Virial Thm & Equipartition Thm

$x_i \in (p_i, q_i)$

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{\int d\omega \; x_i \frac{\partial H}{\partial x_j} e^{-\beta H}}{\int d\omega \; e^{-\beta H}}$$

$$\int d\omega \; x_i \frac{\partial H}{\partial x_j} e^{-\beta H}$$

$$= \int d\omega \quad x_i \left(-\frac{1}{\beta} \frac{\partial}{\partial x_j} \right) e^{-\beta H}$$

$$= -\frac{1}{\beta} \int d\omega_{(j)} \; x_i e^{-\beta H} \Big|_{x_j^{(1)}}^{x_j^{(2)}} = 0$$

$$+ \frac{1}{\beta} \int d\omega \; \underbrace{\frac{\partial x_i}{\partial x_j}}_{\delta_{ij}} e^{-\beta H}$$

$$\int d\omega \; x_i \frac{\partial H}{\partial x_j} e^{-\beta H} = kT \delta_{ij} \underbrace{\int d\omega \; e^{-\beta H}}_{Q_N}$$

$$\Rightarrow \boxed{\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = kT \delta_{ij}}$$

$x_i \equiv q_i$

$$\left[\left\langle q_i \frac{\partial H}{\partial q_j} \right\rangle = kT\,\delta_{ij} \right] \delta^{ij}$$

$\delta_{ij}\delta^{ij} = \delta^i_i = d$

if $d = 3$

$$\left\langle q_i \underbrace{\frac{\partial H}{\partial q_i}}_{-\dot{p}_i} \right\rangle = dkT = 3NkT$$

$\Uparrow$ if summed over all particles

$$\boxed{\langle q_i \dot{p}_i \rangle = -3NkT}$$

$\Uparrow$ virial

$\Leftarrow$

$x_i = p_i$

$$\left\langle p_i \underbrace{\frac{\partial H}{\partial p_i}} \right\rangle = 3NkT$$

$$\boxed{\langle p_i \dot{q}_i \rangle = 3NkT}$$

<u>Example</u>

$$\sum_{\text{all particles}} \langle q_i \dot{p}_i \rangle = \sum_{\text{all particles}} \langle \vec{r} \cdot \vec{F} \rangle = -P \oint \vec{r} \cdot d\vec{S}$$

$$\langle \vec{F} \rangle = -P\, d\vec{S}$$

$$-3NkT = -P \oint \vec{r} \cdot d\vec{S} = -P \int \underbrace{(\operatorname{div} \vec{r})}^{3} dV$$

$$-3NkT = -3PV \Rightarrow \boxed{PV = NkT}$$

$$\langle q_i \dot{p}_i \rangle = -3NkT$$

$$\dot{p}_i = F = F^{pressure} + \sum_j F_{ij}$$

$$\langle q_i \dot{p}_i \rangle = -3PV + \langle \sum_{ij} F_{ij} r_i \rangle$$

$$-3NkT = -3PV + \langle \sum_{i<j} F_{ij} r_{ij} \rangle$$

$$F_{ij} = -F_{ji}$$

$$\boxed{\frac{P}{nkT} = 1 - \frac{1}{dNkT} \langle \sum_{i<j} \vec{F}_{ij} \cdot \vec{r}_{ij} \rangle}$$

$$n = \frac{N}{V}$$

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if $\lambda^m H(p, q) = H(\lambda p, \lambda q)$

$$m \lambda^{m-1} H(p,q) = \frac{\partial H}{\partial(\lambda p)} p + \frac{\partial H}{\partial(\lambda q)} q \Big|_{\lambda=1}$$

$$\boxed{p \frac{\partial H}{\partial p} + q \frac{\partial H}{\partial q} = mH}$$

$$H = \sum_i \left(A_i p_i^2 + B_i q_i^2 \right) \Rightarrow m = 2$$

$$\boxed{p_i \frac{\partial H}{\partial p_i} + q_i \frac{\partial H}{\partial q_i} = 2H} \Leftarrow$$

$$\underbrace{\left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle}_{3NkT} + \underbrace{\left\langle q_i \frac{\partial H}{\partial q_i} \right\rangle}_{3NkT} = 2\langle H \rangle$$

$$\Rightarrow \langle H \rangle = 3NkT$$

6N: # of terms in the Hamiltonian.

$$= 3N\, 2\left(\frac{kT}{2}\right)$$

$$U = 6N\left(\frac{kT}{2}\right)$$

Classical Harmonic Oscillator

$$Q_N = [Q_1]^N$$

$$Q_1 = \int \frac{d^3p\, d^3q}{(2\pi\hbar)^3} e^{-\beta\left(\frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2\right)}$$

