$\Rightarrow C_x = T\left(\frac{\partial S}{\partial T}\right)_x$: heat capacity

$$dU = T\,dS - p\,dV + \mu\,dN + \cdots$$

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial S}\right)_{V,N} \qquad \text{Maxwell's Relations}$$

$$-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right) = \kappa \Leftarrow$$

Microcanonical Ensemble: E, N, V: fixed

$\Rightarrow \Omega(E,N,V) = \#$ of microstates for given E, N, V

$$\boxed{S = k_B \ln \Omega}$$

$$dU = T\,dS - p\,dV + \mu\,dN + \cdots$$

$$dS = \frac{1}{T}\,dU + \frac{p}{T}\,dV - \frac{\mu}{T}\,dN \cdots$$

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}\,; \quad \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{p}{T}\,; \cdots$$

$S(E, V, N_i)$

$\Sigma(E,V,N) = \#$ of microstates (for given V,N) whose energy is $\leq E$

$$\Omega(E,V,N) \simeq \frac{\partial \Sigma}{\partial E}\,\Delta E \Leftarrow$$

$$\ln \Omega \simeq \ln \Sigma$$

$$\ln \Omega = \ln \left[\left(\frac{\partial \Sigma}{\partial E} \right) \Delta E \right]$$

$$\Sigma \propto E^N \Rightarrow \frac{\partial \Sigma}{\partial E} \propto N E^{N-1}$$

$$\frac{\partial \Sigma}{\partial E} \simeq N \frac{\Sigma}{E}$$

$$\frac{S}{k} = \ln \Omega = \ln \left(\frac{\partial \Sigma}{\partial E} \right) \Delta E$$

$$\simeq \ln N \frac{\Sigma}{E} \Delta E$$

$$\simeq \underbrace{\ln \Sigma}_{\mathcal{O}(N)} + \underbrace{\underbrace{\ln \left(\frac{\Delta E}{E} \right)}_{-\mathcal{O}(10)} + \underbrace{\ln N}_{\mathcal{O}(23)}}_{\text{negligible}}$$

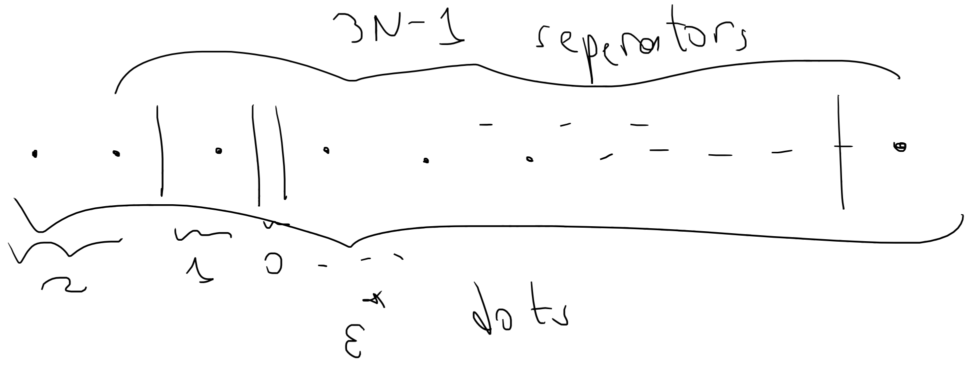
$$N \sim 10^{23}$$

<u>SHO</u> N 3D oscillators

$$E = \sum \hbar \omega \left(n_x^i + n_y^i + n_z^i + \frac{3}{2} \right)$$

$$\varepsilon^* = \left(E - \frac{3N}{2} \hbar \omega \right) \frac{1}{\hbar \omega} = \sum \left(n_x^i + n_y^i + n_z^i \right)$$

$$\varepsilon^* = \sum \left(n_x^i + n_y^i + n_z^i \right)$$



$$\Omega(E) = \frac{(\varepsilon^* + 3N - 1)!}{\varepsilon^*!\,(3N-1)!}$$

$$\Sigma(E) = \frac{1}{\omega_0}\int \prod_i dp_i\,dq_i\,\Theta\big(\tilde{E} - \underbrace{E(p_i,q_i)}\big)\prod_k \frac{1}{N_k!}$$

$\omega_0 \simeq h^{3N}$ (in 3D for N particles)

$$P_r = \begin{cases} \text{constant} & \text{if } E_r = E \\ 0 & \text{if } E_r \neq E \end{cases}$$

