT \ln z_{rot} = -NkT \ln \frac{I_1 kT}{\hbar^2}$$

$$S_{rot} = -\frac{\partial F}{\partial T}\bigg|_N = Nk\left[\ln\left(\frac{I_1 kT}{\hbar^2}\right) + 1\right]$$

$U_{rot} = F_{rot} + TS_{rot} = NkT$! 2 degrees of freedom

Total energy $U = U_{trans} + U_{rot} = \frac{5}{2} NkT$

in general when molecule are not symmetric, I_1, I_2, I_3

$\rightarrow U_{rot} = \frac{3}{2} NkT$

$U = U_{rot} + U_{trans} = 3NkT$