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

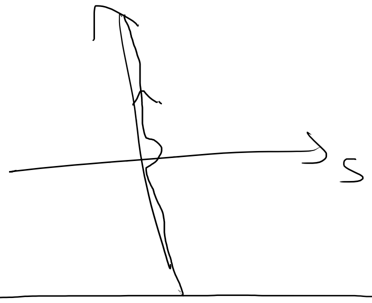
$$Q_1 = \frac{1}{(2\pi\hbar)^3} \left(\frac{4\pi^2}{\beta^2\omega^2}\right)^{3/2}$$

$$= \frac{1}{(\cancel{2\pi}\hbar)^3} \left(\frac{\cancel{2\pi}\, kT}{\omega}\right)^3 = \left(\frac{kT}{\hbar\omega}\right)^3$$

$$\boxed{Q_1 = \left(\frac{kT}{\hbar\omega}\right)^3} = \left(\frac{1}{\beta\hbar\omega}\right)^3 \quad (1)$$

$$g_1(E) = \frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} ds \, \frac{e^{sE}}{(s\hbar\omega)^{3\,(1)}}$$

$$g_1(E) = \frac{1}{(\hbar\omega)^3}\frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} ds \, \frac{e^{sE}}{s^3} = \frac{1}{(\hbar\omega)^{3\,(1)}}\frac{E^2}{2}$$



$$\boxed{g_1(E) = \frac{1}{(\hbar\omega)^3}\frac{E^2}{2}}$$

For the 1D HO

$$g_1(E) = \frac{1}{\hbar\omega}$$

$g_1(E)\,dE$ = # of states in the energy range $(E, E+dE)$

$$g_1(E)\,dE = \frac{dE}{\hbar\omega}$$

$$Q_N = \left(\frac{kT}{\hbar\omega}\right)^{3N}$$

$$A = -kT \ln Q_N = -3NkT \ln\left(\frac{kT}{\hbar\omega}\right)$$

$$\boxed{A = -3NkT \ln\left(\frac{kT}{\hbar\omega}\right)}$$

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{V,T} = -3kT \ln\left(\frac{kT}{\hbar\omega}\right)$$

$$S = -\left(\frac{\partial S}{\partial T}\right)_{V,N} = +3Nk\ln\left(\frac{kT}{\hbar\omega}\right)$$

$$+\,3Nk$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} = 0$$

$$A = U - TS$$

$$U = A + TS = \cancel{-3NkT\ln\left(\frac{kT}{\hbar\omega}\right)}$$

$$\cancel{+3NkT\ln\left(\frac{kT}{\hbar\omega}\right)} + 3NkT$$

$$\boxed{U = 3NkT}$$

$$\left.\begin{aligned} C_V &= \left(\frac{\partial Q}{\partial T}\right)_V \\ C_p &= \left(\frac{\partial Q}{\partial T}\right)_p \end{aligned}\right\} \quad \boxed{C_V = C_p = 3Nk}$$

$$Q = \int d\omega\, e^{-\beta H}$$

$\hbar\omega \ll kT \Rightarrow$ classical results should hold

$\hbar\omega \gg kT \Rightarrow$ quantum mechanical effects should be important.

QM Oscillator (1D): $3N \to N$

$$Q_N = [Q_1]^{3N}$$

$$Q_1 = \sum_r e^{-\beta E_r} = \sum_{n=0}^{\infty} e^{-\beta \hbar w (n+\frac{1}{2})}$$

$$Q_1 = \frac{e^{-\beta \hbar w/2}}{1 - e^{-\beta \hbar w}} \qquad \sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$$

$$Q_1 = \frac{1}{e^{\beta \hbar w/2} - e^{-\beta \hbar w/2}} = \left[2\sinh\left(\frac{\beta \hbar w}{2}\right)\right]^{-1}$$

$$Q_N = \left[2\sinh\left(\frac{\beta \hbar w}{2}\right)\right]^{-3N}$$

$$A = -kT \ln Q_N = -kT(-3N)\ln\left[2\sinh\left(\frac{\hbar w}{2kT}\right)\right]$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} = -\frac{\partial}{\partial T}\left[3NkT \ln\left(2\sinh\left(\frac{\hbar w}{2kT}\right)\right)\right]$$

$$S = -\frac{A}{T} + 3N\cancel{k}\cancel{T} \frac{\cosh\left(\frac{\hbar w}{2kT}\right)}{\sinh\left(\frac{\hbar w}{2kT}\right)} \left(+\frac{\hbar w}{2kT^2}\right)$$

$$U = A + TS = T\left(S + \frac{A}{T}\right)$$

$$U = T\,3Nk \frac{\cosh\left(\frac{\hbar w}{2kT}\right)}{\sinh\left(\frac{\hbar w}{2kT}\right)} \left(\frac{\hbar w}{2kT}\right)$$

$$U = 3NkT\, f\left(\frac{\hbar\omega}{2kT}\right)$$

$$f(x) = x\,\frac{\cosh x}{\sinh x}$$

high temperature: $\frac{\hbar\omega}{2kT} \equiv x \ll 1$

$$f(x) \Rightarrow x\,\frac{e^{x}+e^{-x}}{e^{x}-e^{-x}} \Rightarrow x\,\frac{(1+x)+(1-x)}{(\cancel{1}+x)-(\cancel{1}-x)}$$

$$f(x) \Rightarrow x\,\frac{2}{2x} = 1$$

$$f(x) \xrightarrow[x\to 0]{} 1$$

$$U \xrightarrow[kT \gg \hbar\omega]{} 3NkT$$

Low temperature limit: $\frac{\hbar\omega}{kT} \equiv x \gg 1$

$$f(x) = x\,\frac{\cosh x}{\sinh x} = x\,\frac{e^{x}+e^{-x}}{e^{x}-e^{-x}} \xrightarrow[x\gg 1]{} x$$

$$U = 3NkT\, f\left(\frac{\hbar\omega}{2kT}\right) \to 3N\cancel{kT}\,\frac{\hbar\omega}{2\cancel{kT}}$$

$$U \to 3N\left(\frac{\hbar\omega}{2}\right)$$

$$Q_N = \sum_r e^{-\beta E_r}$$