Canonical Ensemble

$$P_{\underline{r}} = \frac{e^{-\beta E_r}}{Q}$$

r: label of <u>the</u> microstate

$P_E(\varepsilon)$ = probability that the system has energy ε

$$= \sum_{E_r=\varepsilon} P_r = P_r(\varepsilon)\sum_{E_r=\varepsilon} 1 = P_r(\varepsilon)\,\Omega(\varepsilon)$$

$$E = \sum_r E_r P_r = \frac{\sum E_r e^{-\beta E_r}}{Q \equiv \sum e^{-\beta E_r}}$$

$$U \equiv \bar{E} \equiv \langle E \rangle = \frac{1}{Q} \sum_r \left(-\frac{\partial}{\partial \beta} e^{-\beta E_r} \right)$$

$$= \frac{1}{Q} \left(-\frac{\partial}{\partial \beta} \right)_{V,N} Q$$

$$\boxed{U = -\left(\frac{\partial \ln Q}{\partial \beta} \right)_{V,N}}$$

$$\ln Q = -\beta A$$

$$A = E - TS \Rightarrow dA = -S\,dT - P\,dV + \mu\,dN \ldots$$

$$\boxed{S \equiv -\sum_r P_r \ln P_r}$$

$$P_r = -\frac{\partial E_r}{\partial V}$$

$$P = \langle P_r \rangle = \sum \left(-\frac{\partial E_r}{\partial V} \right) \frac{e^{-\beta E_r}}{Q}$$

$$= \frac{1}{Q} \frac{1}{\beta} \sum \left(\frac{\partial e^{-\beta E_r}}{\partial V} \right)_{T,N}$$

$$\boxed{P = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{T,N}}$$

$$\boxed{Q = \sum_r e^{-\beta E_r}}$$

classical case $\displaystyle = \prod_k \frac{1}{N_k!} \int \prod_i \frac{dp_i\, dq_i}{h} e^{-\beta E(p,q)}$

If $\displaystyle E = \sum_i E_i(p_i, q_i)$

$$Q = \frac{1}{N!} \int \prod_i \left(\frac{dp_i\, dq_i}{h} e^{-\beta E_i(p_i, q_i)} \right)$$

$$= \frac{1}{N!} \prod_i \underbrace{\left(\int \frac{dp_i\, dq_i}{h} e^{-\beta E_i(p_i, q_i)} \right)}_{Q_1}$$

$$Q_N = \frac{1}{N!} Q_1^N \Leftarrow$$

If $\exists$ interactions

$$= \prod_k \frac{1}{N_k!} \int \prod_i \frac{dp_i\, dq_i}{h} e^{-\beta E(p,q)}$$

$$Q_N^{int} = Q_N^{non\text{-}int} \frac{1}{Q_N^{non\text{-}int}} \prod_k \frac{1}{N_k!} \int \prod_i \frac{dp_i\, dq_i}{h} e^{-\beta E^{non\text{-}int}} e^{-\beta V^{interactions}}$$

$$= Q_N^{non\text{-}int} \underbrace{\left\langle e^{-\beta V} \right\rangle}_{} {}^{int}$$

non-interacting $\Downarrow$ ($\cong$)

$$Q_N^{int} \simeq Q_N^{non-int} \left\{ 1 - \beta \langle V^{int} \rangle^0 + \frac{\beta^2}{2} \langle (V^{int})^2 \rangle^0 + \cdots \right\}$$

$$\langle \mathcal{O} \rangle = \frac{1}{Q} \sum_r \mathcal{O} e^{-\beta E_r}$$

$$= \frac{1}{Q} \prod_k \frac{1}{N_k!} \int \prod_i \frac{dp_i \, dq_i}{h} \mathcal{O} e^{-\beta E(p_i; q_i)}$$

$$dU = dQ - P\,dV$$

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

$$\sum dQ = \int (dU + P\,dV) = (U_2 - U_1) + P_0(V_2 - V_1)$$

$$= \underbrace{(U_2 + P_0 V_2)}_{H_2} - \underbrace{(U_1 + P_0 V_1)}_{H_1}$$

$$\Delta Q = \Delta H$$

$$dA = -S\,dT - P\,dV$$

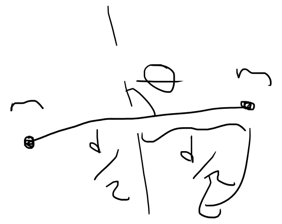
at constant T

$$dA = dW$$

$$\Delta W = \Delta A$$

$T_{Earth} \sim 7^{\circ}C$

$$A = E_{sun} - TS$$



$$L_1 = \frac{1}{2} m \left(\frac{d}{2}\dot{\theta}\right)^2 \cdot 2$$

$$L = \frac{1}{2} \underbrace{\left(m \frac{d^2}{2}\right)}_{I} \dot{\theta}^2$$

$$L = \frac{1}{2} I \dot{\theta}^2$$

$$p_\theta = \frac{\partial L}{\partial \dot{\theta}} = I\dot{\theta} \equiv M$$

$$H = \frac{1}{2I} p_\theta^2$$

$$\Sigma(E) = \int_{|p_\theta| < M} d\theta \, dp_\theta$$

$$= (2\pi)(2M) = \boxed{4\pi M = \Sigma(E)}$$

$$L = \frac{m}{2}\left[\dot{r}^2 + r^2\left(\sin^2\theta\, \dot{\phi}^2 + \dot{\theta}^2\right)\right]$$

rigid rotator: $\dot{r} = 0$

$$L = \frac{r^2 m}{2}\left(\sin^2\theta\, \dot{\phi}^2 + \dot{\theta}^2\right)$$

$$p_\theta = \frac{\partial L}{\partial \dot\theta} = m r^2 \dot\theta \qquad \dot\theta = \frac{1}{mr^2} p_\theta$$

$$p_\phi = \frac{\partial L}{\partial \dot\phi} = m r^2 \sin^2\theta\, \dot\phi \qquad \dot\phi = \frac{p_\phi}{mr^2 \sin^2\theta}$$

$$H = \frac{p_\theta^2}{mr^2} + \frac{p_\phi^2}{mr^2\sin^2\theta} - \frac{mr^2}{2} \sin^2\theta \frac{p_\phi^2}{m^2 r^4 \sin^4\theta}$$

$$- \frac{mr^2}{2} \frac{1}{m^2 r^4} p_\theta^2$$

$$\boxed{H = \frac{1}{2mr^2} p_\theta^2 + \frac{1}{2mr^2\sin^2\theta} p_\phi^2}$$

$$\Sigma(E) = \frac{1}{h^2} \int d\theta\, dp_\theta\, d\phi\, dp_\phi$$

$$\Theta\left[M^2 - \left(p_\theta^2 + \frac{1}{\sin^2\theta} p_\phi^2\right)\right]$$

$$\vec{M} = \vec{r} \times \vec{p}$$

$$M^2 = (\vec{r} \times \vec{p})^2 = r^2 p^2 - (\vec{r} \cdot \vec{p})^2$$

$$\dot r = 0 \qquad \vec{r} = r\hat{r}$$

$$\vec{r} \cdot \vec{p} = 0 \qquad \dot{\vec{r}} = \underset{0}{\dot r}\hat r + r\dot{\hat r}$$

$$M^2 = r^2 p^2 = m^2 r^2 \dot{\vec{r}}^2 \qquad \dot{\vec{r}} = r\left[\dot\theta\hat\theta + \sin\theta\dot\phi\hat\phi\right]$$

$$= m^2 r^2 \dot{\hat{r}}^2 \qquad \frac{\partial \hat r}{\partial \theta} = \hat\theta \qquad \frac{\partial \hat r}{\partial \phi} = \sin\theta\hat\phi$$

$$M^2 = m^2 r^4 \left[\dot\theta^2 + \sin^2\theta\, \dot\phi^2\right]$$

$$\dot{\theta} = \frac{1}{mr^2} p_\theta$$

$$\dot{\phi} = \frac{p_\phi}{mr^2 \sin^2\theta}$$

$$M^2 = \cancel{m^2 r^4}\left[\overbrace{\frac{1}{\cancel{m^2 r^4}} p_\theta^2}^{\dot{\theta}^2} + \cancel{\sin^2\theta}\,\overbrace{\frac{p_\phi^2}{\cancel{m^2 r^4} \sin^{4\,2}\theta}}^{\dot{\phi}^2}\right]$$

$$\boxed{M^2 = p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}} \qquad M^2 \neq p_\theta^2 + p_\phi^2$$

$$H = \frac{1}{2mr^2} p_\theta^2 + \frac{1}{2mr^2 \sin^2\theta} p_\phi^2 = \frac{1}{2mr^2} M^2$$

$$\vec{M} = M_\theta \hat{\theta} + M_\phi \hat{\phi}$$

$$M_\theta \overset{?}{\simeq} p_\theta$$

$$M_\phi \overset{?}{\simeq} p_\phi$$

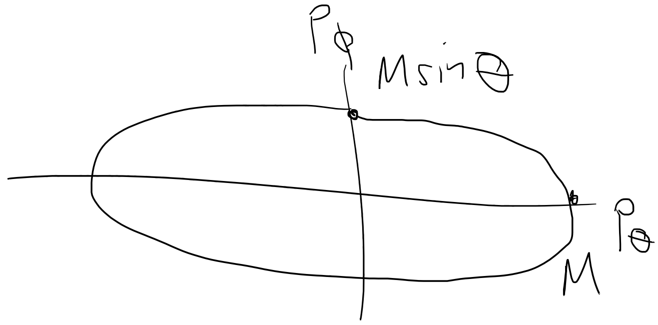
$$\Sigma(E) = \frac{1}{h^2} \int d\theta \, dp_\theta \, d\phi \, dp_\phi \; \Theta\left[M^2 - \left(p_\theta^2 + \frac{1}{\sin^2\theta} p_\phi^2\right)\right]$$

$$= \frac{1}{h^2} 2\pi \int d\theta \, dp_\theta \, dp_\phi \; \Theta\left[\left(M^2 - \frac{p_\phi^2}{\sin^2\theta}\right) - p_\theta^2\right]$$

$$= \frac{2}{h^2} 2\pi \int_0^{\pi} d\theta \int_0^{A} dp_\phi \; 2\sqrt{M^2 - \frac{p_\phi^2}{\sin^2\theta}} \;\Theta\left[M^2 - \frac{p_\phi^2}{\sin^2\theta}\right]$$

$$\Sigma(M) = \frac{1}{h^2} 2\pi \int d\theta \, dp_\theta \, dp_\phi \;\Theta\left[\left(M^2 - \frac{p_\phi^2}{\sin^2\theta}\right) - p_\theta^2\right]$$

$$1 = \frac{p_\phi^2}{M^2 \sin^2\theta} + \frac{p_\theta}{M^2}$$



$$= \frac{1}{h^2} 2\pi \int_0^{\pi} d\theta \;\pi M \; M\sin\theta$$

$$= M^2 \frac{2\pi^2}{h^2} 2 = \frac{M^2}{\hbar^2}$$

$$\Sigma(M) = \left(\frac{M}{\hbar}\right)^2$$

$$\Sigma_j = j(j+1)$$

$$\Omega(j) = \Sigma_j - \Sigma_{j-1}$$

$$= j(j+1) - (j-1)j = 2j\,(+1)$$

$$\Omega(j) = \Sigma_{j+\frac{1}{2}} - \Sigma_{j-\frac{1}{2}} = \left(j+\tfrac{1}{2}\right)\left(j+\tfrac{3}{2}\right) - \left(j-\tfrac{1}{2}\right)\left(j+\tfrac{1}{2}\right)$$

$$= \left(J+\frac{1}{2}\right)(2) = 2J+1$$

In canonican ensemble

$$H = \frac{1}{2mr^2} p_\theta^2 + \frac{1}{2mr^2 \sin^2\theta} p_\phi^2$$

$$\boxed{Q_1 = \frac{1}{h^2}\int d\theta\, d\phi\, dp_\theta\, dp_\phi\, e^{-\frac{\beta}{2mr^2}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right)}}$$

$$= \int d\theta\, 2\pi \sqrt{\frac{\pi}{\frac{\beta}{2mr^2}}} \sqrt{\frac{\pi}{\frac{\beta}{2mr^2 \sin^2\theta}}}$$

$$= \frac{1}{h^2} 2\pi\, \pi\, \frac{2mr^2}{\beta} \underbrace{\int d\theta \sin\theta}_{2}$$

$$\boxed{Q_1 = \frac{1}{\hbar^2} 2mr^2 kT}$$

$$Q_N = \left(\frac{2mr^2 kT}{\hbar^2}\right)^N = \left(\frac{2mr^2}{\hbar^2 \beta}\right)^N$$

$$U = -\frac{\partial}{\partial\beta} \ln Q_N = -\frac{\partial}{\partial\beta}\left[-N\ln\beta\right]$$

$$U = \frac{N}{\beta} = \boxed{NkT = U}$$